Pre-adsorbed Selektope®

Creation of a new carrier system for Selektope® via pre-adsorption on Zinc Oxide for enhanced antifouling performance

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Abstract

Over the past five years, I-Tech's team of R&D scientists have discovered new ways in which the first-of-its-kind biocide, Selektope® can be introduced to marine antifouling coatings with little or no effect on formulation chemistry and in combination with other biocides.

Selektope is the brand name of the active agent medetomidine patented and registered for use in marine coatings by I-Tech AB. It has a unique mode of action amongst other biocides used in marine antifouling coatings because it repels the target organism rather than killing them. This is achieved by receptor stimulation whereby medetomidine interacts with the octopamine receptor of the barnacle larva causing the rapid kicking of the larva's swimming legs. This technology induces the effect that the barnacle has no option but to swim away from the coated surface.

Currently, the most common way to introduce Selektope into a self-polishing copolymer (SPC) coating matrix and to prevent its premature depletion is via Selektope interacting with a carrier (e.g., pigment particle) in the paint mixture. The introduction of Selektope, which is supplied as a powder, into a paint during the manufacturing processes is preferably done by first dissolving it in a solvent and then adding it into the wet paint matrix. By adding the active substance early in the paint making process, the chances of Selektope adsorbing onto the surface of other paint components (e.g., inorganic metal oxide pigments) are maximised. The Selektope attaches to the pigment surface through molecular interactions, rather than being free in the wet paint.

Although the controlled release of Selektope in SPC coatings has proved successful using the introduction method described above with multiple products commercialised to-date, recent I-Tech R&D efforts have focussed on obtaining proof of concept that pre-adsorbing Selektope on the carrier compound zinc oxide (ZnO) improves coating stability, reduces the risk of viscosity increase and improves biocidal leaching for sustained antifouling performance. By "pre-adsorbed" we mean adsorbing Selektope on the surface of a pigment from Selektope solution, followed by separation evaporation of the solvent to obtain a powder additive of Selektope adsorbed on the surface of the pigment. This pre-adsorption process is completely external from the actual paint manufacturing process. Tests conducted to-date show strong results and I-Tech is continuing work in this research field.

An additional proof of concept was obtained for the addition of Selektope pre-adsorbed on ZnO to silicone-based foul release coatings. If Selektope is not properly incorporated into a foul release coating matrix it will leach to the surface of the coating too fast. Therefore, this new method of introducing Selektope pre-adsorbed to ZnO could open a route for the use of the biocide in these types of coating systems. Another major benefit is that the addition of Selektope, pre-adsorbed on pigment particles, does not require fundamental reformulation. By contrast, it is even possible to add it into ready-made paint. Positive test results have been obtained to-date and further testing is underway in this research field.

What is Selektope®?

Selektope (common name: medetomidine) is an active agent developed, patented and registered by I-Tech AB for use in antifouling coatings. It is a highly selective technology that induces effect on the target organism at very lowsmall concentrations (nano molar).

When a barnacle larva comes into contact with Selektope, they become hyperactive, and their swimming legs perform around 100 kicks per minute. This is due to their octopamine receptor being stimulated by the medetomidine. The effect is reversible, and the larvae quickly return to their normal state when not exposed to Selektope. In this way, the larvae cannot attach to a surface painted with Selektope and, at the same time, there is no fatal impact.

Selektope can coexist with all existing, approved biocides and other ingredients in a paint matrix. However, how and when it is added during the production process is key to controlling its release rate from an antifouling paint.

This active agent is preferably dissolved in a solvent before being added into the paint matrix. The conventional formulation method is to add the Selektope solution together with fresh metal oxide pigment, such that the Selektope molecules are able adsorb on the pigment surfaces in-situ during paint production. Cuprous oxide (Cu^2O), zinc oxide (ZnO) and iron oxide (Fe^2O^3) are commonly used. Selektope adsorbed on ZnO in-situ during the paint production process is the most common method.

