Reducing copper oxide biocides used in antifouling paints for ships in Baltic sea

This case study aims to illustrate a chemical substitution process. It is based on publicly available information on company's experience as well as on substance hazards, alternative to the hazardous substance and regulatory information. The case study is neither complete nor comprehensive in illustrating all substitution options of a substance but rather exemplary.

1. Introduction

Antifouling technologies have been used from early times to prevent marine organisms from adhering to the surface of the vessel and preventing increased friction and therefore – fuel consumption as a result, and possibly preventing even ship damage. From earlier times, various technologies have been used such as lead and copper sheets, arsenic, sulphur and pitch [1] and more modern options include organotin compounds, copper oxides, zinc pyrithione and organic biocidal substances. Copper has a long history of use and even nowadays copper oxide accounts for the most used biocide in anti-fouling paints, but it has shown to have serious environmental concerns. Even though alternative technologies exist, but they are not so widespread yet.

2. Hazards of copper oxide

Copper oxide (CAS-number 1317-38-0; EC-number 215-269-1) is very toxic to aquatic life with long lasting effects. The following risk phrases are listed in the classification and labelling inventory:

- H410 (Very toxic to aquatic life)
- H410 (Very toxic to aquatic life with long-lasting effects)

2.1. Copper affects marine life

Studies have shown that dissolved copper may affect not only target species but also has negative effects on a number of other marine species by disrupting enzymatic activity and increasing mortality [2]. Free copper ions Cu^{2+} and Cu^{+} are the most bioavailable, while metallic copper is available to lesser extent. Typically, copper concentration in coastal and estuarine water does not exceed 5 µg/l. However, very often the copper bound to dissolved organic carbon is not accounted for and it is known that concentrations in the bottom sediment, where it accumulates, are higher than in free water column. Some species have shown particular sensitivity to copper while other, such as fish species are more resilient to this type of pollution [3]. The levels of copper in the Baltic sea have been increasing in recent times. [4]

2.2. Discarding old paints

Large quantities of antifouling paint particles (APPs) are generating in boat and shipyards during maintenance and repair. In some countries waste produced from ship maintenance is collected and properly disposed while in others, proper disposal is not practised or

regulated. Recreational boat industry is much less controlled, therefore contributing to significant amount of APP generation.
Copper, zinc and even tin containing antifouling paint particles are found both along the shore and contaminating the sea bed, where they behave similarly to bottom sediment particles and they are ingested by filter feeders and over time leach toxic heavy metals into the marine environment. [5]

3. Baltic Sea region situation

3.1. Biofouling and antifouling use

It is known that around 3 million leisure boats are docked in ports around Baltic sea. It is known that in Sweden, around 80% leisure boats have copper or zinc containing antifouling paint. Furthermore, around 30% of boats use antifouling paints containing unnecessarily high amounts of copper biocide. Baltic sea is considered a brackish environment and not fully "marine", therefore, the biofouling pressure is much lower. A lot of users still have layers of organotin compound containing antifouling paint underneath the top layer of paint and during the boat maintenance this paint may be carelessly scrapped to the ground and possibly contaminating soil, and water bodies. In Sweden, a recent survey found this is most often the case, with 80% user leaving the scrapped off paint simply on the ground. [6]

3.2. Regulatory status

3.2.1. Union legislation

The authorisation of antifouling biocides can largely be divided into two parts: the authorisation of the active substances used in the anti-foulant and the authorisation of the antifouling biocide itself. Active substances used exclusively for biocides (single-use substances) are regulated by Biocidal Products Regulation, while substances used also for other chemical products (dual-use substances) have to be registered according to REACH. However, antifouling products are one of the product-types that are not granted Union authorisation, thus allowing for increased national influence on which products are approved and ability to adjust to local conditions.

It is important to refer to Water Framework Directive and the Marine Strategy Framework Directive. It is the national implementation of the directives assesses the current status, sets the environmental goals and standards and determines the measures to be taken to reach good status. While some of the substances used in antifouling are recognized as priority substances by the European Union, for others, such as copper, a standard must be implemented by the Member States' themselves. For the Baltic Sea, the HELCOM is central for the regional cooperation. All states surrounding the Baltic Sea, as well as the European Union itself, are members of HELCOM and it provides a platform for harmonization of legislation and common monitoring and actions to jointly work on issues regarding the marine environment. [7]

3.2.2. Country-specific requirements

Copper use in antifouling paints in the Baltic sea is restricted by some countries. In Sweden Baltic Sea is considered environmentally sensitive and due to this reason Swedish authorities applied the precautionary principle and placed restrictions on the use of copper antifouling paint for leisure boats in early 2000s, however this restriction has been lifted and now Chemical Agency authorises antifouling products that have limited concentration of biocides, including copper that are allowed to be used in Sweden. [8]

In Denmark, there are also requirements that limit the release of copper into the seawater for leisure boats. The copper release rate in the paint may not exceed 200 micrograms Cu / cm^2 after the first 14 days and 350 micrograms Cu / cm2 after the first 30 days. It is also prohibited for the boat owner to use antifouling paints on leisure boats that predominantly sail in freshwater. [9]

In 2009 Dutch government proposed a ban on copper antifouling paint in leisure boats, but it was removed after the EU Scientific Committee on Health and Environmental Risks concluded the ban being insufficiently backed by evidence and thus it was rejected.

