Technical Paper

Sustainable antifouling by controlled release from polymer-bound Selektope®.

November 2022

Key facts

- **Project end:** 2022
- **Project partners:** I-Tech & RISE Research Institutes of Sweden
- **Compounds:** Selektope® (common name: medetomidine).
- **Type of testing:** Static panel tests - 10 months
- **Test location:** Kristineberg Center for Marine Research and Innovation - West Sweden

Introduction

Biocide-containing antifouling coatings are widely used to prevent the accumulation of marine biofouling on vessel underwater surfaces. The adhesion of microbial slimes, macroalgae and hard-shelled organisms such as barnacles on vessels create increased friction as the hull glides through the water. This can lead to reductions in vessel manoeuvrability, increased weight and reduced speed, all of which can result in increased fuel consumption and maintenance costs.

A study conducted by I-Tech and Safinah Group found that of 44% of 249 large,-ocean-going vessels inspected in dry dock had over 10% of their underwater hull surface covered with hard fouling. If you extrapolate that to global fleet scale, we estimate that (based on data published in study by Michael P. Schultz in 2011 for added resistance due to hard fouling) just 10% hard fouling coverage could be responsible for at least 110 million tonnes of excess carbon emissions per year, and an additional US $6 billion spent annually on fuel from the international shipping industry.

As the first line of defence against biofouling, antifouling coatings must ensure continued protection, as biofouling conditions change and intensify in warming waters due to climate change.

Today, there are a limited number of biocides available for use in marine antifouling coatings. For these biocides, a sustainable release rate of across the entire intended lifespan of a coating product is essential for effective biofouling prevention. For example, antifouling coatings for large, merchant vessels need to deliver adequate antifouling protection for up to five years vessel operational time between drydocking, as dictated by safety obligations at an international level.

If we look to the past for inspiration on how to create better antifouling coatings for the future, unrivalled biocide release rate control is achieved when a biocide is covalently attached to a polymer chain, with the biocide release only occurring when the covalent bond between the biocide and the polymer is hydrolysed upon contact with water at at the coating surface. This was the highly effective controlled release rate method used for the high-performance tributyltin (TBT)-based coatings of the past.

In recent years, I-Tech AB and RISE Research Institutes of Sweden (RISE) have collaborated to prove the concept that the barnacle-repelling biocide, Selektope® can be attached to a polymer chain as an alternative method for its introduction into antifouling coatings and to improve the control of its release.

Background

For over forty years Tributyltin (TBT), an organotin biocide, was used in antifouling paints, mostly commonly as a booster biocide alongside cuprous oxide. Due to its strong ecotoxicity and its negative ecological effects observed worldwide, TBT was phased out of use from 1st Jan 2008 by the International Maritime Organization (IMO). Unfortunately, coatings that made use of if TBT in the past delivered superior antifouling performance that can, in part be attributed to its mode of controlled release facilitated by being covalently attached to a polymer chain.

Since the TBT ban, the number of other biocides available for use has decreased and R&D efforts to develop new antifouling technologies has intensified in a quest to ensure continuously high antifouling performance.

Today, the three most common types of marine antifouling coatings are: self-polishing copolymer (SPC), controlled depletion polymer (CDP) coatings and, foul release (FR). In SPC and CDP coating types, the biocide is not chemically bound to anything, it is evenly dispersed in the matrix and is released as the matrix erodes/polishes. Alternatively, the biocide could be dissolved as water penetrates the paint film and the biocide would diffuse out to the coating surface. However, there is a risk that biocide molecules could diffuse out too early.

One way to stop biocidal molecules from diffusing out of the coating film prematurely is to attach them to a large carrier, such as a polymer. In this set up, the biocide is covalently bound to the polymer chain. The bond must be hydrolysable so that it breaks upon contact with water and the biocide gets released as the coating film erodes/polishes. You can control the release rate of the biocide based on the chemistry of the covalent attachment and the composition of the co-polymer and so, ultimately control the polishing rate of those coating systems. This is what made TBT so successful as a biocide in antifouling coatings with a long lifespan for commercial, ocean-going ships.

What is Selektope?

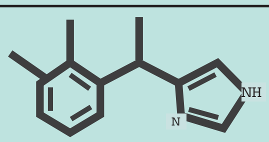
selektope®

Selektope (common name: medetomidine) is an active agent developed, patented and registered by I-Tech AB for use in antifouling coatings. It can be used to reduce hard fouling (primarily barnacle growth) on vessels and other underwater structures.

Currently, the most common way to introduce Selektope into a coating matrix and to prevent its premature depletion is via the Selektope interacting with a carrier (pigment particle) in the paint mixture. The Selektope remains in the matrix through electrostatic interactions with the metal pigment where it “interacts” with the inorganic particles. It does not form a new molecule.

Cuprous oxide, zinc oxide and iron oxide are commonly used. ZnO is advised as the best pigment particle for maximum Selektope adsorption.

For this method of introduction, the strength of electrostatic interactions is controlled both by pH and ionic strength of the surrounding medium, which might vary the rate of release in different waters, although most marine waters are similar.

