Evaluating organotin-free catalysts as EU-REACH compliant solutions for biocidal silicone-based marine coatings

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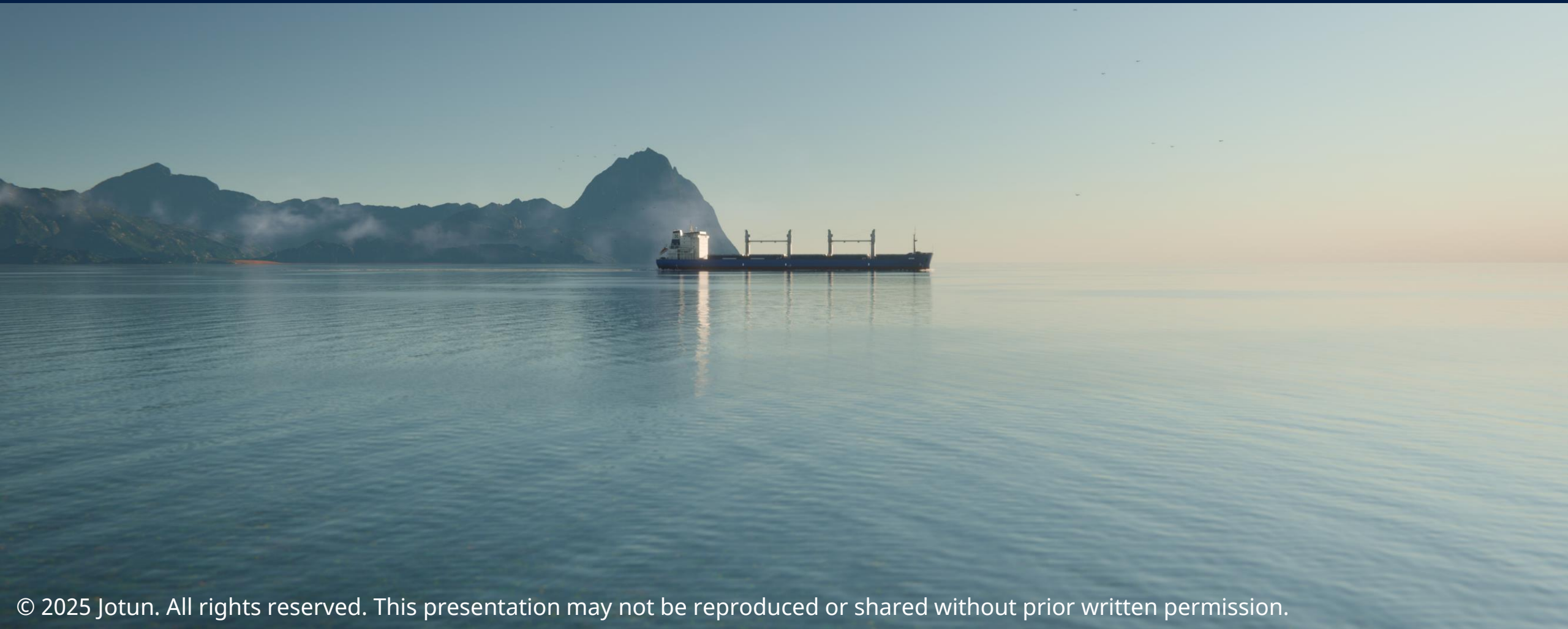


Outline

- Introduction
- Workflow
- Lab test results
- In-service test results
- Conclusions

Clean hull, cleaner operations

The need to improve sustainability in the shipping industry is accelerating. The global industry must cut carbon emissions, protect marine biodiversity and leverage the use of data for smarter decision making.

