selektope®

Advancing Marine Coating Formulations with Selektope®

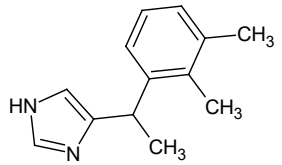
-Insights from Silyl Acrylate Systems

Ida Friberg

selektope®

Selektope®

-Keeps the Hull Barnacle-Free



- Organic molecule (medetomidine)
- Efficient against barnacles in low concentrations
  - 0.1 % by weight
- Non-lethal, temporary and reversible effect
- Biodegradable
- Tested and approved
  - On over 3000 vessels
  - In more than 30 commercial paints
  - By 7 of 9 the largest paint companies

- As little as 10% barnacle coverage on the hull requires 36% extra shaft power to keep the same speed*
- 1/3 of inspected ships had more than 10% barnacles based on in-docking study** made by Safinah Group

** Schultz et al. (2011), **Report availble at Selektope.com*

selektope®

Target organism and mode of action of Selektope

Making barnacle larvae swim away.

Receptor stimulation

Selektope stimulates the octopamine receptor in barnacle larvae.

Repelling mode of action

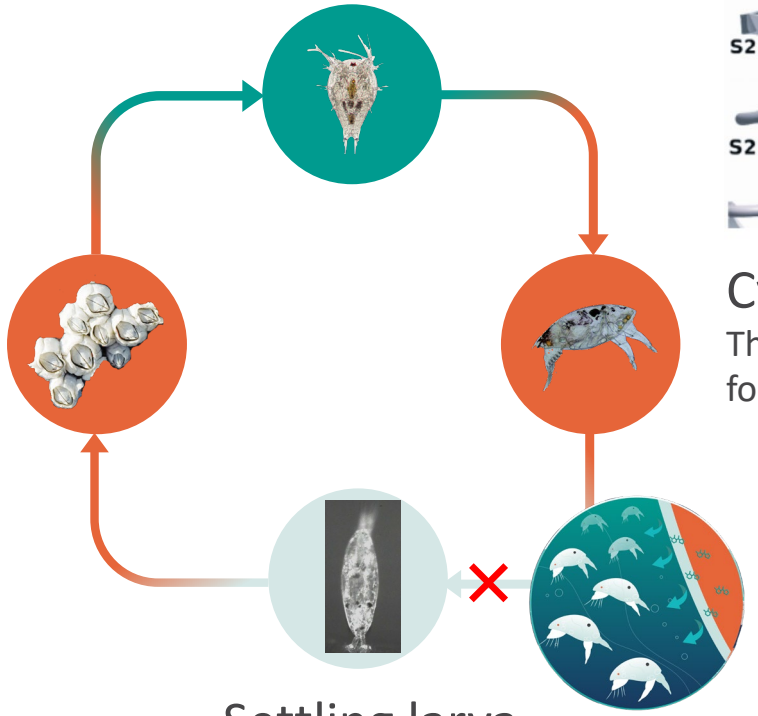
Their legs will start to kick with a frequency of around 100/min. Interfering with the surface exploration behavior necessary to settle.

Temporary effect

The effect is reversible and lasts for 2-3 hours. There are no long-lasting effects on the larvae.

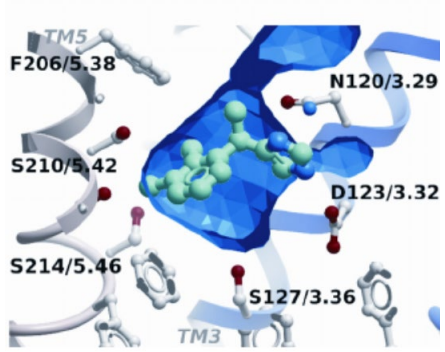
Nauplii larvae

Adult barnacles produce nauplii larvae.



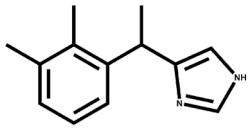
Adult barnacle

Once barnacles have started to grow, they attract more larvae, forming colonies.



Cyprid larvae

The cyprid larvae look for places to settle.