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

Concept and strategy

I-Tech AB and RISE Research Institutes of Sweden created a synthesis method for a Selektope-containing monomer and the polymerisation of that monomer was developed as a means to improve/control the release rate of the biocide in marine antifouling coatings.

The theory behind polymerising a Selektope-containing monomer was that if Selektope was covalently attached to the backbone of a polymer it would hydrolyse and its rate release would be significantly improved.
(A monomer is a small molecule that can be reacted with itself or with other monomers to make a polymer, each monomer is like a link in the polymer chain. A homopolymer is a polymer made up of the same type of monomer. A co-polymer is built up of two or more different monomers.)

A secondary objective was to ascertain whether polymerising the Selektope-containing monomer solved any previously encountered gelation issues in paint products during storage. For example, silyl acrylate coatings are sensitive and usually do not have a shelf life of more than six months when stored.

For the coating of larger vessel hulls this is not an issue since the paint is produced and supplied "on demand" at the shipyard. However, for leisure boats using SPC coatings as opposed to CDP paints, gelation and shelf life of paint products are an issue.

Therefore, the intended outcomes of this research were to:

- Prove the concept of using polymer-bound Selektope to achieve the same control of release rate achieved by TBT-coating systems of the past.

- Solve any issues with gelation in stored paint products.

The approach

Initially, work was conducted by I-Tech and RISE to screen various monomers and synthesis routes as well as attempting the polymerisation of them.

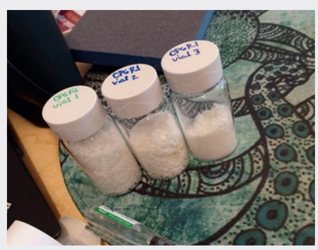
Finding ways to create hydrolysable covalent bonds to Selektope is not only of interest to create monomers but can potentially be used in other carrier structures.

Equipped with better understanding of what monomers might be feasible, during the second phase I-Tech and RISE commenced work to refine the method and to synthesise some polymers.

After this, I-Tech and RISE had some success creating the monomer and the chemistry used to attach the Selektope molecule to the monomer was patented.

I-Tech and RISE then proceeded to scale-up and develop synthesis methods. In the end, four different monomers were used to make a co-polymer. Since the collaborative R&D teams were equipped with much more knowledge and experience from the initial phases, they knew which combinations worked best.

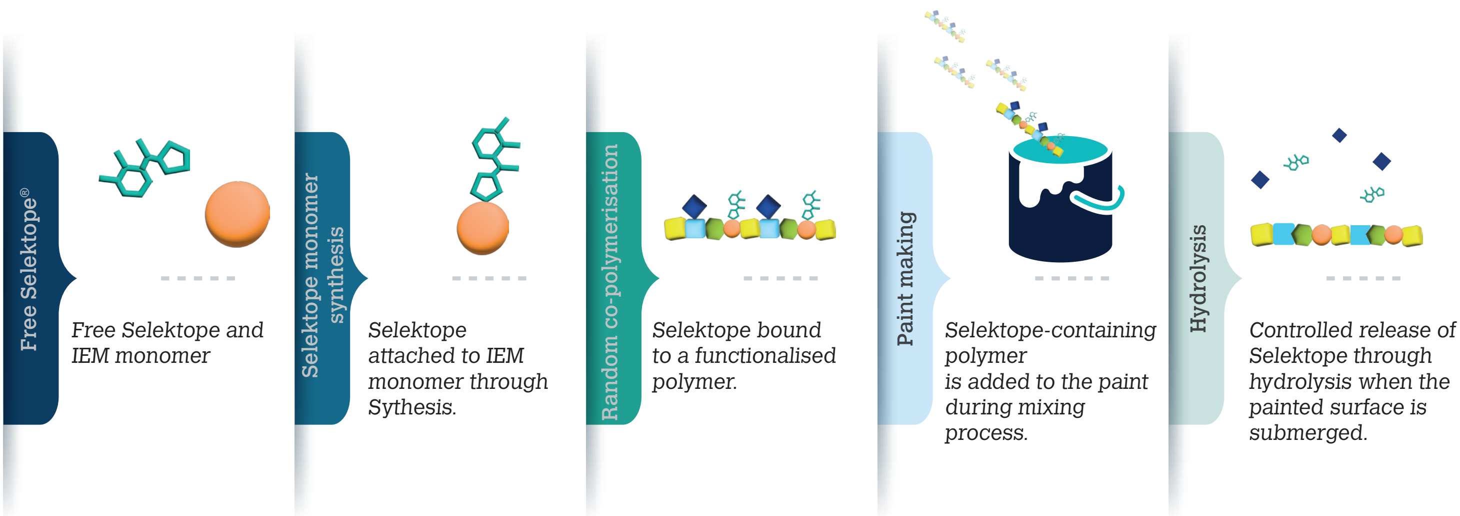
Therefore, the aim of the final phase was to refine the polymerisation and to create a polymer that can be used as a binder system in paint.



Today, zinc acrylate and silyl acrylate are common binders used in SPC coatings. Therefore, I-Tech and RISE tried to make a monomer that could be added in the polymerisation of silyl acrylate to make them even better.