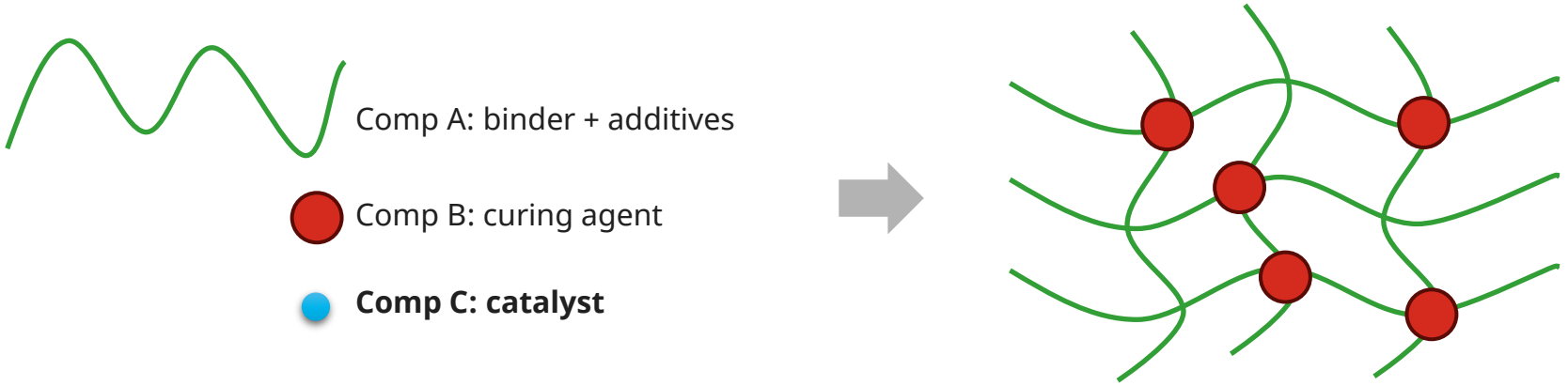
CUT CARBON EMISSIONS

PROTECT BIODIVERSITY

PRESERVE FUEL

Fouling release silicone-based coatings

Fouling release coatings - crosslinking process



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An ecotoxicological study on tin- and bismuth-catalysed PDMS based coatings containing a surface-active polymer

Carlo Pretti [a,*], Matteo Oliva [a], Elvira Mennillo [a], Martina Barbaglia [a], Marco Funel [a,1], Bhaskar Reddy Yasani [b,1], Elisa Martinelli [b], Giancarlo Galli [b]

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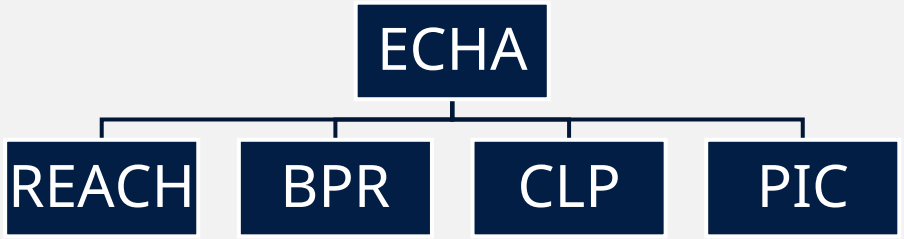
5. Conclusions

Bismuth neodecanoate was an effective catalyst for the condensation curing of PDMS coatings that exhibited no toxicity against *V. fischeri*, *D. tertiolecta*, *A. salina* and *S. aurata*, while dibutyltin diacetate, even if effective catalyst, showed toxicity toward *V. fischeri* and *A. salina*.

This encourages further exploitation of this catalyst and suggests that it may represent an eco-sustainable alternative to dibutyltin diacetate for the preparation of PDMS coatings incorporating a surface-active polymer to combat marine biofouling.

Pretti C, Oliva M, Mennillo E, Barbaglia M, Funel M, Yasani BR, et al. Ecotoxicol Environ Saf. 2013;98:250–6.

Regulatory landscape



Annex XVII of REACH specifically restricts the use of hazardous substances.

Entry 20 targets organotin compounds.

