Development of environmentally acceptable anti-fouling products for large ships in commercial use

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(Udvikling af miljøvenlig bundmaling til store skibe i kommerciel fart)

Performed by: EnCoat ApS

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Preface

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This project has benefited from our cooperation partners given below. We like to thank them for their patience and help:

Professor Sergey Dobretsov, Sultan Qaboos University, Muscat, Oman have assisted us with static raft tests.

Henrik Tofte Jespersen, Aproxi ApS, performing drying of silica aerogels with supercritical CO_2.

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Summary

Based on our patented encapsulation technology the aim was to combine the use of active compounds (co-biocides) with high efficacy at low concentrations in fouling control coatings for the trade fleet. Significant amounts of these active compounds leach to the sea from commercial fouling protect products. The encapsulation technology keeps the active compound in the surface film (leaching layer) and allows for a reduction of excess amounts of these compounds.

The effect of silica encapsulation technology was proven in antifouling coatings for yachts in 2018. Adapting fouling control coatings for the trade fleet and documenting effectiveness and environmental advantages is though more demanding as longevity is essential and needs to match current commercial fouling control products. To reach this goal it is essential both to document the encapsulation technology further as well as adapt coating formulations and document its fouling efficacy.

It has been shown that it is possible to produce and reproduce encapsulated co-biocides using different drying methods for the wet gel to achieve a dry aerogel encapsulated material. The significant difference between the encapsulated materials produced with the two drying methods (freeze-dried and supercritical CO_2-dried) was the porosity of the encapsulated co-biocides, which decreased using freeze-drying compared to supercritical drying. Both types of gels can be used in an Anti-Fouling coating achieving acceptable technical properties.

Parallel to the encapsulation work self-polishing coatings have been produced and optimized regarding wet stability and dry film properties. The binder systems used are Zinc acrylate and Silyl acrylate.

The initial raft tests showed no clear difference between the antifouling efficacy comparing coating including freeze-dried encapsulated material with a coating including supercritical dried encapsulated material (accounts for both CuPT and Tralopyril). To be able to compare encapsulated co-biocide with free co-biocide it is necessary to do long-term tests or as a minimum tests in aggressive environments.

Copper containing antifouling products with encapsulated CuPT have been produced with a reduction of both Cuprous oxide as well as CuPT. Testing in a high fouling pressure area (Oman) gives promising results after 6 months of static raft exposure. A few barnacles occurred on some panels, but small adjustments of the coating formulation gave results comparable to commercial products.

High fouling pressure shows that Tralopyril is protecting against hard fouling like barnacles. As soon as a complementary co-biocide against soft fouling is included in the formulation the dominant fouling is biofilm.

Patch tests made on Danish Home Guard vessels have shown good results for a traditional control depletion product over 3 years compared to a commercial reference coating. Following up with a self-polishing AF-product shows very promising results after approximately 1 year. This test is on-going.

Overall, the development has been very successful. Industrial interest has been growing significantly due to legislation, which is reducing the allowed use of biocides. This challenge is under our evaluation with further adaptation of AF-formulations and exposure tests. The encapsulation technology allows for further reduction of active compounds and is one of the technologies that can be used, further optimized, used and adapted to different fouling control systems.

Sammenfatning

På grundlag af vores patenterede indkapslingsteknologi har projektets målsætning været at bruge aktivstoffer med høj effektivitet og lavt indhold af i bundmaling til handelsflåden. I kommercielle bundmalinger bliver væsentlige dele af aktivstofferne (som modvirker begroning), udvasket i havet. Med indkapslingsteknologien fastholdes og virker aktivstoffet i malingens overflade film, hvorved der er mulighed for at reducere mængden af biocid.

Effekten af silika indkapsling af aktivstof anvendt i Anti-Fouling (AF) produkter til lystbåde blev dokumenteret 2018. Tilpasning af AF-produkter til handelsflåden med dokumentation af antibegronings effektivitet og miljømæssige fordele stiller væsentlige større krav, da det er afgørende at levetiden svarer til nuværende kommercielle AFprodukter. For at opnå denne målsætning er det afgørende at dokumentere indkapslingsteknologien yderligere, tilpasse produktformuleringer til store skibe og dokumentere antibegronings effekt.

Det er vist at det er muligt at producer og reproducere indkapslede co-biocider ved at anvende to forskellige tørremetoder til den våde gel for at fremstille tørt indkapslet materiale. Den signifikante forskel mellem indkapslet materiale der er tørret med to forskellige tørremetoder (frysetørret og superkritisk CO_2-tørret) var den indkapslede co-biocids porositet, som mindsker med frysetørring sammenlignet med superkritisk tørring. Begge typer af gel kan anvendes I en AF produkt, hvor acceptable tekniske egenskaber opnås.

Paralllelt med indkapslingsarbejdet er der produceret og optimeret selvpolerende produkter, der er stabile og har acceptable film egenskaber. Binder systemerne der anvendt er Zinc akrylat og Silyl akrylat.

De indledende raft test viste ingen tydelig forskel i antibegroningseffekt mellem et product med frysetørret indkapslet materiale og et produkt med superkritisk tørret indkapslet materiale (gælder både for CuPT og Tralopyril). For at kunne sammenligne indkapslet co-biocid med frit co-biocid vil det være nødvendigt med lang tids test eller som et minimum aggressive begroningsbetingelser.

Kobberholdige AF-produkter med indkapslet CuPT er fremstillet hvor både mængden dikobberoxid og CuPT er reduceret. Raft test I et område med aggressiv begroning (Oman) I 6 måneder gav lovende resultater. Der var nogle få ruer, men små formuleringsændringer viser resultater der er sammenlignelige med kommercielle reference produkter.

I områder med meget begroning kan det tydeligt ses at Tralopyril beskytter mod ”hard fouling” som ruer. Når et co-biocid mod “soft fouling” tilføjes I formuleringen bliver den dominerende begroning biofilm.

Patch test er udført på et Dansk hjemmeværns skib og viser gode resultater for en traditionel polerende produkt i 3 år sammenlignet med en kommerciel reference produkt. Opfølgningen med et selvpolerende produkt viser meget lovende resultater efter knap 1 år. Denne test fortsætter.

