Application of Biotechnology in Antifouling Solutions for Hard Fouling Prevention

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Abstract

This paper describes the development, subsequent application and success of using biotechnology in marine coatings for hard fouling prevention purposes. Existing self-polishing and controlled depletion polymer coating types that are suitable for the addition of 'Selektope®' are described. Current market uptake and in-service performance data for selected case studies are also presented. The paper also shares insight into I-Tech's research and development efforts to advance next generation antifouling materials that make use of Selektope®.

1. Introduction

Since the worldwide ban of the use of tri-butyl-tin (TBT) in antifouling coatings in 2003, suppliers of marine coatings have faced increasing pressure to offer antifouling products that deliver the same level of effectiveness as those that previously contained TBT for preventing the build-up of biofouling on ship wetted hard surfaces.

The banning of TBT use forced the marine coatings sector to reconstruct their formulations to accommodate different biocides, with copper designated as the favoured candidate, supplemented with booster biocides. Soon after, biocides faced new regulatory challenges in the shape of the EU Directive on Biocidal Products (98/8/EC). The effect of this was the number of certified biocides available for use in antifouling coatings reducing in number to just 12 active substances, including Selektope®.

Neither scheduling penalties, nor increased fuel costs were acceptable to a globalised industry reliant on just in time delivery. A solution had to be found and, for barnacle fouling, that solution was Selektope®.

Some two years earlier, in February 2000, biologists at the University of Gothenburg published a research paper on biofouling in Swedish waters. Researchers had been investigating how a range of substances that would prevent the settlement of hard fouling when dissolved in seawater could be used.

This research focused on the barnacle *Amphibalanus improvisus*, and its 'colonisation' of man-made surfaces at the larval stage. The goal of the research was to discover 'adrenoceptor active compounds' that manipulated the barnacle larvae's behaviour to inhibit invertebrate larvae from settling. Dahlström, et al. (2000) found that larval-stage receptors were remarkably responsive to one substance in particular– medetomidine. This bioactive substance prevented barnacle larvae attempting to settle on a hard substrate.

Medetomidine was also distinguished by its reversible effects. Larvae that came into contact with the substance could still later metamorphose into juvenile barnacles with no apparent ill effect.

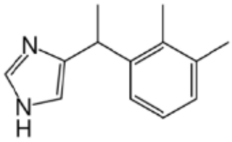
CAS-No. **EINECS-no**	86347-14-0 Not listed
IUPAC Name	4-[1-(2,3-dimethylphenyl)ethyl]-*1H*-imidazole
Other common name	Medetomidine
Molecular formula	$C_{13}H_{16}N_2$
Structural formula	
Molecular weight (g/mol)	200,28 g/mol

Fig 1. Medetomidine identity

In collaboration with two Finnish universities, Swedish researchers discovered that medetomidine could bind to a specific group of receptors, the octopamine receptors. The receptors were cloned and the causality between the receptor and medetomidine was established. Further study led the researchers to link the binding to octopamine receptors to changes in the larval behaviour at a surface. This explained the high efficacy in preventing and deterring barnacle larvae in an antifouling paint without its being toxic to the barnacles.

In a counter-intuitive discovery, given its sedative effect on vertebrates, medetomidine was found to induce hyperactivity in the barnacle larvae to disrupt the settling process; similar to the effects to a small dose of adrenaline in humans.

Fig 2. Cyprid larvae stage of the barnacle.

Fig 3. Adult stage of the barnacle.

During initial panel testing, a further discovery was made. Remarkably, a polymer film containing medetomidine in a concentration equivalent to 0.02% by weight volume rejected 97% of the aggressive *Barnacle improvus* after two weeks, and 96% after four weeks. No other macro-fouling organisms were present at all. A further distinction pointed towards medetomidine's potential for "large scale synthesis": its "tendency to accumulate at the solid/liquid interface" across the full extent of a surface.