ECHA
EUROPEAN CHEMICALS AGENCY

ANNEX XVII TO REACH – Conditions of restriction

Restrictions on the manufacture, placing on the market and use of certain dangerous substances, mixtures and articles

Entry 20
Organostannic compounds

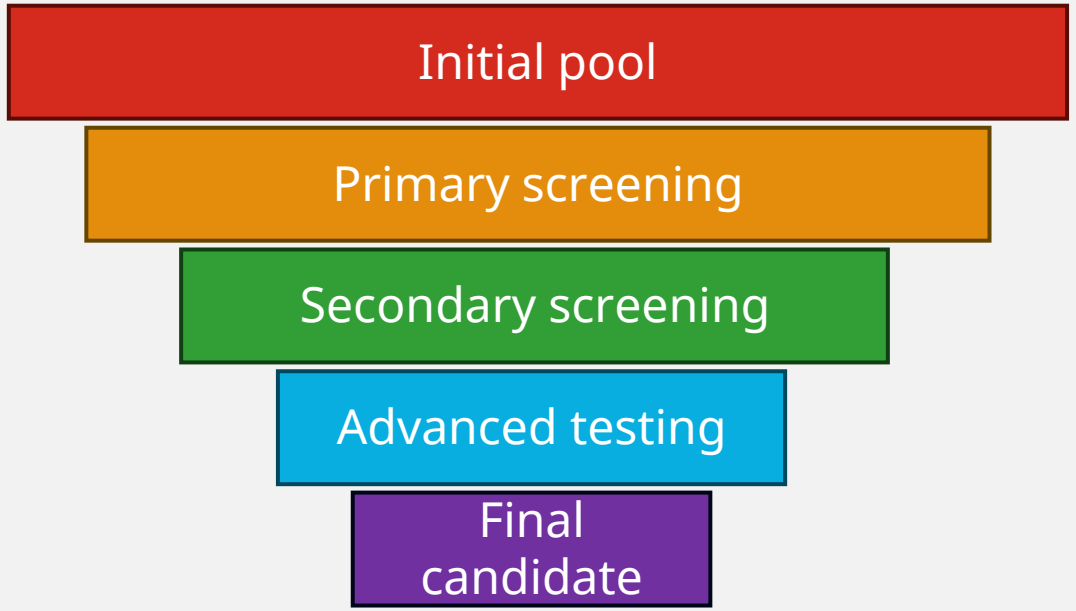
Conditions of restriction
1. Shall not be placed on the market, or used, as substances or in mixtures where the substance or mixture is acting as biocide in free association paint.
2. Shall not be placed on the market, or used, as substances or in mixtures where the substance or mixture acts as biocide to prevent the fouling by micro-organisms, plants or animals of: (a) all craft irrespective of their length intended for use in marine, coastal, estuarine and inland waterways and lakes; (b) cages, floats, nets and any other appliances or equipment used for fish or shellfish farming; (c) any totally or partly submerged appliance or equipment.
3. Shall not be placed on the market, or used, as substances or in mixtures where the substance or mixture is intended for use in the treatment of industrial waters.

Strategy for tin catalyst replacement

Approaches to eliminate tin catalyst

1. Modify binder technology
2. Explore alternative crosslinkers
3. Evaluate catalyst options
   - Organic catalysts
     e.g., aminosilane, amidine, guanidine
   - Metal-based catalysts
     e.g., Bi-based, Zn-based, or other metal systems
   - Catalyst mixtures
     Explore synergistic effects of combined catalysts