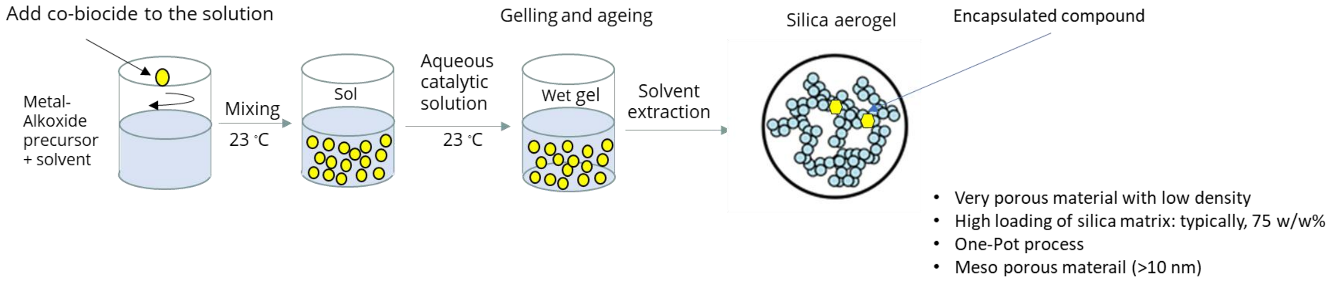
Overordnet har denne udvikling været meget succesrig. Den industrielle interesse har vokset significant grundet lovgivning, som reducerer den tilladte mængde brug af biocider. Denne udfordring evalueres af os med yderligere tilpasning af AF-formuleringer og eksponeringstest. Denne indkapslingsteknologi tillader yderligere reduktion af aktivstoffer og er en af de teknologier som kan anvendes yderligere optimeret , brugt og tilpasset andre typer af bundmalinger.

1 Laboratory production of encapsulated active compounds using silica aerogel technology

1.1 General principles

The general principle of producing gel samples is seen in figure 1. The silica precursors are mixed with solvent to create an alkoxide solution. After a couple of minutes, the active compound (biocide) is added to the alkoxide solution, so the silica precursors can form initial hydrogen bonding. When the biocide has been added, the alkoxide solution and the biocide form the ‘Sol’, which is one part of the ‘Sol-gel’ process. A basic catalyst solution is then added to the sol, and the gelling process slowly begins. All these steps are performed under ambient temperature and mixed with either a mechanical mixer or a magnetic stirrer.

The gel is considered a ‘Wet gel’ when it has settled. The next step in the process is drying said gel. This solvent extraction is either done by supercritical drying or freeze drying. We have seen that the drying properties create different pore structures depending on the chosen active compound. Therefore, choosing the best suitable drying method for the active compound is important. The main findings are that the wet gels with metal-organic compounds (which are described in the next section) can be dried by either method. Whereas the wet gels with the tested organic compounds are best suited for freeze drying.



- Very porous material with low density
- High loading of silica matrix: typically, 75 w/w%
- One-Pot process
- Meso porous materail (>10 nm)

Figure 1. Silica precursors mixed with alcohol, active compounds mixed in together with the alkoxide and finalized with a basic catalyst.

1.2 Used active compounds (biocides) for marine antifouling coatings

The different active compounds must be handled according to their solubility. If they are easily soluble in water or alcohol, it is important to find the optimal conditions. The materials used for encapsulating the active compounds in this case are mixtures of TEOS (silica precursor) and MTMS (silica precursor). The co-biocides tested here are shown in figure 2.

Metal-organic antifouling compounds

Even though the method’s general principle of encapsulation is the same, adjustments to the recipe are needed for each co-biocide. The encapsulation process for the metallic active compounds (Copper pyrithione, Zinc pyrithione and Zineb) has been produced in an easily reproducible way, and the dried gel has had similar properties when tested.

Organic antifouling compounds

Tralopyril is rather soluble in ethanol, which has consequences for the supercritical CO_2 drying procedure. The drying procedure was adapted to avoid loss of active compound. We have produced gels with similar properties using the freeze-drying and supercritical-drying methods.

The organic active compounds are more delicate during the encapsulation process. Therefore, the sol-gel formulations had to be adjusted to accommodate these delicacies. DCOIT has been encapsulated at a laboratory scale under acidic conditions during the encapsulation process. If the compound reaches a pH above 9 it will degrade, and its effectiveness will be parred to zero.

Medetomidine has also been encapsulated at a laboratory scale. The solubility of Medetomidine is very high both in water as well as ethanol. This makes Medetomidine difficult to work with, so the encapsulation can be further optimized.

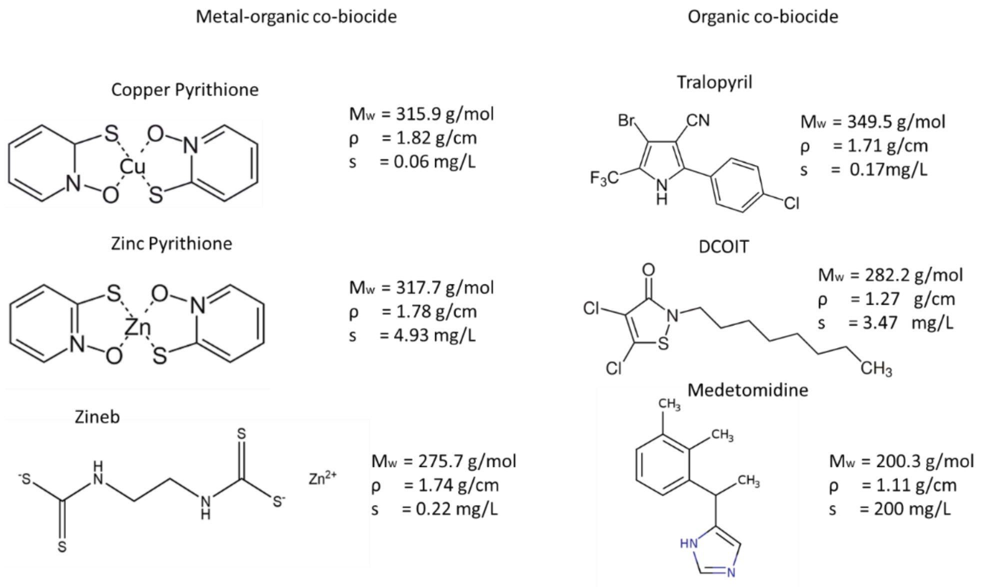


Figure 2. The active compounds used as co-biocides in antifouling coatings can be categorized into metal-organic- and organic-co-biocides. These compounds will be discussed further in the next section.

As the different active compounds also called co-biocides have different effect on marine fouling species it is often necessary to use more than one co-biocide in aggressive marine environments. Below there is an overview of the target organisms for the 6 co-biocides used for encapsulation with the technology described in this study.

Table 1. Overview over co-biocides used in this project.

Biocides	**Target organisms**	
Metal-organic compounds	*Soft Fouling*	*Hard Fouling*
Copper Pyrithione	Bacteria, fungi, algae	Barnacles (at high conc.)
Zinc Pyrithione	Bacteria, fungi, algae	Barnacles (at high conc.)
Zineb	Bacteria, fungi, algae	Barnacles
Organic compounds	*Soft Fouling*	*Hard Fouling*
Tralopyril	Bacteria, fungi, algae	Barnacles, polychaete, tubeworms, and bivalve mollusks to ascidianz, hydroids, bryozoans, and sponges
DCOIT	Bacteria, fungi, algae	Barnacles
Medetomidine		Barnacles

Ref.: M. Fink, T. Slothuus, and P. B. Larsen. Survey of Cybutryne. Environmental project No.: 1476.
(Danish Ministry of the Environment, 2013).