These significant research findings catalysed the development of the industry's first biotechnology approach to biofouling prevention. I-Tech AB commercialised the use of medetomidine in marine coatings, owning all IP and regulatory rights to the antifouling agent under the brand name Selektope®. I-Tech also controls the largest and most efficient source of medetomidine production.

In 2009, buoyed by the further confirmation of earlier research, I-Tech entered a new stage in the development of Selektope®, by initiating the registration of the marine antifouling agent for regulatory approvals. Few can doubt the dedication required to submit a new substance to the BPR's evaluation process; the dossier BPR (EU528/2012) consists of more than 20.000 pages 528 files and refers to 90 investigations regarding human and environmental safety. Even so, Selektope® was granted full approval in 2016 for use as a marine biocide under EU Biocide Product Regulation (EU) (528/2012).

Today, Selektope® has received approvals in all leading markets for new builds and dry-docking including China, South Korea and Japan. In the EU, Selektope® has been approved for all relevant use-types l. For Africa, South America and the rest of Asia, no registration is needed for the use of Selektope®. Following 15 years of development time and numerous regulatory hurdles, the first commercial antifouling coating product containing Selektope® was applied to the vertical sides of a ship in 2015 with the first commercial product containing Selektope® being officially launched into the market in 2016.

2. Increasing demand for advanced antifouling coatings

Ocean going vessels are increasingly at risk from negative commercial impacts associated with biofouling accumulation on the hull. Marine fouling is the biological process of single celled organisms, algae and hard-shelled organisms, predominantly barnacles, attaching to submerged surfaces and colonising at a rapid rate.

Any organisms anchored on the hull create increased drag (commonly referred to as added resistance) which significantly decreases hull performance. A biofouled vessel must burn more fuel to attain the same speed through water when in active service, resulting in higher fuel costs for the ship operator. A hull suffering from heavy fouling is also extremely impactful on maintenance costs. Costs associated with hull cleaning services are factored into a ship operator's operating expenditures (OPEX) but as global biofouling risk increases, hull cleaning is likely to be required more frequently, in-creasing maintenance costs. Repeated cleaning of the hull can also remove layers of the antifouling coating, reducing its service life.

Different types of biofouling require different hull cleaning practices. Soft fouling can be removed by diver cleaning with brushes or by Remote Operated Vehicle (ROV) cleaning technology. However, hard fouling presents a greater cost and risk for the ship operator. Encrusted colonies of barnacles or other hard-shelled organisms must be removed with methods such as scraping or blasting which are much more damaging to the antifouling coating.

Biofouling accumulation on vessels experiencing extended periods of static activity is also becoming an increasingly dominant issue on the agenda for many shipyards. Newly launched vessels remaining stationary for three or four months at shipyards located in biofouling hotspots, or longer in the case of LNG carriers, during the fitting out process are becoming so fouled that they perform badly during sea trials.

In addition, growing regulatory focus on the transportation of invasive aquatic species (IAS) by the international shipping fleet creates an increased risk of potential commercial impact. Some regional regulations are already in force that allow ports to refuse entry of heavily bio-fouled ships, resulting in greater financial costs for the operator. On an international level, IMO has recently shifted its focus on tackling IAS transfer via ballast water onto hull biofouling.

The afore-mentioned issues are driving the need for high performance, advanced antifouling technology in the maritime industry. Ship operators are increasingly demanding antifouling paints that are both well-suited to specific ship trading patterns, and varying activity levels in addition to protecting against both soft and hard fouling. When looking at the future trading potential, ship operators need to ensure that their ship is protected whether it be in constant active service, idle for long periods of time, or is at risk of fluctuating between the two.

This future-proofing approach to antifouling coating selection, without any certainty of future trade, is exerting great pressure on the coating suppliers, prospering great innovation and new approaches of fouling prevention technology using the active substance Selektope®. This is supported by increasing demand for antifouling coatings that contain the anti-barnacle active agent from ship owners and operators.