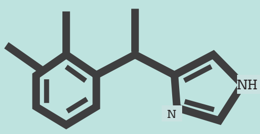
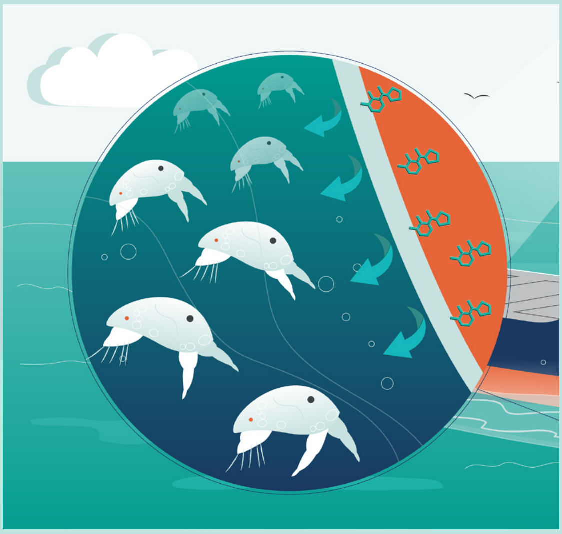
CAS-No. EINECS-no	86347-14-0 Not listed
IUPAC Name	4-[1-(2,3-dimethylphenyl)ethyl]-1H-imidazole
Other common name	Medetomidine
Molecular formula	$C_{13}H_{16}N_2$
Structural formula	
Molecular weight (g/mol)	200,28 g/mol

Figure 1. Selektope: molecular and structural formula



The Challenge

Reinforcing paint stability

To-date, Selektope has been introduced as a co-biocide into a range of self-polishing co-polymer (SPC) systems. The first antifouling coating systems commercially introduced to the ocean-going vessel market that made use of Selektope were silyl acrylate SPC coatings, with one premium coating developed as a copper-free solution.

Selektope can also be used in zinc acrylate, copper acrylate and nano acrylate SPC coatings.

Silyl acrylate SPC coatings are generally sensitive, and gelation and instability problems can arise if the paint products are stored for too long. In fact, most silyl acrylate systems have a shelf life of around one year only. This issue being that the viscosity of the paint products increases over time, a process known as gelation. Gelation in antifouling coatings creates issues during the application process since paint with a higher viscosity can clog up the tip of the spraying nozzle, resulting in the paint not being sprayed well, or even at all. If the paint is thinned to make it spray-able, it may no longer have the right properties. Gelation may also influence the general performance of the coating, e.g., its polishing and antifouling properties.

The presence of free Selektope molecules may influence the shelf-life of silyl acrylate-based paint. In the presence of trace amounts of water, Selektope catalyses hydrolysis of the silyl ester bonds in the silyl acrylate polymer. Hydrolysis causes the formation of carboxylates on the polymer chain which upon coordination to metals in the paint formulation cause gelation. It is, therefore, important to anchor Selektope molecules with other paint components, preferably through adsorption on metal oxide pigments, and thereby minimise the amount of free Selektope molecules in the wet paint and slow the rate of gelation. To prevent the hydrolysis, and subsequent gelation, it is also important to remove traces of water in the silyl acrylate paint. Selektope is, therefore preferably combined with a water scavenger additive in the formulation.

Although the paint manufacturer that first commercialised Selektope-containing silyl acrylate SPC coatings reports that they have encountered no issues to date, this is an area of R&D focus for I-Tech since minimising the effect of Selektope on silyl acrylate instability will further future-proof the use of the biocide in advanced marine coatings.

Concept and Strategy

Although the conventional method of adsorbing Selektope on pigment in-situ during the paint production process has been proven to extend the shelf life of silyl acrylate-based paints, to obtain controlled release and improved in-can stability , I-Tech R&D scientists have investigated a new concept of easy-to-use pre-adsorbed Selektope/pigment powder additive. This would offer the benefits of:

- Improved dispersion of the biocide.
- Reduced risk of high viscosity.
- Reduced exposure risk of the biocide during the paint production process.
- No redevelopment or change to formulation chemistry is required.
- Controlled release of Selektope from the coating.

By adsorbing Selektope on a carrier particle, such as ZnO, the amount of free Selektope molecules in the wet paint formulation can be limited. If there is no free Selektope, incompatibility is reduced . When Selektope pre-adsorbed on a metal oxide pigment is used together with a water scavenger, the rate of gelation is significantly lower since there will be fewer free Selektope molecules and water molecules available to promote the hydrolysis of the silyl acrylate polymer, which consequently slows down the gelation process.