2. Drying of aerogels

Depending on the drying method, the silica aerogel formulation must be changed. Less water for supercritical dried active compounds and less ethanol for the freeze-dried aerogels. The framework of the active compounds has also been shown to determine what drying method is most suitable for them. The metal-organic biocides are typically well suited for supercritical drying, while organic biocides are more suited for freeze-drying.

2.1 Supercritical drying of aerogels – Description of principle

Supercritical drying is a common method for producing aerogels from wet gels by replacing the solvent in the pores of the gel with air. When the solvent of a wet gel is evaporated under normal conditions, the capillary forces acting on the gel network by the solvent lead to a collapse of the gel network. Using supercritical CO_2 to exchange the solvent in the gel pores makes it possible to extract the solvent and keep the pore structure of the gel when going to ambient temperature and normal pressure where CO_2 is a gas. Extraction conditions for supercritical carbon dioxide are above the critical temperature of 31 °C and critical pressure of 74 bar. In commercial drying equipment the gas is circulated in a closed system and reused.

2.2 Freeze drying of aerogels – Description of the principle.

The wet gel has to be frozen at a temperature that is below the freezing temperature of the solvent mixture in the wet gel. Freeze drying, also known as lyophilization, is a process that involves removing moisture from a material by sublimating frozen water directly into vapor, bypassing the liquid phase. It is commonly used to preserve perishable or heat-sensitive materials while maintaining their integrity and extending their shelf life.

3. Characterization of encapsulated active compounds

In this chapter examples are given of characterized samples that has been encapsulated and dried either with supercritical CO_2 or freeze drying.

3.1 Methods

The samples, listed in Table 2, were characterized to compare supercritical-dried and freeze-dried silica gels loaded with 75% biocide by weight. Prior to the characterization study, all samples were dry-milled on a small ball mill (RJM-30D, MRC lab) using 7 mm balls for 10-25 mins at 500 rpm.

Table 2. Specification overview of gel samples characterized.

Sample name	Batch number	Drying method	Biocide	Biocide loading
SCD ZnPT gel	EN20072022	supercritical	Zinc pyrithione	75 wt%
FD ZnPT gel	B184	freeze drying	Zinc pyrithione	75 wt%
SCD CuPT gel	EN23082022	supercritical	Copper pyrithione	75 wt%
FD CuPT gel	B183	freeze drying	Copper pyrithione	75 wt%
SCD TP gel	B164	supercritical	Tralopyril	75 wt%
FD TP gel	B178	freeze drying	Tralopyril	75 wt%

Scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDX) analysis was performed by FORCE technology using ZEISS EVO MIK-015 BRUKER X-Flash DET—011 scanning electron microscope. The powder samples were applied on carbon tape and sputtered with a thin layer of Iridium to avoid charging effects. Analyses were conducted at 5-10 keV.

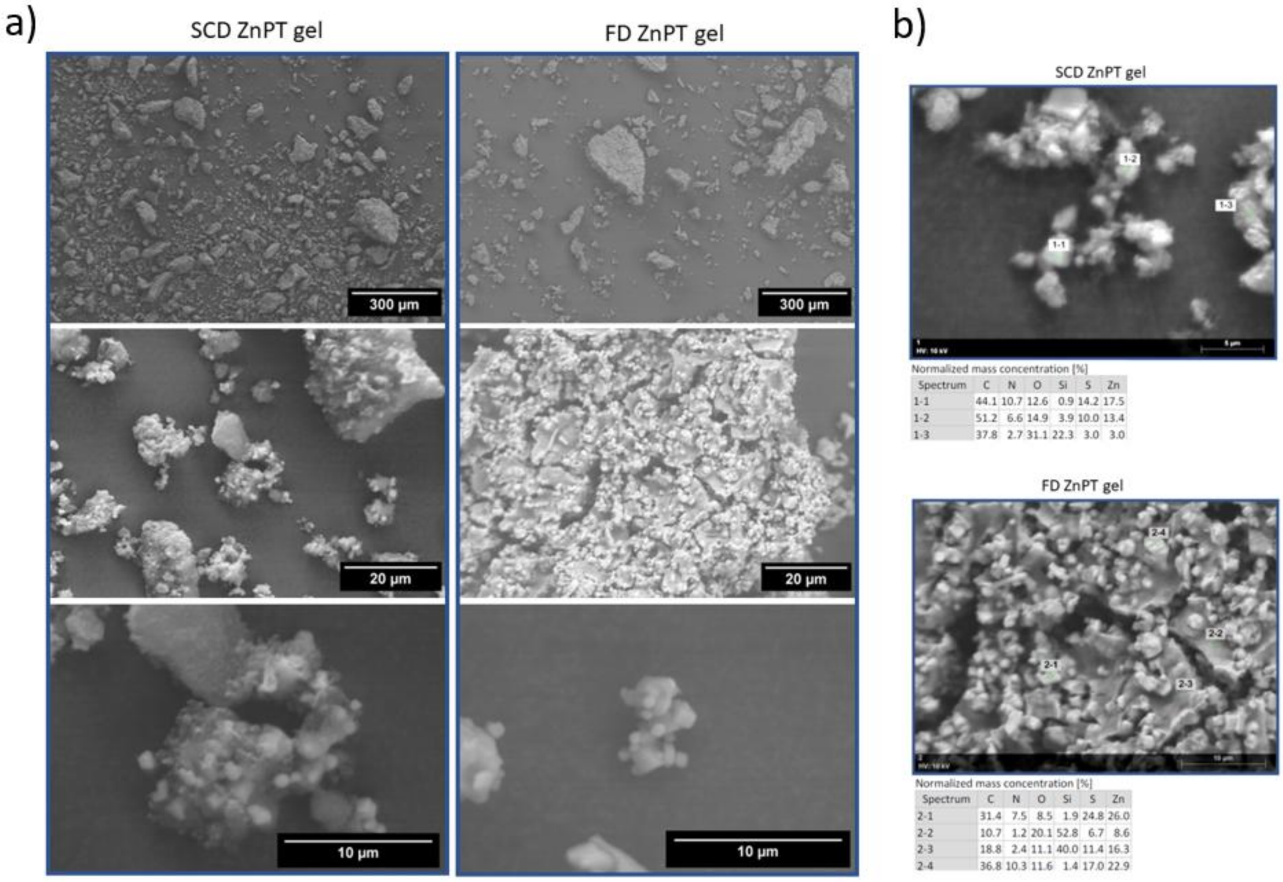
Mercury intrusion porosimetry (AutoPore V, Micromatic) was used to calculate the median pore diameter, bulk density, apparent density, total porosity, and pore volume. While apparent densities were achieved by raising the pressure to 200 MPa, bulk densities were measured at 100 kPa. An apparent density included space between particles and pores down to 6.6 nm in diameter. The method is based on the Washburn model, assuming cylindrical-shaped pores with open ends, closed pores, and that narrow-opening pores are not included. The median pore diameter is calculated based on the distribution of pore sizes from low to high pressure.

The oil absorption (OA) value for the dry gels was determined according to the standard method ISO 787-5:1980.