3. The use of Selektope® in self polishing coatings

Selektope® cannot be used in 'foul release' coatings with low surface energy based on siloxane elastomers and fluoropolymers, yet. Selektope® is a biocide that is currently suited for use only in coatings that are 'self-polishing' (SPCs) or 'Controlled Depletion Polymers' (CDPs) types. SPCs rely on the friction generated by the ship's motion through water causing tiny quantities of the base polymer paint to hydrolyse and to leach at a predetermined rate, while the active antifouling maintains its performance evenly through the paint's lifetime.

Selektope® is a biocide that has highly favourable antifouling properties at low concentrations (nano Molar). To obtain full protection against barnacle fouling, 0.1 - 0.3% w/w of Selektope® should be used in a wet paint formulation. Just 2 grams Selektope® is used per litre of paint, comparable to 500-700 grams of copper oxide used per litre of paint for barnacle prevention.

Selektope® binds to pigment and other particles in the paint system and is therefore continuously released in the same way as other active substances and components. This contributes to long-term performance as long as the paint remains on the hull. The paint formulation, which mainly comprises binding agents, biocides, pigment and filler material, is applied to the hull using a traditional spraying method. The compatibility between Selektope® and the paint matrix in the marine coatings industry, ensures as slow and steady release secures the antifouling effect over time.

However, how and when Selektope® is added during the formulation process is key to controlling the release rate of Selektope® from an antifouling paint. To prevent premature depletion of Selektope® the molecule should be able to interact with a carrier in the paint mixture. A carrier could be an inorganic particle such as zinc- or cuprous oxide. It could also be a metal ion such as Zn2+ or Cu2+, or an acid group on a binder, for example the carboxylic acid on rosin.

I-Tech advises that Selektope® should be added early in the process, rather than adding it post formulation. I-Tech also advises that Selektope® should be added as a solution in a suitable solvent. Preferably the Selektope® solution and the carrier should be mixed first and then the rest of the components can be added. Selektope® will adhere to metal ions and metal oxide such as zinc oxide and cuprous oxide. This has been shown to be an effective way to control the release of Selektope® and prevent premature depletion.

Inorganic materials such as Al_2O_3, SiO_2, CuO, ZnO, TiO_2 and MgO can be used. Cuprous oxide, zinc oxide and iron oxide are commonly used. ZnO is advised as the best pigment particle for maximum Selektope® adsorption in xylene.

If Selektope® is added later in the paint formulation process the surface of the metal oxide pigment may already be occupied and Selektope® adsorption will not take place in an adequate or linear way with uneven distribution and weaker adhesions. This may cause Selektope® to leach out of the paint too quickly and result in premature depletion of Selektope® from the treated surface.

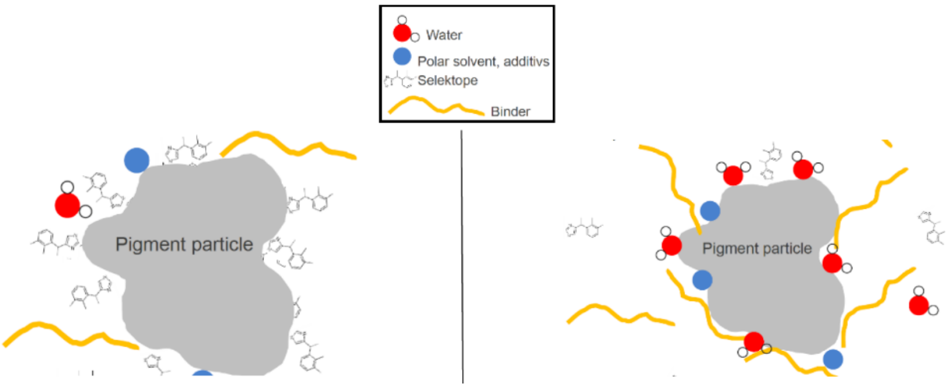


Fig.3. Selektope® added before the binder and other components - good adhesion will occur versus if Selektope® added at the end of the formulation process – weaker or no adhesion occurs potentially leading to premature depletion of Selektope®

Although most Selektope®-containing antifouling paint products on the market are combinations of copper oxides and Selektope®, Chugoku Marine Paints have launched a paint that is copper free. Therefore, the concentration of biocides in the paint has been reduced, while other qualities, such as prevention of soft fouling (e.g. slime and seaweed) have been notably improved.