No such restrictions are placed for large ships. No international plans to band copper use in antifouling paint have been announced.

4. Case description and alternatives

4.1. Case description

It is aimed to replace antifouling coating containing both zinc oxide and copper oxide that pose risk to aquatic environment and also other components that pose a risk to human health with an environmentally friendlier option. The coating also needs to be suitable for large vessels since the company is operating a ship with underwater surface area of around $800m^2$. However, the research is also very useful for leisure boat owners.

4.2. Alternatives technologies

Below – a table listing available and other currently researched antifouling paint technologies as environmentally friendlier alternatives.

Technology type	Mode of action	Chemistry	Available?
Ablative/self-polishing **(Currently used)**	Slow continuous release of biocide	Mostly copper or zinc based.	yes
Low emission antifouling	Slow continuous release of biocide	Contain alternative more effective biocides, e.g. medetomidine.	yes
Foul release/non-stick	Low surface energy, foul easily detach, e.g. at high speeds or are easily cleaned.	Silicone, fluoropolymer or hybrid polymer based.	yes
Enzyme based	Enzymes hydrolyse the marine organism footprint, so they do not settle onto surface	Enzymes	no
Nano-coatings, biocide free	Non-attractive surface for foul organisms		no
Biomimetic coatings	Based on biotechnology. Non-attractive surface for foul organisms		no

4.3. Alternative techniques

Although these options are hardly applicable to large ships, this is still very useful information for recreational boat owners on how to avoid antifouling paint whatsoever.

- Hauling out boat and keeping the boats in air whilst not in use.
- Scrubbing hull during infrequent hauls (but do not attempt dry sanding)
- Cover the boat with boat hull protectors in water to cover from light and thus prevent growth of fouling organisms.
- Mechanical methods – boat brushers. A boat is taken through rotating brushes and fouling organisms are brushed off.

Also, it is worth to note that during boat renewal, when scraping of old paint, it is important to collect and manage it, preventing it from getting into the environment. And also, it is important to avoid dry sanding.

5. **Substitution**

5.1. Alternative products assessment

	Technology	Mode of action	Hazardous substances	Available?
1.	Currently used product	ablative	Copper and zinc oxides, solvent naphtha (H340, H350)	
2.	Foul release, silicone based	Hydrogel microlayer prevents organisms from adhering and has self-cleaning properties.	"Biocide free" however, dibutyltin dilaureate (H400, H410, H360) present (function: crosslinker-stabiliser)	yes
3.	Low emission semi-hard antifouling	Abamectin-based (0,1% content), bacterial compound. Acts on contact – no release to seawater (theoretically)	Xylene, zinc oxide (H400, H410), zync pyrithione (H400), abamectina (H400, H410)	Possibly available in near future.
4.	Biological, enzyme based	Enzyme immobilised in aerogel, enzymes hydrolyse the marine organism footprint, so they do not settle onto surface	Enzymes, degrade 10-12days in aquatic environment.	Possibly available in near future.
5.	Poly- siloxane fluoro-polymer technology (proprietary hybrid siloxane)	Foul release. Valence of coating changes in presence of floating water. Low surface energy and low friction. Does not deplete or leach. Self-clean.	Polyamide resin (possibly H411)	yes
6.	Hydrophilic / hydrophobic modified siloxane combined with an epoxy resin	The modified siloxane aids in the formation of a slick film on the surface of the coating that inhibits the settlement of marine larval organisms	-	yes

5.1.1. Choosing alternative and justification.

Two possible alternatives were chosen, that according to product description have a long service life, decrease friction through water and provide fuel savings, have no biocidal release and have no or very little hazardous ingredients. Both products theoretically provide around 10% fuel savings or possibly even more and have a longer service life. Alternative no.5 according to the manufacturer is guaranteed to have 10 or possibly even 15-year service life, which is 2-3 times that of conventional copper-based antifouling coating. Manufacturer provided info about the actual cases of application of this paint proving its' long service life. After preliminary economic assessment, it was decided to choose alternative no.5. Even though it is much more expensive than copper-based option, but possibly provided fuel savings over 10 years period is economically beneficial and even more over longer 15 years period, thus providing financial gains. Alternative no.6 is also a considerable option from an environmental point of view, but it is less economically favourable.

5.2 Implementation

The implementation has not started yet.

6. References

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