Catalyst screening workflow



Hazard comparison of different catalysts

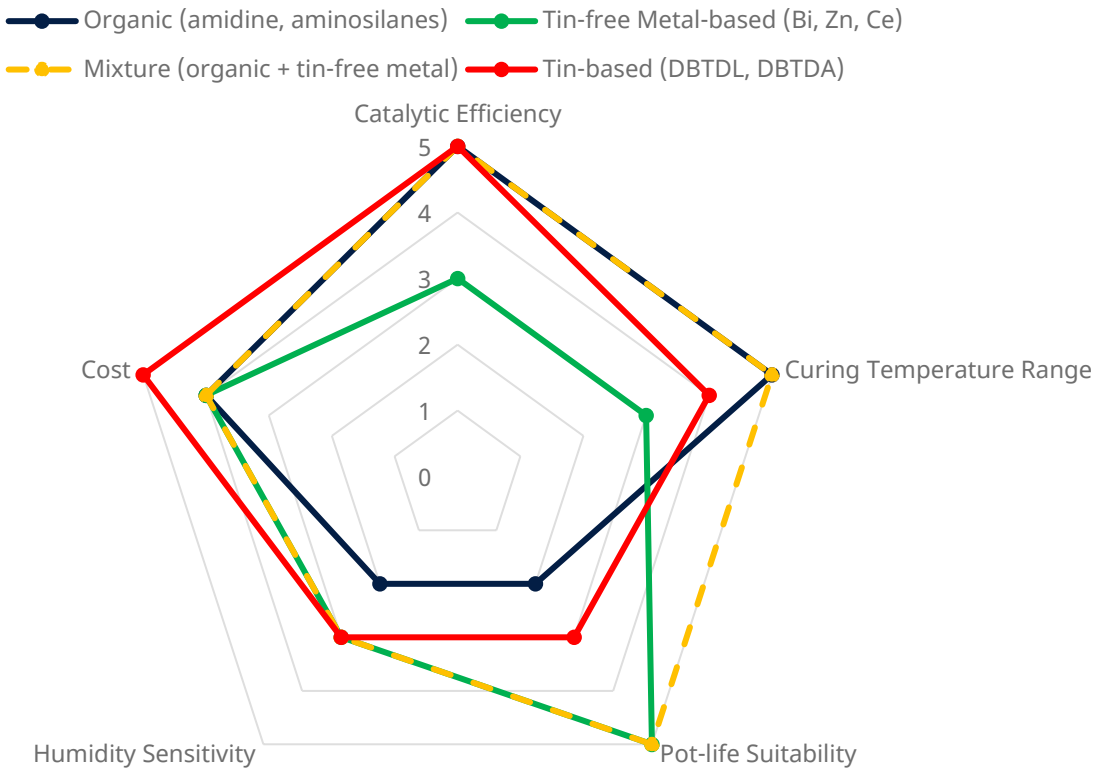
Catalyst	Warning/Danger	Acute Toxicity	Sensitization	Repro/Mutagen/ Organ Toxicity	Environmental Hazard	Corrosiveness
Bismuth neodecanoate	🟡	🟡	🟢	🟢	🟢	🟢
Cerium neodecanoate	🟡	🟡	🟢	🟢	🟡	🟢
Potassium neodecanoate	🟡	🟡	🟢	🟢	🟢	🟡
Zinc neodecanoate	🟢	🟢	🟢	🟢	🟢	🟢
Amidine	🔴	🟡	🟢	🟢	🟢	🔴
Aminosilane	🔴	🟡	🔴	🟢	🟢	🔴
Dibutyltin diacetate/Dibutyltin dilaurate	🔴	🟡	🔴	🔴	🔴	🔴

Legend: 🟢 **Low/No hazard** 🟡 **Moderate hazard** 🔴 **High hazard**

Disclaimer: Commercial metal neodecanoates may contain neodecanoic acid.