4. Current market uptake and in-service performance data

Application data, as provided by paint manufacturers, suggest that to-date the total of ships coated with a Selektope®-containing antifouling totals over 300. There are 10 antifouling coating products available to the market that contain Selektope® (correct as of April 2019).

In this paper, a selection of case studies that demonstrate the hard fouling prevention effectiveness of Selektope®-containing antifouling coatings are presented.

4.1. CASE STUDY: 36-month medium range tanker trial

The vertical sides of the IMO II 2009-built chemical and products tanker *Team Calypso* were coated with a copper free Selektope®-based antifouling product with a service life of 60 months.

At the 36-month position in its drydock interval *Team Calypso* had a hull completely free of barnacle fouling after spending more than 50% of its operating time spent in areas of high biofouling with up to 32ºC water temperatures. The tanker had also encountered several extended idling periods of 25 days or more.

		
MONTH 27: VERTICAL SIDE	**MONTH 27: UNCOATED LETTERS**	**MONTH 27: UNCOATED BALLAST SUCTION**

Fig 4. *Team Calypso* dive inspection report, Month 27

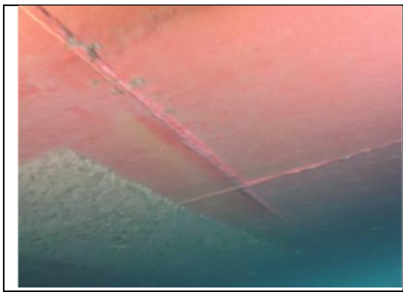
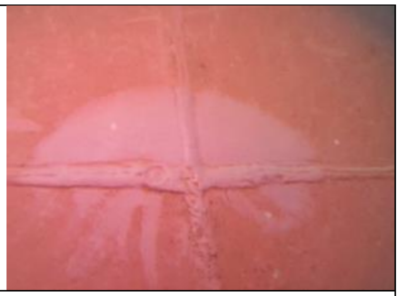
		
MONTH 32: FLAT BOTTOM WITH PATCH OF UNCOATED SURFACE	**MONTH 32: UNCOATED BALLAST SUCTION**	**MONTH 32: FLAT BOTTOM**

Fig 5. *Team Calypso* dive inspection report, Month 32

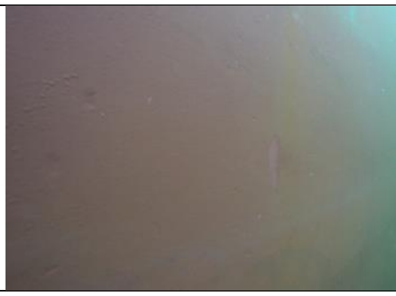
		
MONTH 36: VERTICAL SIDE	**MONTH 36: VERTICAL SIDE**	**MONTH 36: VERTICAL SIDE**

Fig 6. *Team Calypso* dive inspection report, Month 36

Independent, third party analysis of hydrodynamic data used to calculate the MR tanker hull's added resistance also reinforced the underwater hull inspection findings at month 36. Data analysis confirms that the added resistance on the MR Tanker's hull and propeller due to fouling was exceptionally low compared to that expected for a reference ship of similar age, size and trading patterns.

The independent data for *Team Calypso* at Month 36 is described in Fig. 7 below.

Total added resistance	12 %
Hull added resistance	8 %
Propeller added resistance	4 %
Development rate of added resistance (normally 0.5% to 1.5%)	0.4 %
Excessive fuel consumption since last drydock at loaded condition	2.7 t/24h
Months since latest dry-docking	36
Months since latest hull cleaning	36
Months since latest propeller polish	6

Fig 7. *Team Calypso* added resistance data: Month 36

The performance of the Selektope®-containing SPC applied to *Team Calypso* was compared to two other sister ships in the fleet (ship A and ship B). Ship A coated with a foul release coating type and ship B coated with an SPC type. The added resistance data for each ship is presented in Fig. 8 below.