A secondary challenge that the I-Tech R&D team is continuously working on is to enhance the processes for introducing Selektope during the paint production process. The production of marine antifouling paints is done on industrial scale and so, improving the ease of use and reducing worker exposure to the biocide is of immense importance. The advantage of this concept is that supply of adsorbed Selektope on ZnO promotes and easier use of the biocide during the paint production process, this is because it is easier to handle (it is heavier and airborne contamination risk is reduced) and the risk of exposure is lowered. This also facilitates fast and easier production since time is saved by the pre-dissolving of Selektope in solvent having already been completed before the material is received at the paint production facility.

The omission of the dissolving Selektope in solvent stage also reduces dermal absorption risk. Although currently inhalation and dermal penetration risks are addressed by the sealed, dissolvable packaging in which Selektope powder is supplied that is added directly into the paint batch during the production process.

To further this concept, small amounts of metal oxide pigments with Selektope pre-adsorbed can be added to silicones, epoxy silicones etc. This opens up a route for Selektope to be used in silicone-based foul release coatings. This may require some reformulation to existing formulation concepts, but not a fundamental reformulation.

The approach

I-Tech R&D scientists used Selektope/ ZnO material in powder form produced by the adsorption method.

The Selektope was first mixed with solvent and ZnO powder. The suspension of ZnO and Selektope solution was stirred for period long enough to allow for the Selektope molecules to adsorb on the ZnO surface followed by evaporation of the solvent, yielding a dry Selektope/ZnO powder.

Test paint formulations containing the produced Selektope/ZnO powder were created to mimic commercially available antifouling coatings. Viscosity analysis was conducted for the silyl acrylate SPC coatings in order to assess the gelation and shelf-life. Water scavenger (TEOS, tetraethyl orthosilicate) was added to the SPC formulations to remove traces water, hence further inhibit the gelation process.

The antifouling properties of the produced Selektope/ZnO powder were tested in silicone-based foul release coatings. This was done by addition of the powder material to ready-made commercially available silicone-based foul release coatings. The painted test panels were submerged in the sea on the Swedish west coast and the fouling on the coating surface was assessed regularly.

Results

Viscosity analysis of silyl acrylate SPC coatings

It is known that in-situ adsorption, i.e., adsorption as one step in the paint production process, of Selektope on the surfaces of commonly used pigments slows down the gelation of silyl acrylate-based paint. However, the research conducted by I-Tech R&D scientists investigated ex-situ adsorption of Selektope onto the surface of ZnO, i.e., the use of Selektope/ZnO additive in the form of a dry powder, produced in a process completely separated from paint production itself.

The results in Figure 2 clearly show that when Selektope is pre-adsorbed on ZnO as a carrier prior to being introduced to a paint matrix, i.e., ex-situ adsorption, the process of gelation is slowed, and the in-can stability of the silyl acrylate paint is improved.

The data in Figure 2 also show that it is particularly efficient to inhibit the gelation by combining pre-adsorbed Selektope/ZnO together with water scavenger.

Gelation is highly dependent on Selektope concentration. The paint samples tested in Figure 2 were prepared with higher Selektope concentration (0.3 wt.%) in order to accelerate the gelation process. In order to get a sufficient barnacle protection, usually a lower Selektope concentration of around 0.1 wt.% is sufficient for optimal antifouling effect. When testing with lower Selektope concentrations, gelation occurs, but at much lower rates.

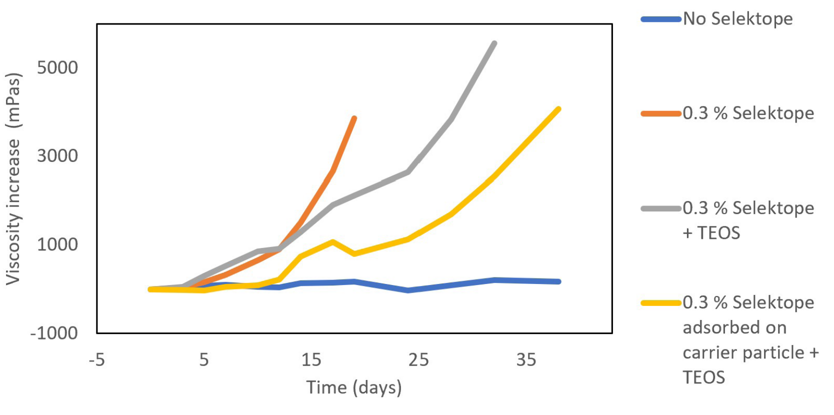


***Figure 2.** Viscosity increase (mPas) over time (days) for paint formulations containing no Selektope (blue), 0.3 wt.% Selektope added as solution (orange), 0.3 wt.% Selektope added as solution and TEOS (tetraethyl orthosilicate) (grey) and 0.3 wt.% Selektope adsorbed on carrier particle and TEOS (yellow).*

Static panel testing of foul release coatings with Selektope

Selektope adsorbed on ZnO was added to a commercial silicone-based foul release coating. The Selektope content in the Selektope/ZnO was 10 wt. % and the total Selektope content in the wet paint was 0.1 wt. %. The Selektope/ZnO powder was added to ready-made paint containing no other biocides.