Comparative evaluation of catalyst systems

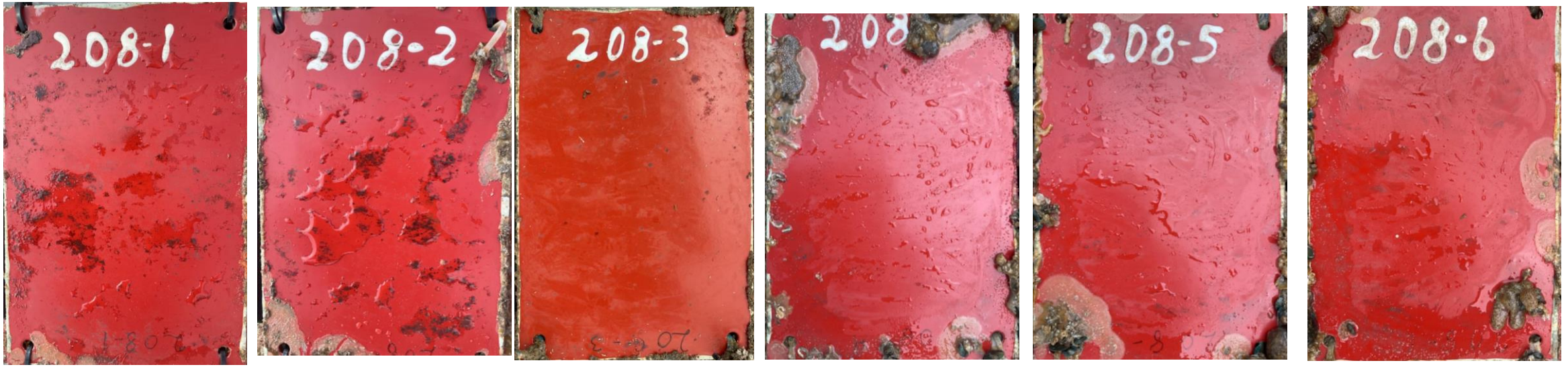
- The mixture catalyst (organic + tin-free metal) offers **the most balanced performance** across all five criteria.
- It effectively **combines the strengths of organic and tin-free metal-based catalysts**, making it the most promising candidate for applications requiring both performance and sustainability.



1 Very Poor - performs poorly; ineffective, unstable, or problematic.
2 Poor - below average; limited use with significant drawbacks.
3 Moderate - acceptable; suitable but not optimal.
4 Good - strong performance; reliable with few limitations.
5 Excellent - optimal; highly effective, safe, and preferred.