Settling larva

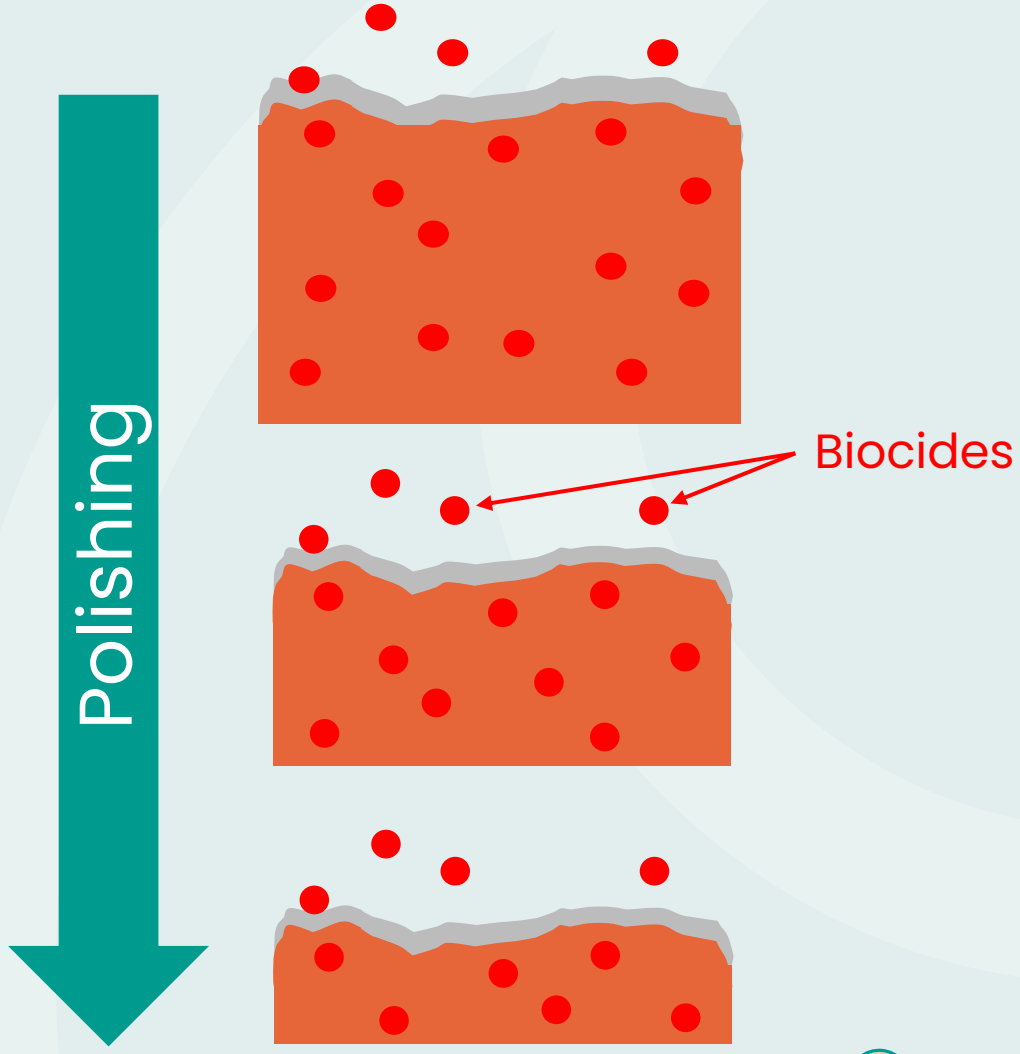
The settled larva metamorphose into hard shelled barnacles.

Octopamine Receptors from the Barnacle Balanus improvisus Are Activated by the α2-Adrenoceptor Agonist Medetomidine
Ulrika Lind, Magnus Alm Rosenblad, Linda Hasselberg Frank, Susanna Falkbring, Lars Brive, Jonne M. Laurila, Katariina Pohjanoksa, Anne Vuorenpa¨a¨ , Jyrki P. Kukkonen, Lina Gunnarsson, Mika Scheinin, Lena G. E. Mårtensson Lindblad, and Anders Blomberg

selektope®

Silyl Acrylate Co-Polymer (SAP) -based Coatings

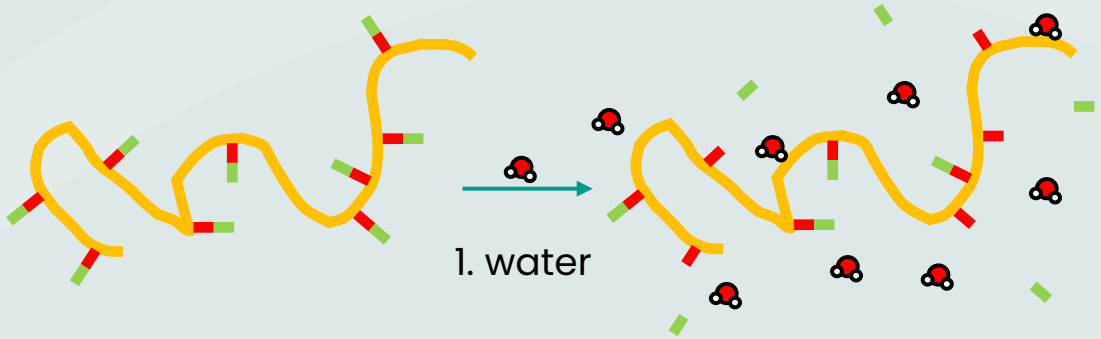
- SAP is a self-polishing coating (SPC) type widely used for marine antifouling.
- Biocides for fouling control.
- Hydrolysis in sea water
  - Controlled polishing
  - Maintained thin leach layer
  - Consistent biocide release
- Proper formulation principles important for achieving long shelf-life
  - Sensitive to water