Two comparative reference samples were made. The first reference did not contain Selektope, hence containing no biocides at all. The second reference contained 0.1 wt.% Selektope added as a solution (Selektope dissolved in 1-methoxy-2-propanol). The Selektope solution was added to ready-made paint containing no other biocides. The foul release coating topcoats were applied by brush in two layers on PMMA panels pre-coated with primer and tiecoat. The panels were divided into three sections where the upper sections were left untreated (undamaged), the middle sections were cut with a knife in the shape of a cross and the surface of the bottom sections were roughened with a sandpaper.

a.) No Selektope | **b.) 0.1% Selektope added in solution** | **c.) 0.1% Selektope pre-adsorbed on ZnO**

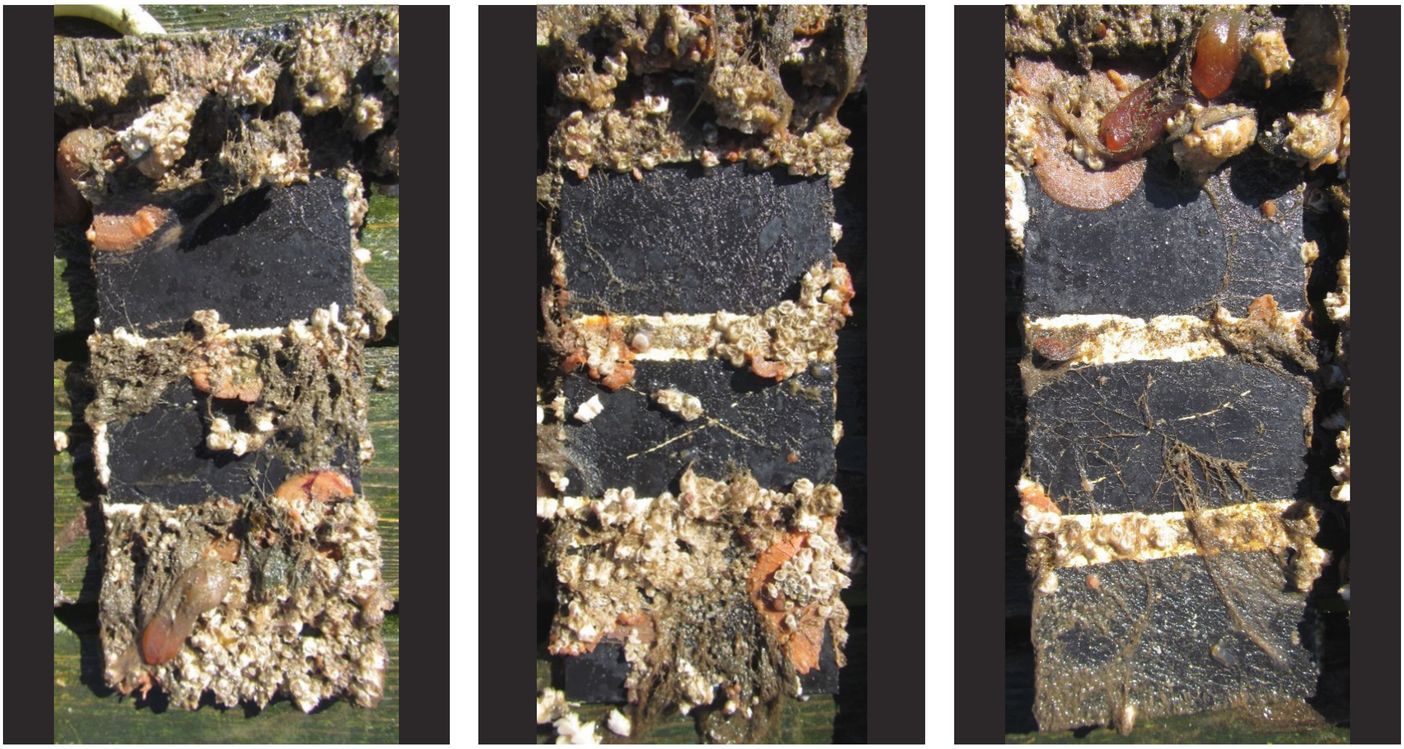


Figure 3. Panels with foul release topcoat after 419 days submersion in the sea outside of Tjärnö (west coast of Sweden). The panels are divided in three sections where the top sections were left undamaged, the middle sections have a cross cut with knife and the surface of bottom sections were roughened with sandpaper. The topcoats contain the following additive, from left to right a) no additive, b) 0.1 weight% Selektope added as solution and c) 0.1 weight % Selektope added as a powder additive consisting of 10 weight % Selektope adsorbed on the surface of ZnO.

The images in Figure 3 show that whereas the undamaged foul release coating generally are efficient in preventing fouling, damaged foul release coating surfaces are easily subjected to fouling. The roughened surfaces of the reference samples in Figure 3a and 3b were particularly densely populated with barnacles primarily, but also other fouling species. For the same panels there were also barnacles settled in the cross-cut in the middle sections of the panels.

By contrast the sample containing Selektope/ZnO only showed a few barnacles on the roughened surface and no barnacles in the cross-cut. Hence, post addition of Selektope/ZnO powder additive to ready-made foul release coatings inhibits the barnacle settling on damaged surfaces significantly compared to the reference samples without Selektope or with Selektope post added as a solution.

The results clearly show that damaged foul release coating surfaces need additional biocidal protection against fouling. It is also clear that the post addition of Selektope solution to ready-made paint entails a risk of premature depletion of Selektope from the coating, due to lack of available adsorption sites on the surfaces of other paint components for Selektope. This shows the importance of anchoring the Selektope to other paint components in order to control the leaching rate of the Selektope. One way to do this is to adsorb the Selektope on the surface a pigment, for instance ZnO as described in this paper.

Conclusion