3.2 Results and Discussion

To compare freeze-dried and supercritical-dried samples, the morphology and size of synthesized gel samples were investigated by SEM-EDX. The results given are concentrated for two samples where both drying methods have been applied.

Figure 3a presents SEM images of the samples SCD ZnPT gel and FD ZnPT gel with different magnifications. It can be seen that the freeze-dried ZnPT gel sample appears denser than the supercritical-dried ZnPT gel. This is caused by shrinkage or collapse of the aerogel pores during the freezing drying process, resulting in less porous materials. The slow (days) freeze-drying process impeded the formation of a compact sheet-like structure. Optimizing the freeze-drying steps is expected to be focused on reducing the drying time and a less dense silica aerogels structure.



Normalized mass concentration [%]

Spectrum	C	N	O	Si	S	Zn
1-1	44.1	10.7	12.6	0.9	14.2	17.5
1-2	51.2	6.6	14.9	3.9	10.0	13.4
1-3	37.8	2.7	31.1	22.3	3.0	3.0

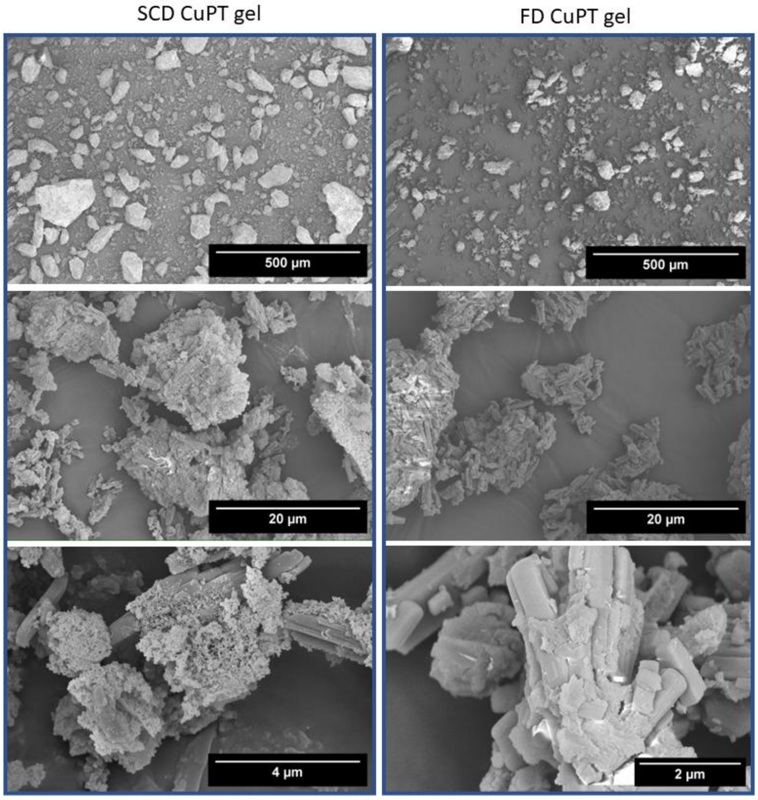
Normalized mass concentration [%]

Spectrum	C	N	O	Si	S	Zn
2-1	31.4	7.5	8.5	1.9	24.8	26.0
2-2	10.7	1.2	20.1	52.8	6.7	8.6
2-3	18.8	2.4	11.1	40.0	11.4	16.3
2-4	36.8	10.3	11.6	1.4	17.0	22.9

Figure 3. Low, medium and high magnification SEM images (a) and elemental analysis (b) of SCD ZnPT gel and FD ZnPT gel.

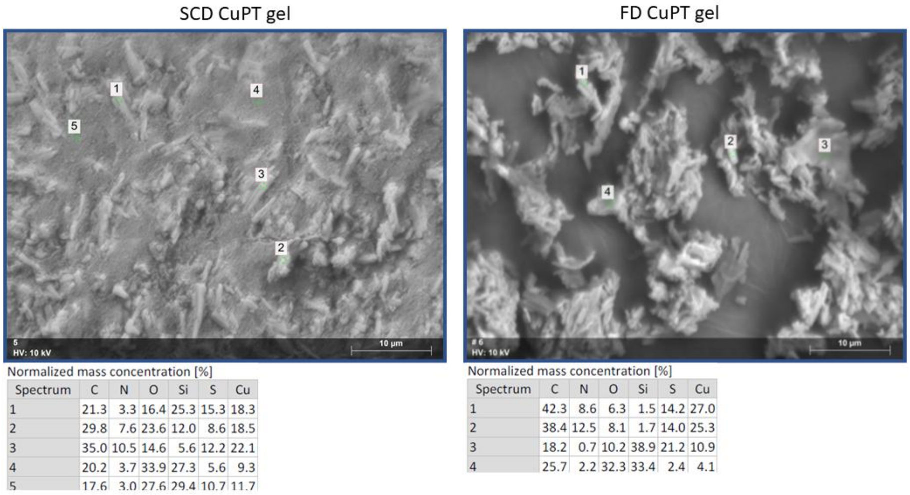
Figure 3b shows an elemental analysis of the SCD ZnPT gel and FD ZnPT gel, where the elements C, N, O, S, and Zn originate from zinc pyrithione and O and Si from the silica aerogel encapsulation. The analysis verifies that small square-shaped and bright zinc pyrithione particles are covered by highly porous silica when supercritical dried, while ZnPT particles are distributed in a compact sheet-like structure of silica.

SCD CuPT gel and FD CuPT gel SEM images are presented in Figure 4aa and the corresponding elemental analysis is in Figure 4b. In the high-magnification images, copper pyrithione is identified as rectangular-shaped particles with silica on the surface. As for the ZnPT samples, the silica appears more porous for the supercritical-dried CuPT gel than the freeze-dried CuPT gel. However, the sheet-like structure was not observed for the FD CuPT gel implying a more efficient drying process despite similar synthesis and drying parameters for the two metal-organic compounds.


SCD CuPT gel

FD CuPT gel

Figure 4a. SEM images of SCD CuPT gel and FD CuPT gel.