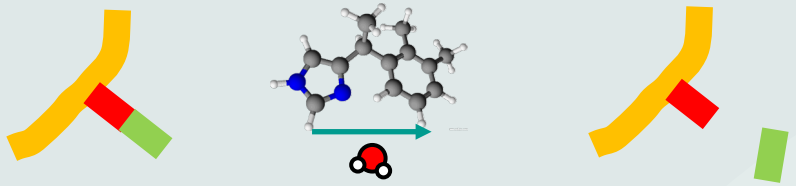
selektope®

Gelation in Silyl Acrylates – Root Cause

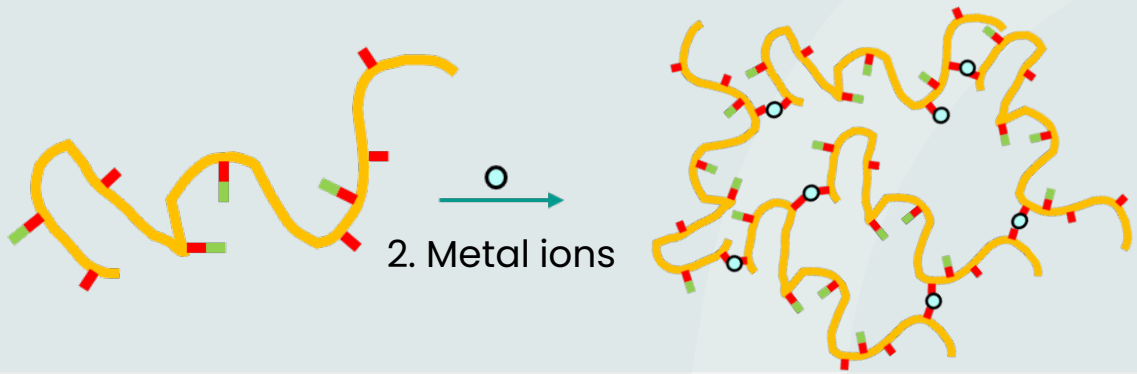
Silyl acrylates polymer hydrolyse in presence of water by design – It happens slowly, in all silyl acrylate paints when water is present, but is slow enough not to cause a big problem at least not at moderate temperatures.



Selektope® catalyses the hydrolysis - the reaction goes faster.



Hydrolysed polymer can **crosslink** in presence of metal ions, such as **Zn^{2+}** and **Cu^{2+}**, causing **gelation**.



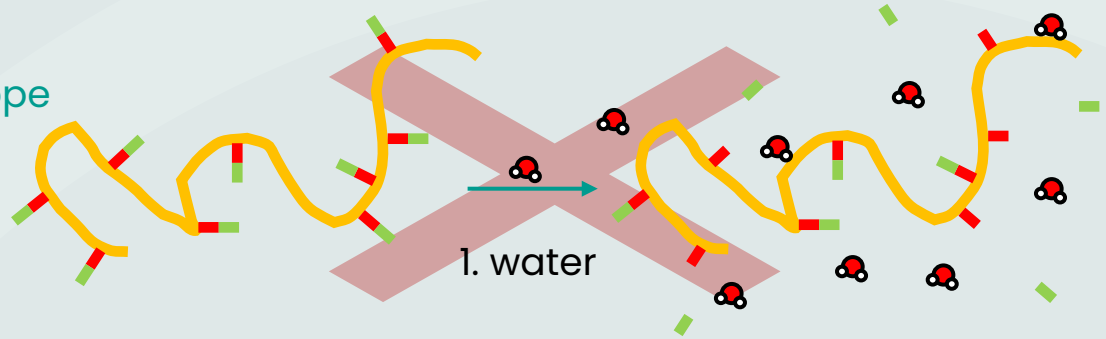
Root Cause: simultaneous presence of water, Selektope and metal cations (Zn^{2+},Cu^{2+})