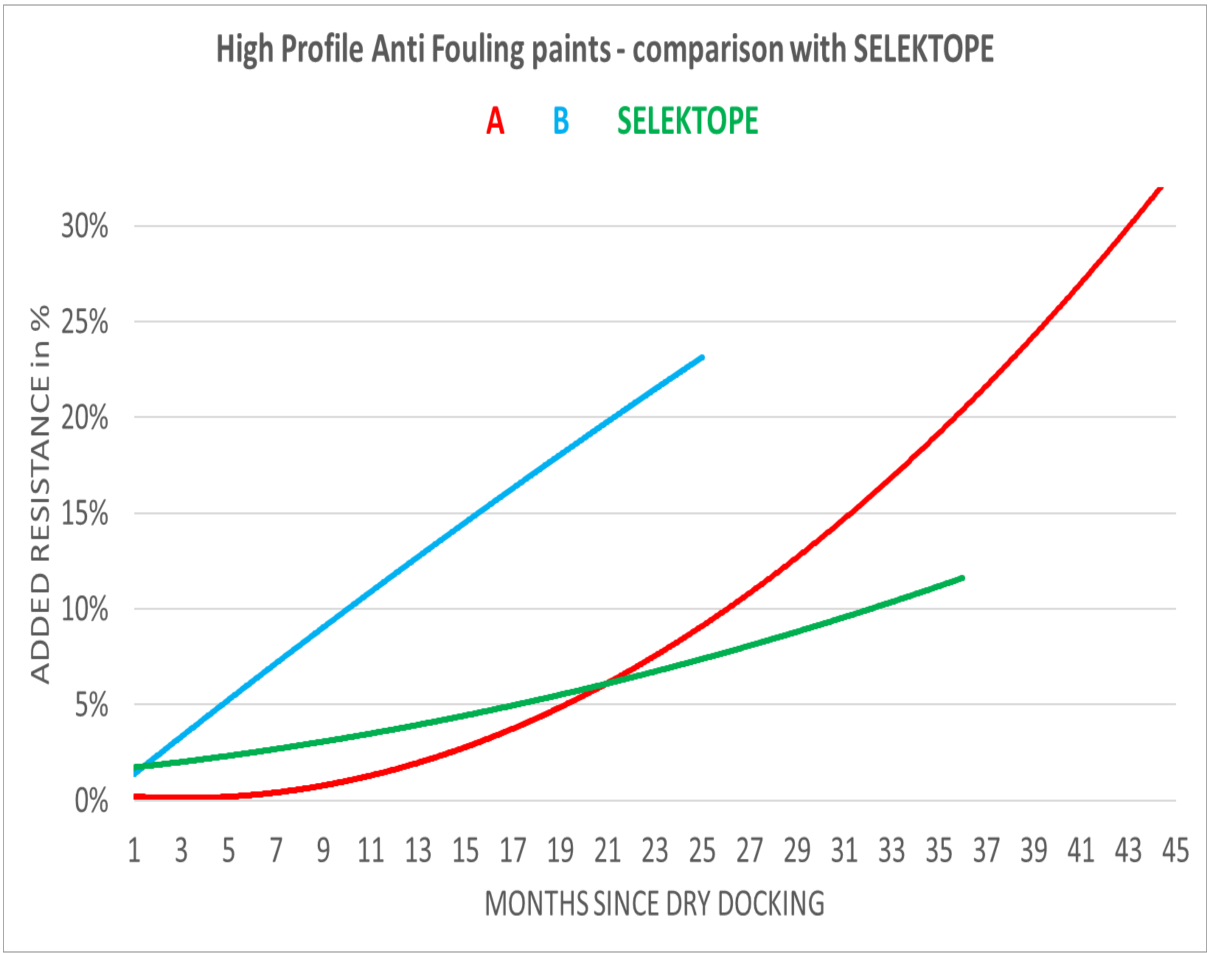


Fig 8. *Team Calypso* development of hull/propeller added resistance versus sister ships

The independent analysis of the tanker's performance data coupled with underwater hull inspections provide yet more convincing long-term performance results for Selektope®-based coatings. These results hold great importance as they confirm the superior efficacy of Selektope® for a vessel engaged in active service that encounters significant exposure to severe fouling conditions and undertakes periodic idling activity. This is proof that I-Tech's unique antifouling ingredient can offer ship operators using Selektope®-based antifouling coatings superior hard fouling prevention for any vessel regardless of its activity and trading patterns.