Selektope/ZnO powder provides a new tool for the incorporation of Selektope into antifouling paints without the need for reformulation. The adsorption of Selektope onto a pigment carrier facilitates a more robust paint production and also mitigates the risk of shorter shelf life for silyl acrylates. Furthermore, it is an efficient tool to for adding Selektope in fouling release systems providing controlled release of Selektope over time.

Test results confirm that Selektope adsorbed on ZnO significantly improves the issue of increasing viscosity (gelation) in silyl acrylate SPC coatings. Also, that the addition of a water scavenger mitigates the gelation issue even further. However, although the viscosity increase is lower when we adsorbed Selektope on ZnO, compared to the presence of free Selektope in the paint matrix, it doesn't completely prevent the increase of viscosity.

Further work is needed to use the full potential and convert the promising results to a commercial product. The next steps for I-Tech R&D scientists are to increase the knowledge base around this work conducted to date. Work to refine the process of adsorbing Selektope on zinc oxide, through the identification of the best solvent and best zinc oxide material combinations that allow for maximum Selektope adsorption will also be undertaken. This will also include the optimisation of the ratio of Selektope and ZnO. Quantification of biocode release rates and upscaling will also be a focus of future work. I-Tech R&D scientists will also evaluate other non-soluble pigments such as ZnO and carbon black to study their performance.

Further study into the introduction of Selektope to non-polishing, foul release antifouling coatings via adsorption to ZnO pigment will be conducted.

Following on from achieving proof of concept for both the adsorption of Selektope to zinc oxide to reduce the issue of increased viscosity in silyl acrylate coatings and also introducing Selektope to foul release coatings using this method, further tests will be completed to study the release rate of Selektope from SPC and foul release coatings containing Selektope/ ZnO particles.

i-tech

I-Tech is a global biotechnology company operating in the marine paint industry. The company has developed and commercialised the product, Selektope. With Selektope, I-Tech is uniquely the first company to ever apply principles from biotechnology research in the marine paint industry to keep ship hulls free from marine fouling.

selektope®

Selektope is an organic, metal-free active agent added to marine antifouling paints to prevent barnacles from settling on coated surfaces by temporarily activating the swimming behaviour of barnacle larvae. This bio-repellent effect makes Selektope the only type of technology of its kind available to the marine paint manufacturers.

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