selektope®

Prevent Gelation in Silyl Acrylates

Minimize water content in wet paint

- Add water scavenger before adding Selektope
  - TEOS*
  - pTSI*



*tetraethyl orthosilicate, para-toulenesulfonyl isocyanate

selektope®

Prevent Gelation in Silyl Acrylates

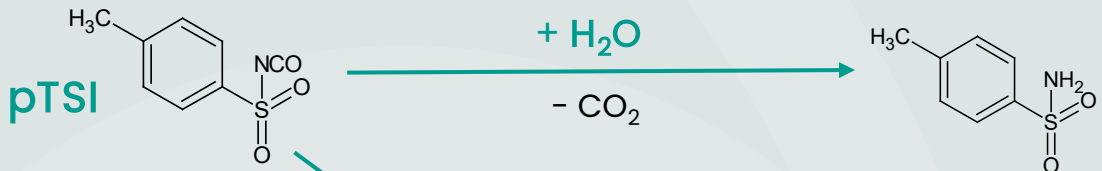
-TEOS and pTSI

TEOS

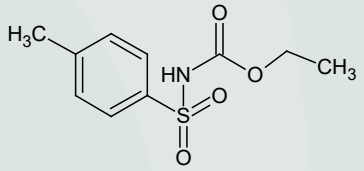
TEOS – water scavenger

pTSI

pTSI – water scavenger



pTSI - ethanol scavenger

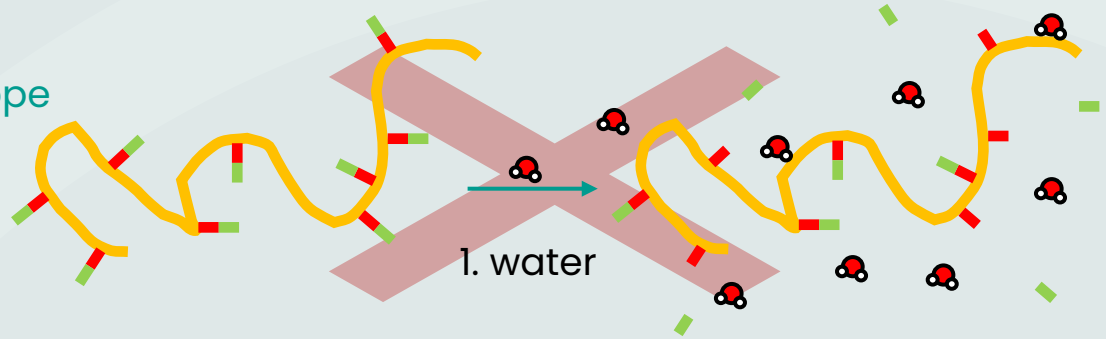


selektope®

Prevent Gelation in Silyl Acrylates

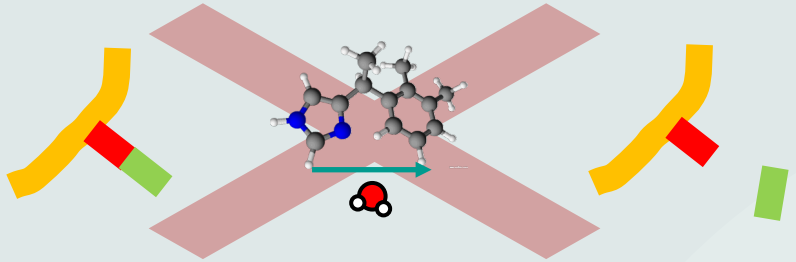
Minimize water content in wet paint

- Add water scavenger before adding Selektope
  - TEOS*
  - pTSI*



Minimize content of free Selektope

- Adsorb Selektope to carrier particles (e.g. ZnO, SiO_2)
  - Adsorption sites must be available
  - Add Selektope early in paint production
  - Keep the content of polar and protic solvents <5 wt.%



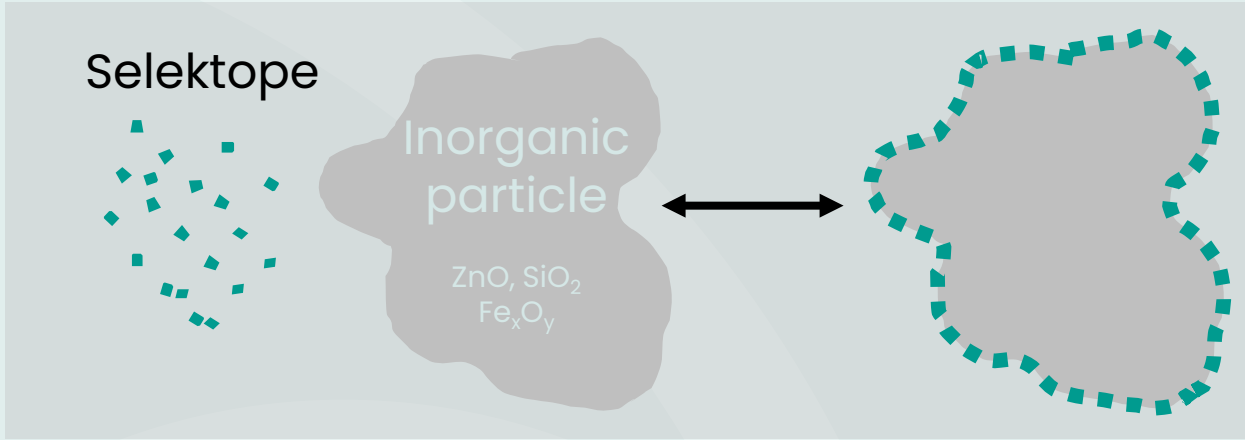
**tetraethyl orthosilicate, para-toulenesulfonyl isocyanate*