SCD CuPT gel

FD CuPT gel

Normalized mass concentration [%]

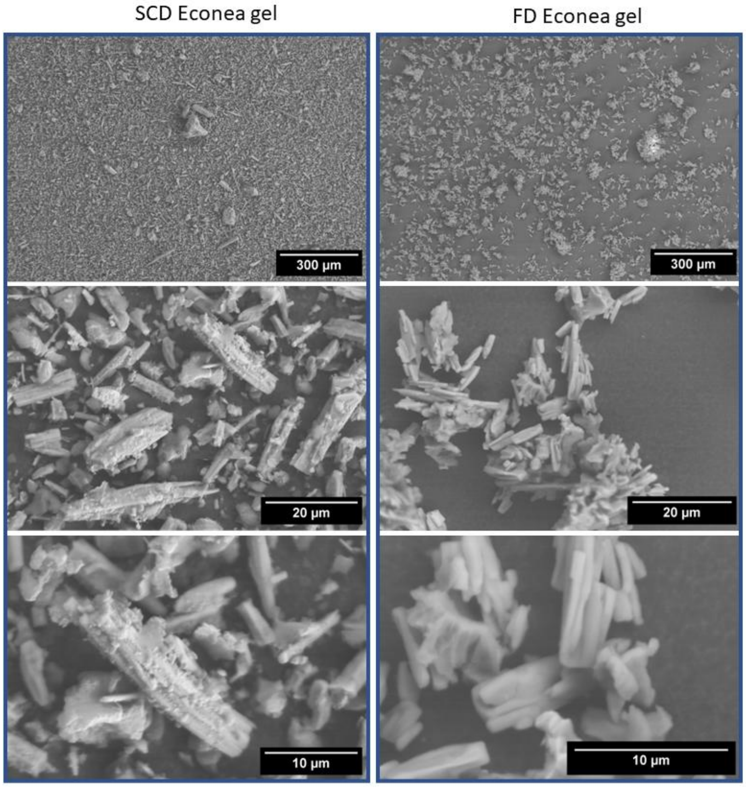
Spectrum	C	N	O	Si	S	Cu
1	21.3	3.3	16.4	25.3	15.3	18.3
2	29.8	7.6	23.6	12.0	8.6	18.5
3	35.0	10.5	14.6	5.6	12.2	22.1
4	20.2	3.7	33.9	27.3	5.6	9.3
5	17.6	3.0	27.6	29.4	10.7	11.7

Normalized mass concentration [%]

Spectrum	C	N	O	Si	S	Cu
1	42.3	8.6	6.3	1.5	14.2	27.0
2	38.4	12.5	8.1	1.7	14.0	25.3
3	18.2	0.7	10.2	38.9	21.2	10.9
4	25.7	2.2	32.3	33.4	2.4	4.1

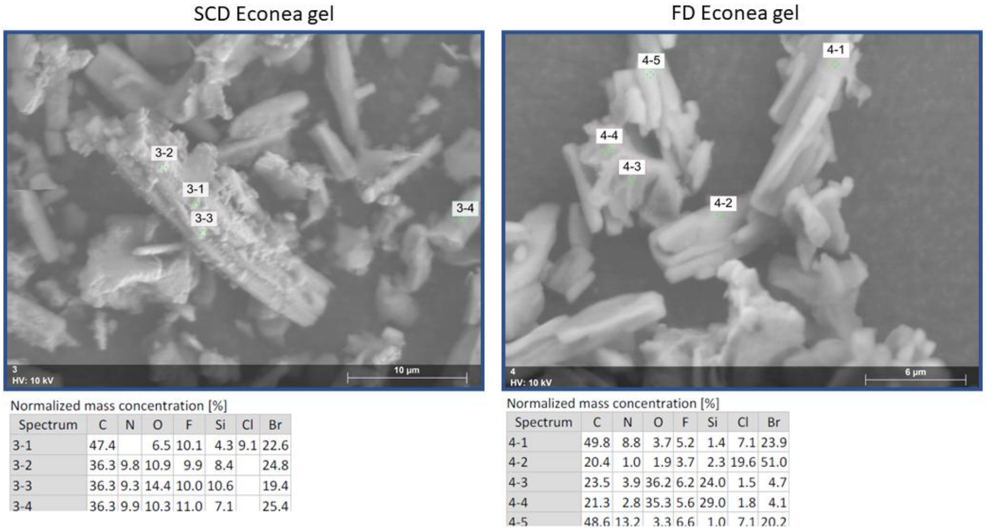
Figure 4b. Elemental analysis of SCD CuPT gel and FD CuPT gel.

Elemental analysis of the particles seen in Figure 5b, where silicon, oxygen, flour, carbon, bromide, and chloride were detected, revealed the presence of both silica and non-metallic organic biocide, tralopyril, as the elongated particles. Figure 5a shows a comparison of the morphology of two Tralopyril (Econea) gel samples obtained by either freeze-drying or supercritical drying. The higher magnification SEM images of both samples show identical rectangular-shaped particles, however, the freeze-dried sample revealed brighter particles which is a result of differences in the encapsulating porous silica.


SCD Econea gel

FD Econea gel

Figure 1a. Comparison of porous silica encapsulated Tralopyril obtained by freeze drying and supercritical drying.


SCD Econea gel

FD Econea gel

Normalized mass concentration [%]

Spectrum	C	N	O	F	Si	Cl	Br
3-1	47.4		6.5	10.1	4.3	9.1	22.6
3-2	36.3	9.8	10.9	9.9	8.4		24.8
3-3	36.3	9.3	14.4	10.0	10.6		19.4
3-4	36.3	9.9	10.3	11.0	7.1		25.4

Normalized mass concentration [%]

Spectrum	C	N	O	F	Si	Cl	Br
4-1	49.8	8.8	3.7	5.2	1.4	7.1	23.9
4-2	20.4	1.0	1.9	3.7	2.3	19.6	51.0
4-3	23.5	3.9	36.2	6.2	24.0	1.5	4.7
4-4	21.3	2.8	35.3	5.6	29.0	1.8	4.1
4-5	48.6	13.2	3.3	6.6	1.0	7.1	20.2

Figure 5b. Elemental analysis of porous silica encapsulated Tralopyril.

The textural properties of the freeze dried and supercritical dried gel samples have been evaluated by oil absorption (OA) and mercury intrusion porosimetry (MIP), summarized in Table 3. The OA value is required and expresses the maximum concentration for hydrophobic (oil) wettability, which depends on the aerogel's surface area and morphology, to determine the critical pigment volume concentration (CPVC) for coating formulations. Generally, Figure 6 shows that the porosity and OA value is directly correlated, and fot the metal-organic co-biocides both values decrease when the samples are freeze-dried compared to the supercritical dried references. The TP gels are more similar to each other, which probably can be explained by solubility effects. As seen in Table 3, the capillary forces of the water meniscus in the porous structure cause the pore diameter to decrease because of water vaporization during freeze-drying.