Performance of tin-free coatings in static exposure

8 months static exposure in Singapore

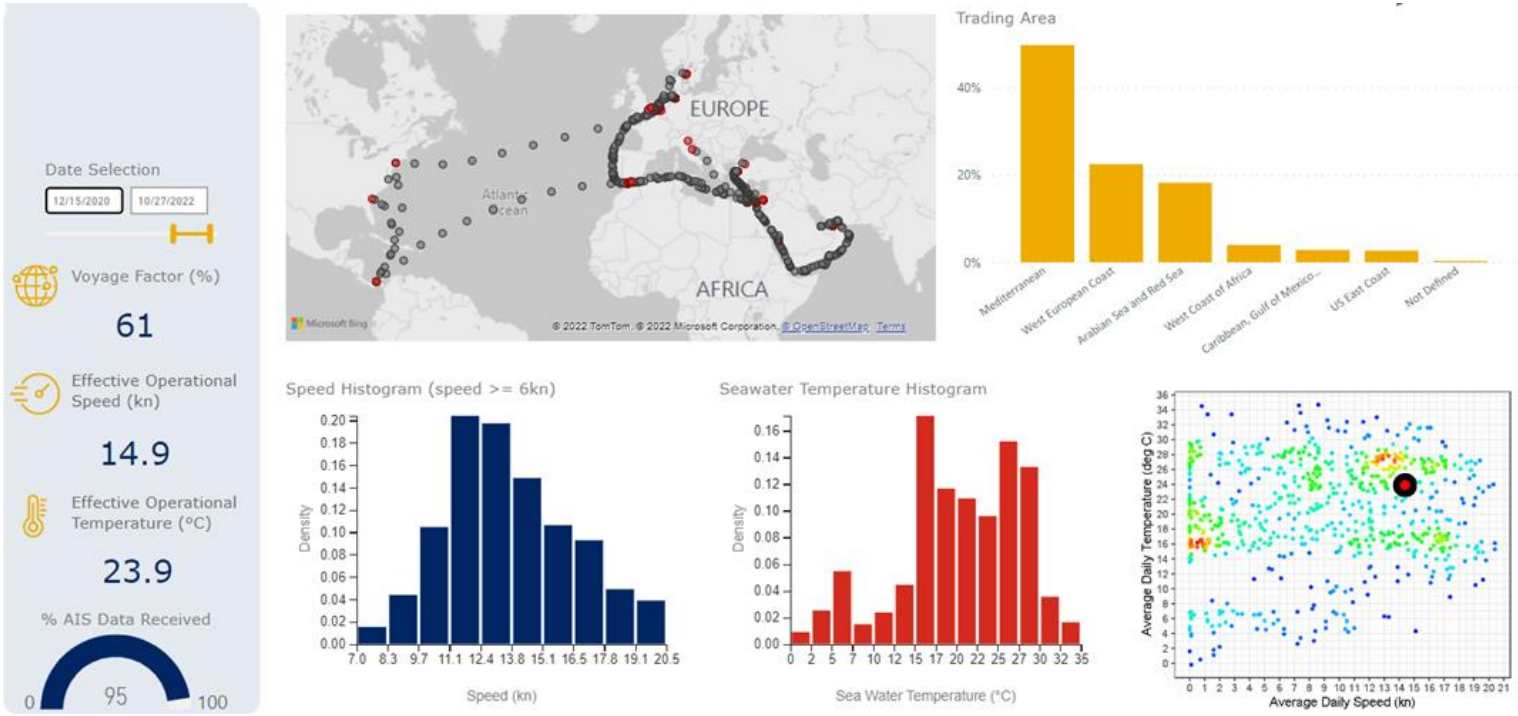


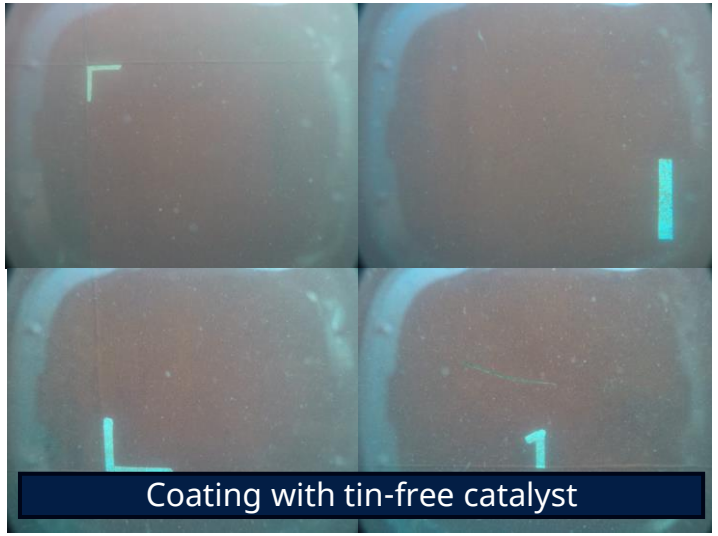
Tin-based catalyst	Bismuth/organic-based catalyst	Zinc/organic-based catalyst	Cerium/organic-based catalyst	Lithium/organic-based catalyst	Organic catalyst

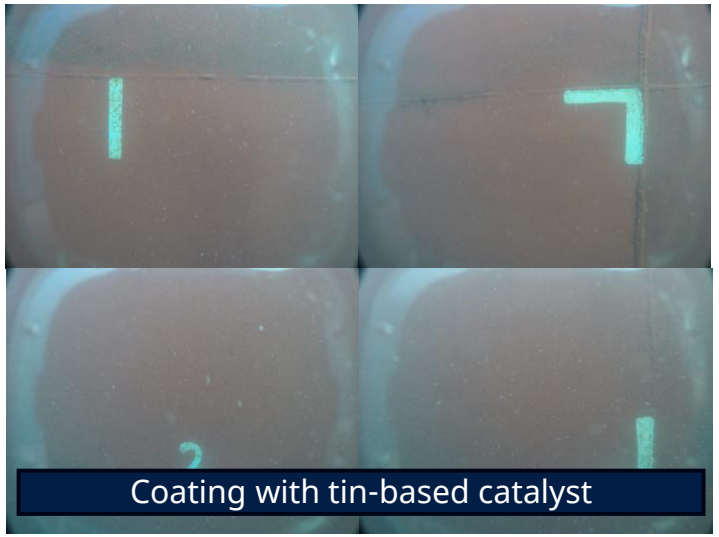
Long term static performance

Singapore 12 months		Florida 24 months		Norway 36 months	
					
Coating with tin-based catalyst	Coating with tin-free catalyst	Coating with tin-based catalyst	Coating with tin-free catalyst	Coating with tin-based catalyst	Coating with tin-free catalyst