selektope®

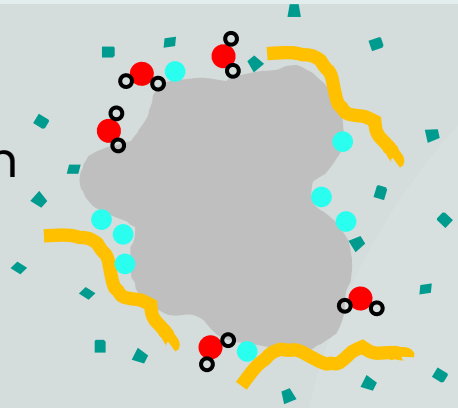
Prevent Gelation in Silyl Acrylates

-Selektope Adsorption on Inorganic Pigments

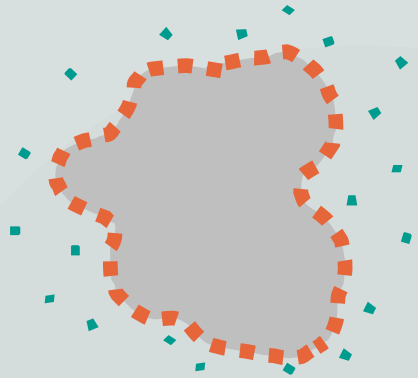
Available surface area



Less Selektope adsorption due to:



Competitive adsorption



Surface treatment

More Selektope adsorption due to:

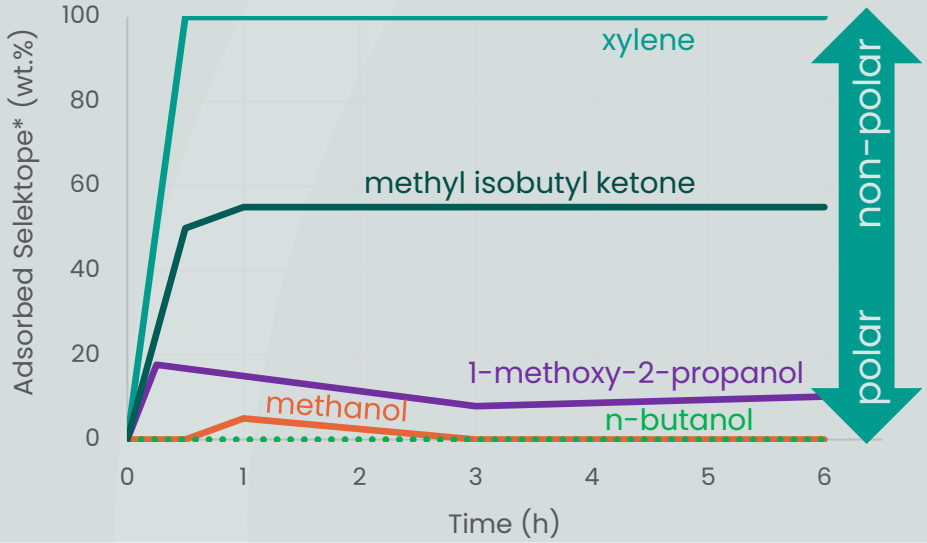
Larger surface area

selektope®

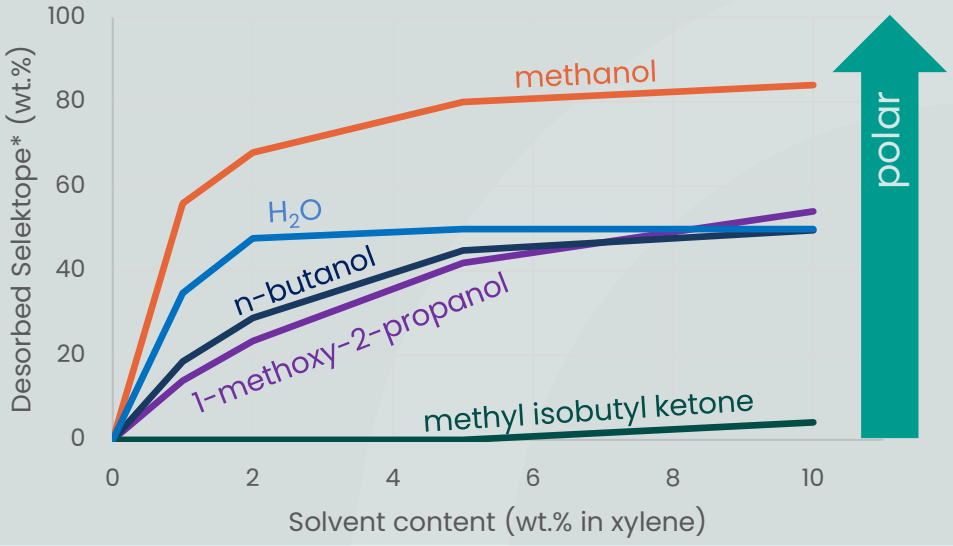
Prevent Gelation in Silyl Acrylates

-Selektope Adsorption on/Desorption from Inorganic Pigments

Adsorption favoured in **non-polar** and **aprotic** solvents (e.g. xylene)