During the final phase, it was found that keeping the monomer mixture close to what is commercially available with the silyl acrylates today yielded the best results.

Attaching Selektope to a polymer chain



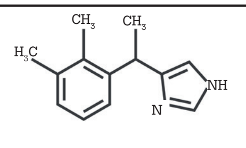
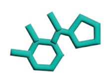
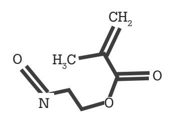
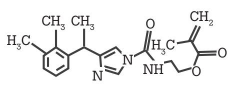
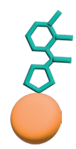
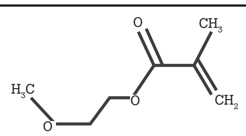
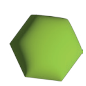
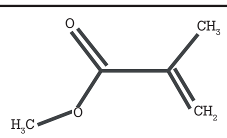
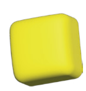
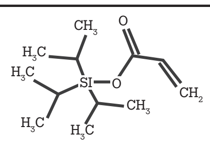
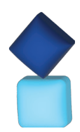
Name	**Structural formula**	**Symbol***
Selektope®		
IEM		
M6 (Selektope monomer) 6 mol %		
2-MEA 9,4 mol %		
MMA 63,45 mol %		
TIPSA 21,15 mol %		

Figure:
The concept of attaching an active agent (Selektope) to a monomer, polymerising it a to a copolymer with other monomers and the hydrolysis of the polymer when in contact with water to release the biocide and form a water soluble polymer.

Table:
List of monomers used in the concept formulations together with their structural formula.

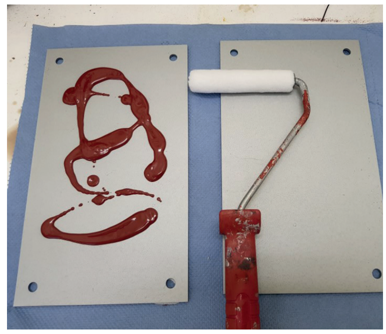
**Symbols were generated for use in illustrations*

Test preparations

The incorporation of the Selektope functionalised monomer in the polymer backbone was verified by diffusion NMR. The release of Selektope due to hydrolysis was verified in artificial seawater by laboratory studies followed by HPLC-measurement.

Formulations were prepared in which the total concentration of Selektope was similar, both when added bound to pigment as well as when added covalently bound to polymer.

The first test panels with coating formulations making use of a Selektope-containing polymer were put into the water in early June 2021 in waters off the west coast of Sweden at the Kristineberg Marine Research Center.

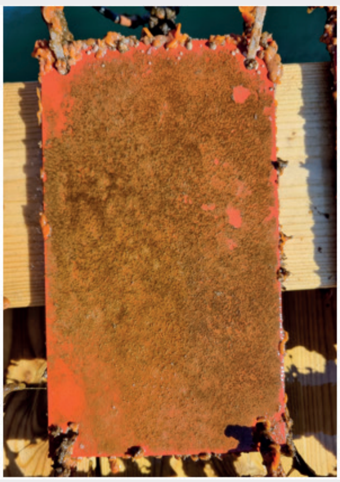


Test panels were coated with SPC copper-free formulations comprising:

- Panel 1: SPC control coating with no Selektope®.
- Panel 2: SPC with pigment-bound Selektope and 1% zinc pyrethione.
- Panel 3: SPC with polymer bound Selektope® and 1% zinc pyrethione.
- Panel 4: SPC with polymer bound Selektope®, no co-biocide.

Results - 10 months

Panel 1: Control



Panel 2: pigment-bound Selektope + ZnPt

Panel 3: polymer-bound Selektope + ZnPt

Panel 4: polymer-bound Selektope

Panel 1 (SPC control coating with no Selektope or biocides) was covered with all kinds of organisms.

Panel 2 (with “free” Selektope and zinc pyrethione co-biocide) had no hard fouling, but some soft fouling.

Panel 3 (SPC with polymer bound Selektope and zinc pyrethione co-biocide) had no hard fouling, but some soft fouling.

Panel 4 (polymer bound Selektope without a co-biocide) had a few organisms attached – this confirms why a co-biocide is required.

Conclusions

- There are no polymers on the market with Selektope. I-Tech and RISE have proven the concept and how it works.

- Self-polishing co-polymers containing Selektope that covalently attach along a polymer backbone can be synthesised.

  - RAFT polymerisation to control kinetics and molecular mass are needed for polymer stability.
  - Selektope was released upon hydrolysis in artificial seawater.
  - Linear release from polymer during months 1-4.
  - Release from formulation with polymer-bound Selektope was below limit of detection.

- The Selektope functionalised acrylic/methacrylic monomer for incorporation in polymers could be synthesised with good yield. Acrylic monomers are very unstable and regularly gelled before homo/co-polymerisation.

- Good antifouling efficacy of the formulation containing polymer-bound Selektope in static field test was achieved over a ten month period. Tests are ongoing.

- Proving this concept in silicone-based, foul release coatings will be a future focus for I-Tech.