Table 3. Mercury intrusion

Sample	Batch no.	Oil no.	Total Porosity [%]	Bulk density [g/cm^3]	Apparent density [g/ cm^3]	Medium pore diameter [nm]
SCD ZnPT gel	EN20072022	95.7	72.5	0.348	1.27	27
FD ZnPT gel	B184	73.4	54.1	0.713	1.55	11
SCD CuPT gel	EN23082022	90.9	70,4	0,342	1.15	29
FD CuPT gel	B183	75.2	56.2	0.566	1.48	15
SCD TP gel	B164	68.9	54.6	0.560	1.23	17
FD TP gel	B178	62.7	58.3	0.618	1.29	12

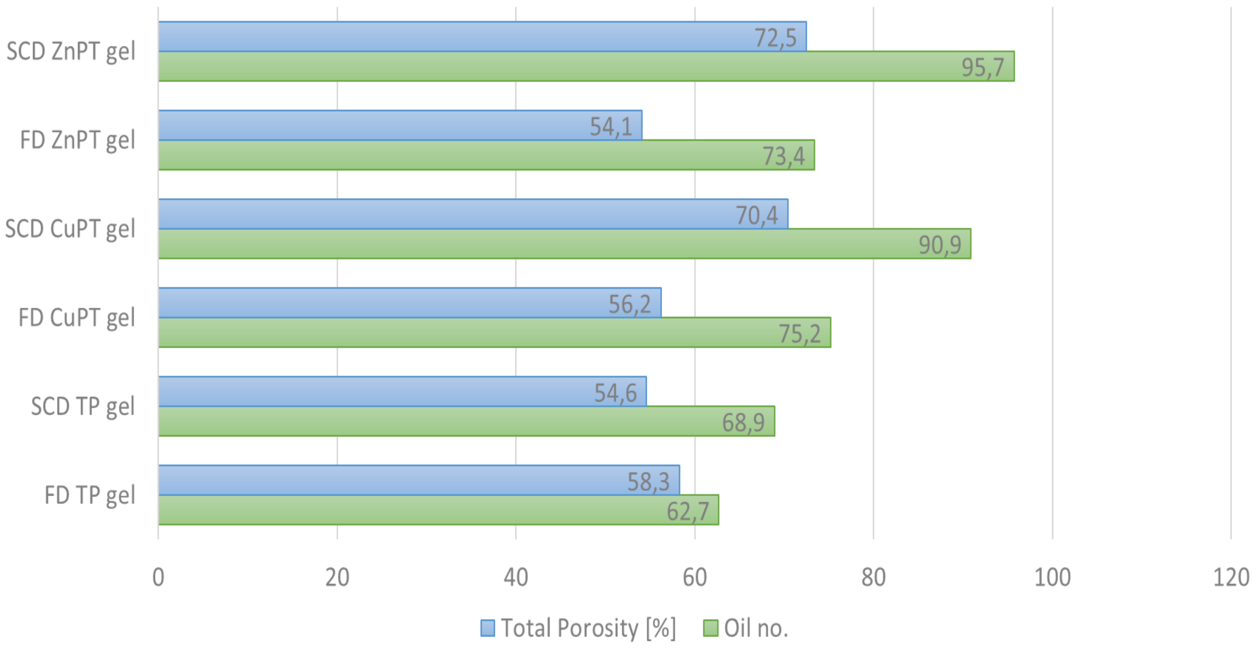


Figure 6. Correlation between the total porosity and oil number of encapsulated co-biocide samples.

3.3 Evaluation of characterized encapsulated active compounds

SEM-EDX was used to evaluate the morphology comparison of freeze-dried and supercritical-dried gel samples. In general, the samples dried with supercritical CO2 seem more porous compared to freeze-drying. The elemental analysis shows the presence of the elements from the silica and the co-biocide in all cases. The textural properties of the freeze-dried and supercritical dried gel samples have been evaluated by oil absorption (OA) and mercury intrusion porosimetry (MIP).

The OA value expresses the maximum concentration for hydrophobic (oil) wettability, which depends on the aerogel's surface area and morphology, and is required to determine the critical pigment volume concentration (CPVC) for coating formulations.

Generally, the total porosity and OA value is directly correlated, and both values decrease when the samples are freeze-dried compared to the supercritical dried references. The capillary forces of the water meniscus in the porous structure cause the pore diameter to decrease because of water vaporization during freeze-drying. When the total porosity decreases the bulk density increases and the material becomes less “fluffy”.

4. Production of antifouling coating samples

To be able to produce test coatings for large vessels it is a must to have the raw materials needed for producing test paint. The most difficult part is the availability of the binder systems. As neither the binder manufacturers nor the coating producers willingly are sharing modern binder systems it was a necessity to buy products from outside Europe. Rosin and acrylic resin can be ordered from traditional raw material suppliers but SPC binders like Zinc acrylate and Silyl acrylate are not easily available. The SPC binders was thus bought from Asia. Below the different binder systems used in this project are described.

Binder systems and their use:

Type binder	Binder system	Usage
CDP	Rosin & acrylic resin	Yachts/Commercial Vessels
SPC	Zinc acrylate	Commercial Vessels
SPC	Silyl acrylate	Commercial Vessels

An antifouling coating includes several raw materials. A general description is:

- Binder system – Typically solvent based
- Dispersion agent(s), pigment and fillers
- Biocide package with a minimum of 2 biocides that prevents hard and soft fouling.
- Solvents
- Other additives like wax and thickeners.

The biocide package used in antifouling coatings is in general containing standard Cuprous oxide in high concentration (25-50 w/w%) combined with at least one co-biocide in typical concentrations of <5 w/w%. In copper free coatings there is typically two co-biocides in concentrations <6 w/w% each. In the commercial market the copper containing products dominate. Estimated to approximately 80 % of the commercial market.

Production of test coating systems, including gel paste:

As the encapsulated co-biocide material has a very low bulk density it is important to adapt the formulation of the antifouling paint. The silica encapsulation material can act as a thickener, why the incorporation procedure is important to ensure both viscosity and stability of the wet coating.

There is basically two possibilities of incorporating the encapsulated material: Either disperse/grind the material in the binder system or producing a gel paste that consists of the encapsulated material, and a part of the binder system (e.g. rosin) and solvent. A gel paste will have approximately 15-20 w/w% of encapsulated material included. The basic idea is to wet the silica material with binder solution to avoid using high amounts of dispersion agent in the wet coating formulation.

The main difference in the production of a coating sample compared to traditional coatings is that the encapsulated material should be included early in the process.

In general, it is important to understand that a raw material with a very low bulk density and a high porosity must be used carefully were the pigment volume concentration (PVC) is reasonable compared to the critical pigment volume concentration (CPVC). This means that standard methods for formulation can be used, but the formulation must be adjusted to make sure that the PVC/CPVC ratio and the viscosity is reasonable compared to commercial standards.

5. Technical properties of test coatings

The samples have been evaluated during the product development work regarding shelf stability in the wet state, water absorption of the test coating film and the test coating film hardness. The methods used for these evaluations and their outcome are described in general below. The aim is to achieve technical properties equivalent to commercial anti-fouling coatings.

5.1 Shelf stability

Marine anti-fouling coatings are expected to have a rather long shelf stability, i.e. 2 years. The accelerated method used to evaluate stability is a standard method where a sample of 100 ml is placed in a closed glass at room temperature and a sample of 100 ml is placed in a closed glass at 54^{o}C for 14 days. The viscosity of the samples was measured at day zero as well as after 14 days with a Brookfield DV2T viscometer. Some of these samples were also saved for 1 year at room temperature.

In general, the rosin-acrylic as well as the zinc acrylate systems were stable regarding shelf stability. The silyl acrylate systems are less stable, why it’s necessary to find a water scavenger and optimize the amount to achieve shelf stability. Without this type of additive, the silyl acrylate systems tend to gel, which increases viscosity and reduces shelf stability significantly. Once a product gels it is no longer possible to stir the mixture into a homogenous liquid. The goal is thus to have stable samples that can be used without risk of gelling, which has been achieved. This goal has been achieved for the binder system used.