4.2. **CASE STUDY: US Navy static panel tests**

The Office of Naval Research Biofouling Program supports field testing at five sites located in Florida, California, Hawaii and Singapore. These sites are characterised by different environmental conditions, and different biofouling communities. Across the sites, however, any coating under evaluation will experience biofouling by the full suite of organisms likely to recruit on a ship hull.

The antifouling performance of a number of coating formulations have been examined during a test period of 12 months using coated test panels under static conditions at the five aforementioned test sites. Each coating formulation is a different product sourced from multiple paint manufacturers.

The first copper based SPC type containing Selektope® supports no macrofouling, with no barnacle growth, or slimes at most of the sites after 12-months static. Some panels at one of the Florida tests sites and at the Singapore site were covered with a layer of slime. At the 6-month point, panels at the California test site also had very little slime growth.

The second coating formulation, a copper-free SPC type containing Selektope®, after 12 months static at all test sites supported no macrofouling, with no barnacle growth. At one of the Florida tests sites, macrofouling, not barnacles, was present and some scattered amphipod tubes. Panels at the Singapore test site supported slightly heavier slime.

For the testing of third coating formulation, one set of panels were coated with a copper-based SPC and one set of panels were coated with a copper-based SPC type containing Selektope® at each test site location, after 12 months there was a clear difference in performance exhibited between the two sets of panels coated, with and without Selektope®. At the Florida test sites the set of panels with Selektope®-containing paint being free of barnacles, while scattered barnacles were present on the set of panels coated with paint not containing Selektope® and both sets of panels also supporting light to moderate slime and scattered amphipod tubes. At the Hawaii tests sites, both sets of panels were essentially clean, while those at the Singapore test site slime was slightly heavier. After 6 months, panels coated with paint containing Selektope® at the California test site remained barnacle free, whereas panels coated with paint not containing Selektope® supported barnacle growth.

Conclusion

This test provided the conclusion that the presence of Selektope®® in antifouling coatings provides superior hard fouling prevention performance, even under static conditions of 12-month duration. This test also demonstrated that copper-free antifouling coatings containing Selektope®® also offer superior colour retention to those copper-containing SPCs tested under the same conditions. This test will continue in 2019.

5. R&D projects advance next generation antifouling materials and surfaces that make use of Selektope®.

The challenges with cleaning submerged surfaces and equipment requires the development of new materials or combinations of materials that withstand cleaning and other kinds of mechanical wear. There is also submerged equipment that could benefit from having an antifouling coated surface that currently may only be coated with ordinary marine paint for corrosion protection. Fenders, buoys, nets, cables, measuring/monitoring devices and energy production devices can suffer from fouling, for example.

I-Tech, together with industry partners, has starting screening suitable materials either as coating or construction materials for submerged objects that are:

- Durable to withstanding cleaning / mechanical wear
- Slippery: to release fouling
- Permeable: to release biocides

Materials already available that can be mixed or tweaked to improve fouling resistance are:

- Polyurethanes
- Silicone epoxies

In this paper, research conducted by I-Tech in the areas of Polyurethanes and Silicone epoxies containing Selektope® is presented.

5.1. CASE STUDY: Polyurethanes with Selektope®

I-Tech has demonstrated that it is possible to protect submerged surfaces/object that are made out of polyurethane material. Test results have confirmed the prevention of barnacle settlement under static conditions over two seasons (summers).