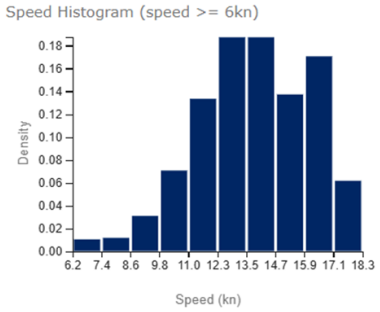
In-service performance

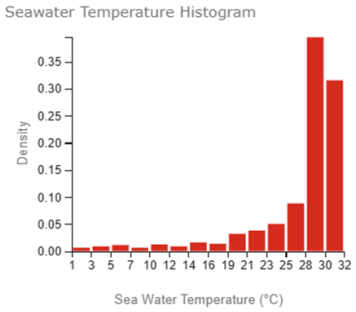


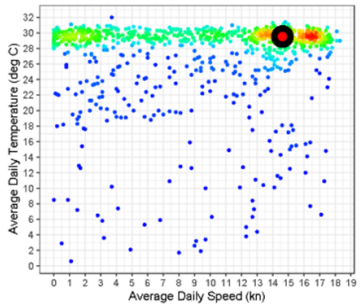


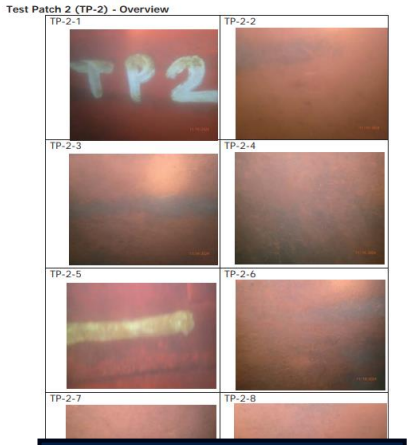


In-service performance

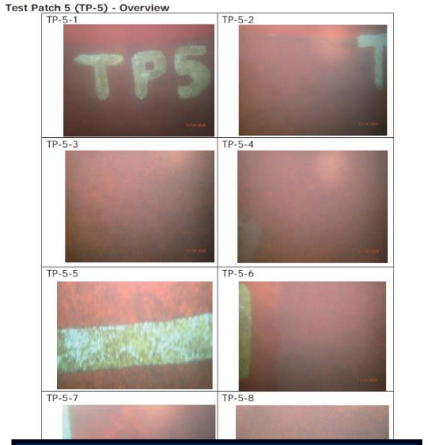




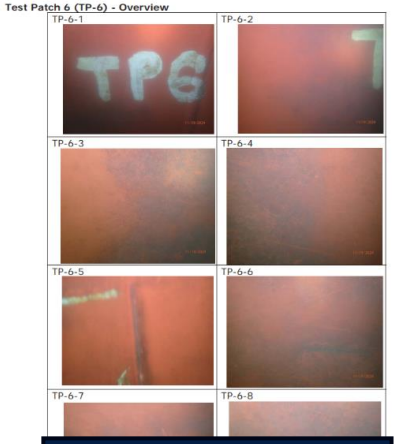




Coating with tin-free catalyst 1



Coating with tin-free catalyst 2



Coating with tin-based catalyst

Summary

- Organotin-free catalysts especially the mixture of organic and metal-based catalysts have demonstrated:
  - Effective curing performance
  - Maintenance of good coating properties
  - Effective against fouling
- Tin-based catalysts present significantly higher toxicity hazards compared to other commercially available metal-based or organic catalysts.
- Thorough evaluation of potential risks is essential prior to catalyst selection and use.

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