5.2 Water absorption

A marine coating must not have water absorption to an extent that can lead to blister formation and loss of adhesion. On the other hand, a low water absorption must be expected and is also affecting the polishing of anti-fouling coatings. To make sure that the water absorption is under control the coatings were applied with an180 µm applicator on glass slides. After three days of drying the paint film was determined by weighing the slides, where the glass slide was subtracted from the total weight. Two slides with each coating were exposed to 2 different salinities at 2 different temperatures for 2 weeks, where the weight increase of the coating film was measured over time. The salinities, 32 ppt and 15 ppt respectively, were achieved using an artificial sea water mixture and demineralized water, where the pH of the resulting liquids was adjusted to 8.2. The aim has been to have water absorptions below 3 wt%.

5.3 Coating film hardness

A König pendulum (according to ISO 1522) has been used to measure hardness after 2 and 4 weeks of aging of dry coating film at room temperature. The coating films were applied on glass panels with a 180 μm film applicator. The aim was to achieve a film hardness close to the commercial references used. In general the measured hardness has been >50 sec to be accepted for further tests.

6. Exposure of coatings in seawater

In the next chapters examples will be presented for results achieved during the project period. The examples cover both SPC and CDP binder systems, with the main focus on SPC systems. The aim is in all cases to further optimize coatings for future commercial anti-fouling use.

6.1 Exposure and evaluation of panels in Denmark 2022

During the exposure season in Denmark of 2022 the focus was both on testing different binder systems commonly used in industry. The formulations with SPC binders were new for us, where Silyl acrylate is sensitive to water/humidity and demanded more optimization than a Zinc acrylate. At the same time, we wanted to see if different drying methods of the encapsulated material showed any difference in anti-fouling performance. It should be noted that these tests were initial and we at this point was not able to test in more aggressive marine environments due to corona close down. These problems occurred first in Denmark and afterwards in Oman, where our preferred cooperation partner is situated. The Danish tests should be regarded as initial screening tests.

The first example shows a functional coating with a Silyl acrylate system, where the biocide package consists of Cuprous oxide and Copper pyrithione. The panels were exposed in Horsens harbor for four months.

In fact, these panels were followed until autumn 2024, but still with no clear difference in fouling. As these test products needed to be optimized regarding stability the follow-up test results will be with new versions of the test products.

Horsens Harbour Ultimo October 2022 Exposed for 4 months. Temperature approx..: 10-25°C Salinity approx.: 18-27 ppt and pH approx.: 7.7-8.1.

Non-coated panel

Silyl acrylate binder, 1,5 wt% CuPT, encap. (SCD) 18 wt% Cu_2O

Silyl acrylate binder, 1,5 wt% CuPT, encap.(FD), 18 wt% Cu_2O

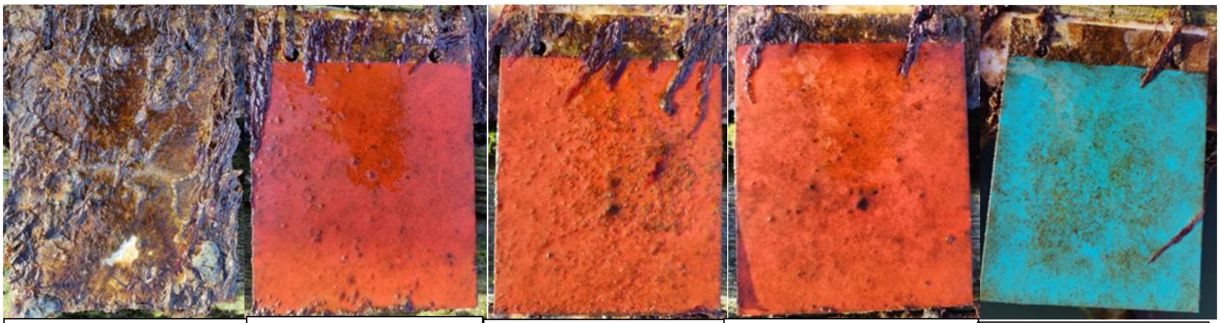
Commercial reference

Figure 7. Coatings with a Silyl acrylate binder system and Encapsulated CuPT (Freeze-dried (FD) and Super critically dried (SCD), and Cu2O after 4 months of static sea exposure.

Coatings with a Rosin-Acrylic binder system and Encapsulated) Tralopyril (Freeze-dried (FD) and Super critically dried (SCD), after 4 months of static sea exposure in Horsens harbor. As Tralopyril is a co-biocide that mainly is targeting hard fouling a longer exposure is not expected to show clearer differences as fouling with algae as main ingredient is taking over at these static conditions.

Horsens Harbour Ultimo October 2022 Exposed 4 months

Salinity approx. 20-30 ppt



Non-coated panel

Rosin/Acrylic system, 2 wt%, free Tralopyril 10 wt% ZnO

Rosin/Acrylic system, 2 wt%, Tralopyril encap. (FD) 10 wt% ZnO

Rosin/Acrylic system, 2 wt%, Tralopyril encap. (SCD) 10 wt% ZnO

Commercial reference

Figure 8. Coatings with a Rosin/Acrylic binder system and Free Tralopyril, Encapsulated Tralopyril Freeze-dried (FD) and Super critically dried (SCD) after 4 months of static sea exposure.

6.2 Patches painted on a Danish Home Guard vessel MHV 802 - 2020-2023

During 2020 EnCoat established a cooperation with the Danish Home Guard mainly to make patch tests on home guard vessels. The cooperation made it possible to start an initial test in March 2021, which was 3-4 months before this project started. The vessel was painted with a red commercial product, where the biocide package was given in the corresponding Safety data sheet (SDS). In this first patch test a CDP binder system was used in combination with a SCD encapsulated co-biocide (Copper pyrithione) and a surface treated Cuprous oxide. The test product was initially developed for yachts. The blue test product was applied on the side of the vessel where film thickness of the dry paint film used in this test was approximately 120-150 μm, which corresponds to three layers of wet paint applied with a roller. The results were very encouraging looking at pictures taken, see below. Our evaluation in this case is that the test product performs has similar anti-fouling efficacy as the commercial product.