Selektope® concentration					
0%	0.1%	0.2%	0.5%	1%	0%

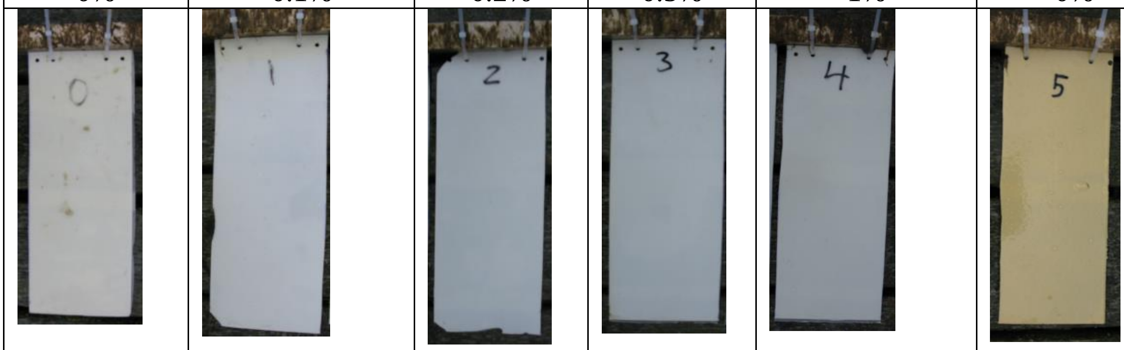


Fig. 13. Reference polyurethane test panels

Selektope® concentration					
0%	0.1%	0.2%	0.5%	1%	0%

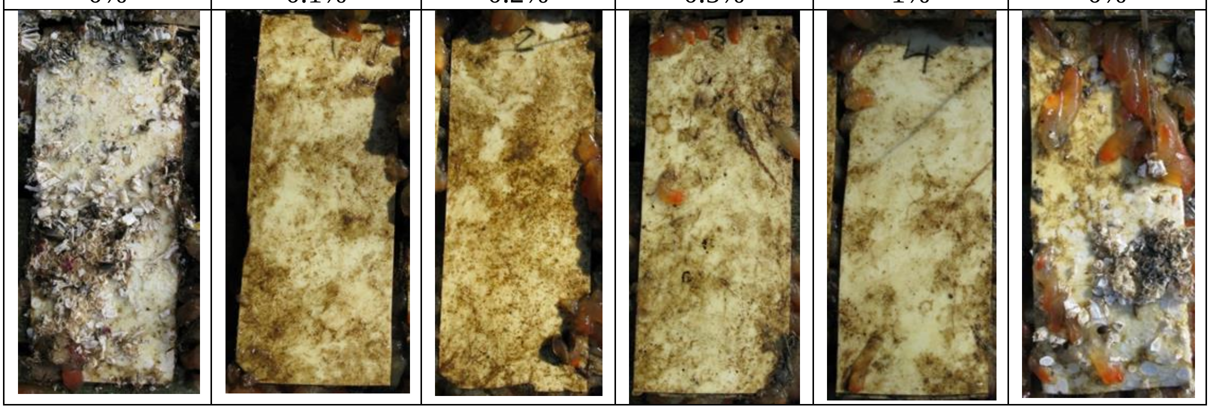


Fig 14. Polyurethane test results: May 2013 - September 2014

Fig 15. Three-panel polyurethane test conducted with only one formulation containing 0.37% Selektope® versus a reference panel with 0% Selektope® - October 2015 - November 2017

Conclusion
This test provided the conclusion that the presence of Selektope® in polyurethane material successfully protects against barnacle fouling.

5.2. CASE STUDY: Silicon epoxy coatings

Whereas epoxy-silicone systems offer abrasion resistance and easy to clean properties, they still have limitations when exposed to sea water at static conditions. The addition of Selektope® enables highly innovative coating systems and, as such American paint specialist Wearlon®, part of Plastic Maritime Corp., trialled the inclusion of Selektope® in its Wearlon Super F-3M range to develop an abrasion-resistant coating with boosted antifouling properties. The trials concluded that the addition of Selektope® to Wearlon®'s epoxy-silicone coating resulted in significantly improved antifouling properties when exposed to raft tests in sea water.