Desorption favoured in **polar** and **protic** solvents (e.g. methanol)



selektope®

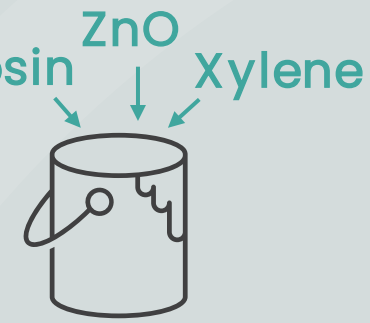
** Percentage of total amount of Selektope in the sample*

Suggested Formulation Procedure

-for High In-Can Stability

1 Resination

Rosin ZnO Xylene

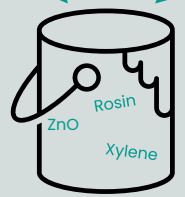


→ H_2O formed

2 Water removal

Addition of water scavenger

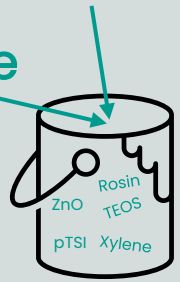
pTSI* TEOS*



3 Selektope adsorption

Carrier material (e.g. SiO_2)

Selektope



4 Other components

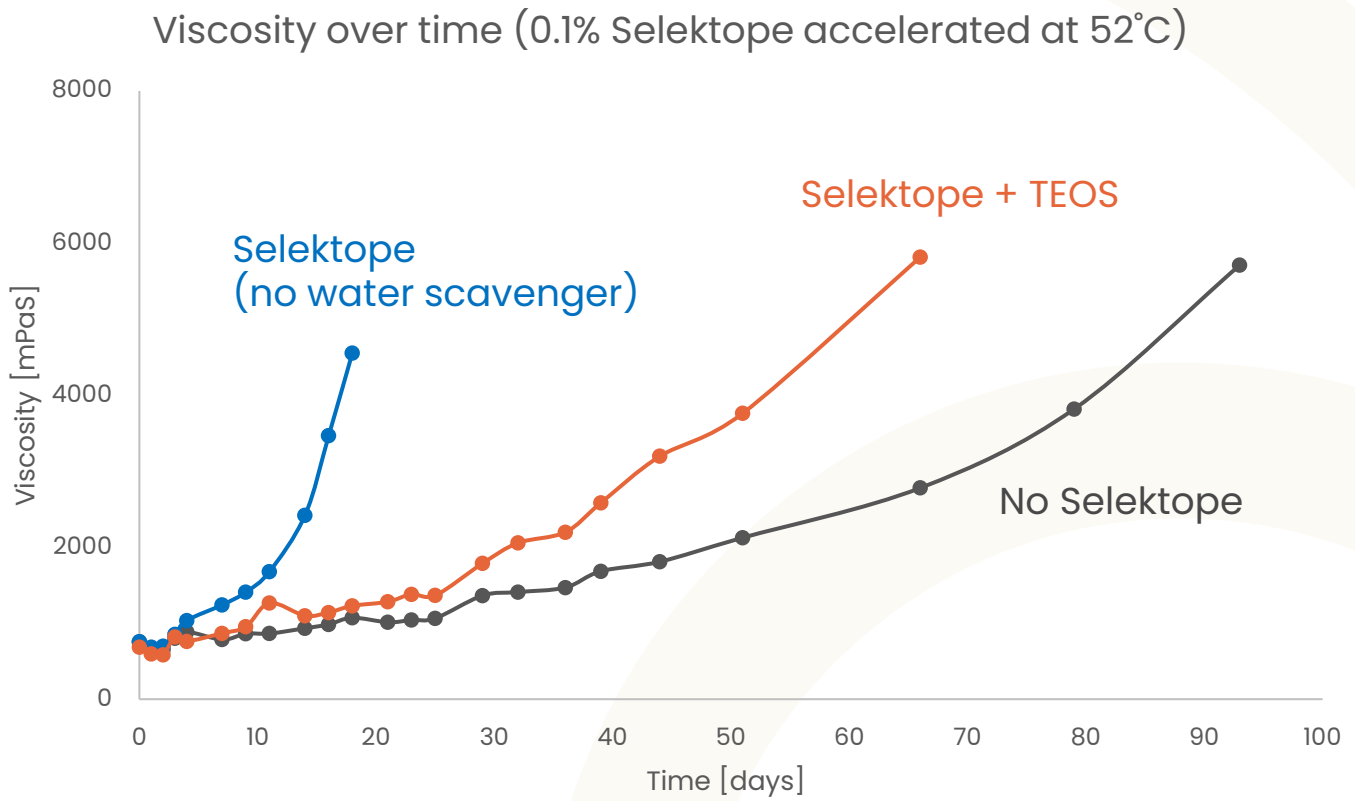
SAP Other

**1 molar eq. with respect to the amount H_2O formed in step 1*

selektope®

Silyl Acrylate Paint In-Can Stability Testing

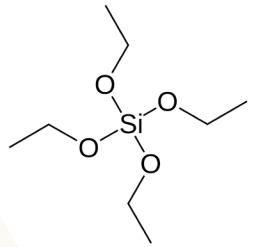
-Tests with Model Formulations



TEOS reduces gelation rate – but more can be done!