March 2021:

Blue Test patch after 10 months

April 2022:

... after 23 months

May 2023:

... after 34 months

Locations: Danish waters

Sailing frequency: 700 hrs within 23 months

Salinity Level (10-25 ppt)

Temperature 10-25°C

Initial barnacles in water line

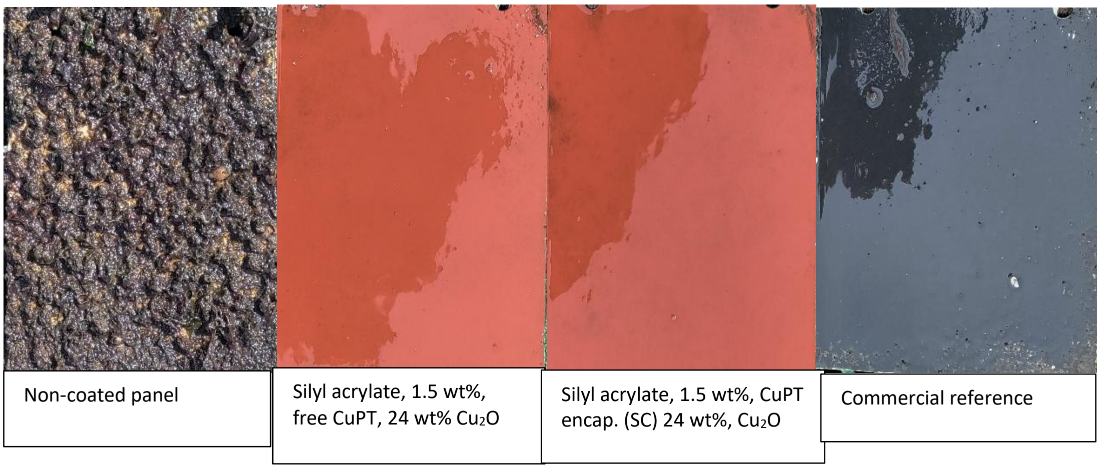
(EnCoat patch <u>and</u> commercial marine coating)

<u>EnCoat biocide package:</u>	<u>Commercial product biocide package:</u>
2 wt% CuPT encapsulated	≥1 - ≤3 wt% CuPT
10 wt% Cu_2O Surface coated	≥25 - ≤50 wt% Cu_2O Standard quality

Figure 9. Patch test with a Rosin/Acrylic test coating on a home guard vessel for 3 years.

6.3 Exposure and evaluation of panels in Denmark 2023 -> 2024

The next example is a silyl acrylate system used with Copper pyrithione (CuPT) as co-biocide. In this case both free and encapsulated co-biocide was used. The panels have been exposed to sea water In Horsens harbor for 14 months. There is no apparent difference between the free and the encapsulated co-biocide in this case. Furthermore, the test products are at least as good as the commercial product tested. This test shows very clearly that there is a need for complementary studies in more aggressive waters to be able to evaluate how the products can function on a commercial level in aggressive marine environments.



Non-coated panel

Silyl acrylate, 1.5 wt%, free CuPT, 24 wt% Cu_2O

Silyl acrylate, 1.5 wt%, CuPT encap. (SC) 24 wt%, Cu_2O

Commercial reference

Figure 10. Coatings with a Silyl acrylate binder system and Free CuPT and Encapsulated CuPT Super critically dried (SCD), and Cu2O after 14 months of static sea exposure

6.4 Patches painted on a Danish Home Guard vessel MHV 814 in 2023 ->

As a follow up on the first patch test we decided to test a test product with a SPC binder system – in this case a Zinc acrylate on one of the home guard vessels. The vessel was painted with a red commercial product, where the biocide package was given in the corresponding SDS. In this second patch test with a SPC binder system the biocide package used was a SCD encapsulated co-biocide (Copper pyrithione) and a standard quality Cuprous oxide. The red test product was applied one on each side of the vessel where the film thickness of the dry paint film used in this test was approximately 120-150 μm, which corresponds to three layers of wet paint applied with a roller. The picture below is taken after almost one year in 2024. The test patch can be seen on the side of the vessel even if the color of the commercial and the test coating film is almost the same, see below. The test product shows superior performance regarding fouling efficacy at this time of exposure. The vessel will be inspected once a year until the vessel needs to be painted again. We will follow the inspections year by year.

MHV 814 – painted autumn 2023 – now almost 1 year

EnCoat biocide package:

1,5 wt% CuPT encapsulated

18 wt% Cu_2O Standard quality

Commercial product biocide package:

≥1 - ≤3 wt% CuPT

≥25 - ≤50 wt% Cu_2O Standard quality

Sailing pattern	
Locations	Danish Waters
Sailing frequency	400 hrs during 11 months

Figure 11. Patch test using a Zinc acrylate test coating on a home guard vessel for almost 1 year.

6.5 Exposure and evaluation of panels in Oman 2023-2024

The reason to expose panels in Oman is that the marine environment is more aggressive than in Scandinavia. Aiming at anti-fouling coatings for large ships it is important to make screenings of our developed products that perform well in Denmark, where the difference in performance can be compared within a reasonable time.

The test started at the end of December 2023 and the results given are exposed for 6 months. In Oman the marine environment is aggressive with multiple species. Both the sea temperature and the salinity is high compared to Scandinavian marine conditions.

Figure 12 shows that it is possible to improve the fouling efficacy with small changes in formulation. Including a third biocide increases fouling resistance significantly as expected. These results are close to commercial standards. The coatings with Silyl acrylate and encapsulated Tralopyril shows that a reduction in concentration can give similar results, se figure 13. It should be noted that concentration must be optimized towards longevity. The polishing rate of the test products in figure 12 compared to the commercial reference seems though to be the same. The panels have been compared by making swabs where the results were very similar.

Non-coated panel	Silyl acrylate, 1.5 wt% CuPT encap. (SCD), 24 wt% Cu_2O, 4 wt% ZnO	Silyl acrylate, 1.5 wt% CuPT encap. (SCD), 24 wt% Cu_2O	Silyl acrylate, 1.5 wt% CuPT encap. (SCD), 24 wt%, Cu_2O, 4.8 wt% Zineb	Commercial reference

Figure 12. Coatings with a Silyl acrylate binder system and Encapsulated CuPT Super critically dried (SCD), and Cu2O after 6 months of static sea exposure

Non-coated panel	Silyl acrylate, 4 wt% Tralopyril (FD), 5 w/w% ZnPT 5 w/w% ZnO	Silyl acrylate, 2 wt% Tralopyril (FD) 5 w/w% ZnPT 5 w/w% ZnO

Figure 13. Coatings with a Silyl acrylate binder system and encapsulated Tralopyril after 6 months of static sea exposure

7 Evaluation of performance

It has been shown that encapsulated materials can perform in several types of binder systems used for large commercial marine ships. The static tests show that even small adjustments of a formulation can improve the overall antifouling performance. It has been shown that co-biocides can be encapsulated and dried with both supercritical as well as freeze drying techniques and can function in a coating on a satisfactory level. There is though a need for long term testing in both cases especially in connection with aggressive marine environments with high sea water temperature and salinity.

8 Following up and future work

In late spring 2024 there have been made scale-up tests with freeze drying of encapsulated materials. The tests showed promising results, where the encapsulated materials were produced on a larger scale with technical properties comparable to the laboratory scale encapsulated materials. As the results were positive it was decided to invest in a laboratory-scale freeze drier.

The patch tests will be followed in the next couple of years and the results are so far promising.

Finally, will antifouling coating formulations intended for aggressive marine environments be adapted towards the new demands of low concentration of each co-biocide. These suggestions for low biocide coatings will be tested during the next fouling season.