The coating is expected to be particularly effective in areas where high-wear strength is required such as around propellers, and for use on off shore equipment.

Wearlon®'s Super F-3M is a water-based silicone-epoxy coating whose silicone epoxies are blocked copolymerised and supplied through emulsion chemistry. The mol % of silicone to epoxy is varied and coupled with surfactant and filler selection to obtain properties that are unique for a variety of applications. Wearlon® Super F-3M is one of the most hydrophobic of all the Wearlon® coatings, having a low surface tension when in contact with water, resulting in drag reduction. Because of its excellent abrasion and corrosion resistance it is being used in a variety of marine applications including zebra mussel control.

Developing a coating that was inclusive of Selektope® has been key to producing a more impactresistant, yet flexible and low abrasive epoxy silicone coating system that shows excellent antifouling performance.

The trialing of the Wearlon® epoxy-silicone product containing Selektope® was conducted at I-Tech's test facility on the west coast of Sweden over a period of 19 months. Test panels were coated with two layers of the test product by a roller. For the formulations that underwent panel testing, a concentration of 0.3% Selektope® w/w of the final wet paint mixture was used to ensure the steady release of the biocide.

A successful formulation was achieved through the addition of a 1-metoxy-2-propanol solution of Selektope® to component B of the two-component system of Super F-3M. Traditionally, when formulating rosin gum-based or acrylic-based antifouling paints, Selektope® is always best added to the paint as a solution. In order to add it to the formulation, it should be dissolved in an appropriate solvent before adding pigments, metal oxides (e.g. ZnO), fillers, binder and other additives.

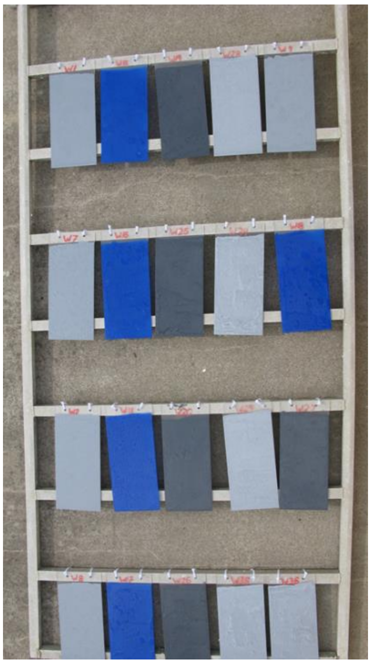


Fig. 16. Reference silicon epoxy-coated test panels submerged in April 2016 off the west coast of Sweden.

Fig. 17. Month 18 results

At the 2-month inspection, all reference panels had plenty of barnacle fouling. Some of the test panels had a few barnacles attached except F-3M with 0.3% Selektope®. At 18 months, panels coated with F-3M with addition of 0.3% Selektope® had no fouling, whereas every other test panel was completely covered in barnacle fouling.

Conclusion

The trial of the Wearlon® Super F-3M range product with Selektope® included concluded that the addition of Selektope® to the Wearlon® epoxy-silicone coating resulted in significantly improved antifouling properties when exposed to raft tests in sea water. In the future, the partners are convinced that epoxy-silicone coating technology will achieve wider acceptance on ocean going vessels due to Selektope®-powered antifouling performance.

5. Conclusion

Selektope® is currently being used on over 300 vessels and I-Tech anticipate this number growing significantly in the near future. Independent data analysis of added resistance on the ship hull, dive inspections and static panel tests confirmed, and continue to confirm, the barnacle repellent power of this biotechnology when used in marine antifouling coatings. Further research efforts conducted by I-Tech confirm that it is possible to add Selektope® to a variety of materials not only to traditional marine paints. This can broaden the scope of use to other areas that are not coated today, but that would benefit from protection against barnacles. I-Tech intends to continue looking for new materials where Selektope® can be incorporated as well as enabling the use of the biotechnology in all currently used antifouling solutions on the market today and in the future.

Acknowledgement

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