Additives to prevent gelation:

- **TEOS** – water scavenger



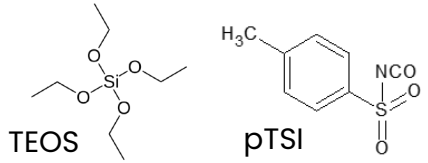
Test parameters:

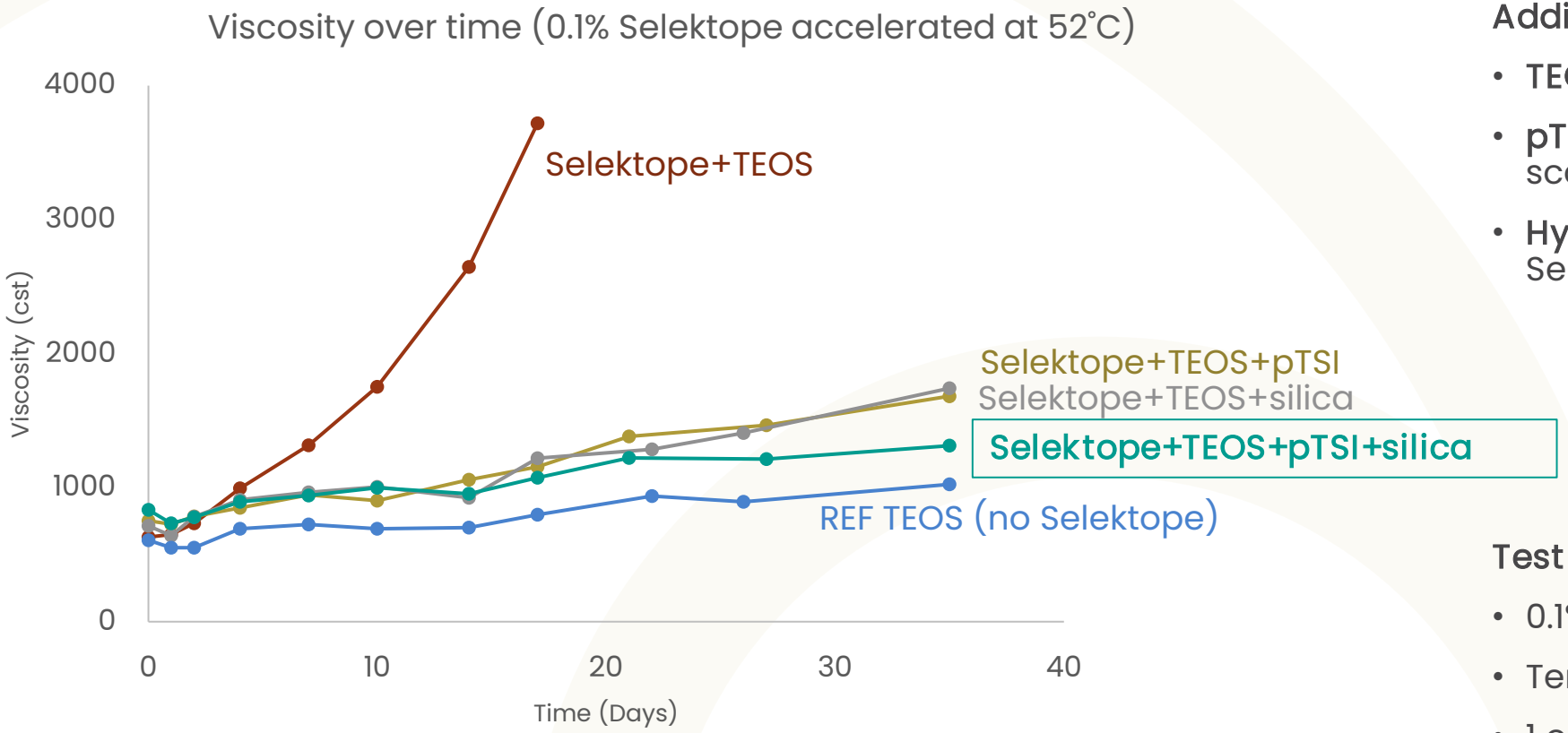
- 0.1% Selektope
- Temp. 52˚C (accelerated test)
- 1 eq TEOS and with respect to the calc. amount of water formed

selektope®

Silyl Acrylate Paint In-Can Stability Testing

-Tests with Model Formulations





The combination of **TEOS**, **pTSI** and **hydrophilic silica** efficiently slows down the gelation

Additives to prevent gelation:

- **TEOS** – water scavenger
- **pTSI** – water and Selektope scavenger
- **Hydrophilic silica-** high Selektope adsorption capacity

Test parameters:

- 0.1% Selektope
- Temp. 52˚C (accelerated test)
- 1 eq TEOS and pTSI with respect to the calc. amount of water formed

selektope®

Field Test to Prove Selektope Release

-Swedish West Coast, 83 days

No Selektope

+0.1% Selektope

+pTSI
+ 0.1% Selektope

Barnacles

Significantly fewer barnacles

Silyl acrylate based coatings

selektope®

Field Test to Prove Selektope Release

-Swedish West Coast, 83 days

No Selektope

+0.1% Selektope

+pTSI
+ 0.1% Selektope

Barnacles

No barnacles

Zinc acrylate based coatings

selektope®

Conclusions

-Successful Inclusion of Selektope® in Silyl Acrylate Antifouling

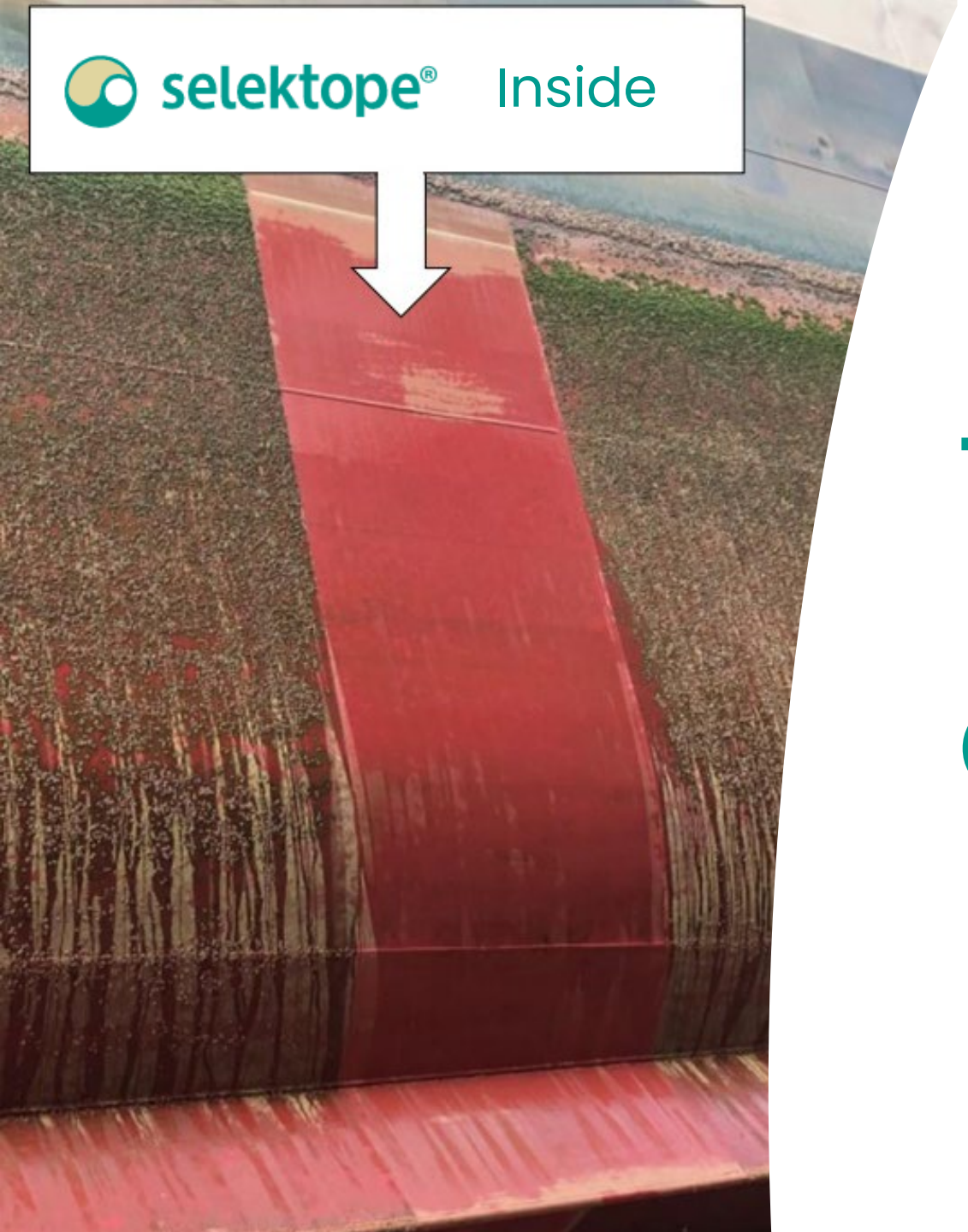
- Stable Selektope-containing silyl acrylate-based paint is made by the following key principles:
  - Minimize water
  - Minimize free Selektope

- The combined use of pTSI and TEOS results in:
  - Efficiently improved in-can stability of silyl acrylate-based paint containing Selektope.
  - Maintained release of Selektope from silyl acrylate-based coatings.

- Addition of hydrophilic silica further improves in-can stability
  - Selektope adsorbs on the surface of the silica

- Selektope is a biocide proven to efficiently repel barnacles and is successfully commercialized in multiple SPCs including silyl acrylate-based paint.

selektope®



Thank you!

Questions?

selektope®