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Survey and risk assessment of chemical substances in non-biocidal antifouling paints for private pleasure boats

Survey of chemical substances in consumer products No. 197

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Summary

An increasing number of antifouling products without biocides are placed on the market as environmentally better alternatives to biocidal antifouling products for protecting pleasure boats against fouling. Even though the non-biocidal coatings may not contain biocides, they may contain other substances with intrinsic hazardous properties both for the human health and the environment. The objective of this study is to clarify whether there are functional, non-biocidal alternatives to biocidal antifouling paints and to gain knowledge about the environmental and health risks associated with the use of non-biocidal antifouling coatings, including whether they can be used without personal protective equipment.

Within the project, data collection about types of non-biocidal antifouling coatings, their efficacy, chemical composition and use was performed by means of literature review, stakeholder consultation and review of available products at Danish retailers. The content of substances of concern in selected non-biocidal antifouling coatings was further investigated by chemical analysis.

Overall, 65 coating products marketed as non-biocidal products were identified. Three different types of non-biocidal antifouling coatings are distinguished based on their antifouling mode of action and chemical composition; silicone-based foul release coatings, self-polishing coatings and hard coatings. Among the non-biocidal antifouling coatings, silicone-based foul release coatings appear to be the most prominent alternative to biocidal antifouling paints.

The efficacy of the non-biocidal antifouling coatings depends on the type of antifouling coating as well as on a variety of environmental and use parameters. A general conclusion on the performance of non-biocidal antifouling coatings compared to biocidal coatings is therefore not possible. Adapted use and mechanical cleaning patterns are recognized as valuable additional tools to improve non-biocidal antifouling performance. Stakeholders recognise that the market of non-biocidal antifouling paints is under strong development with new products arriving every year.

Of the 65 products reviewed, 13 non-biocidal antifouling coatings were evaluated as relevant for inclusion in the risk assessment based on their current and expected future availability for consumers on the Danish market. Based on information from the SDS and the obtained results in the chemical analyses of selected products, seven substances of concern for human health (solvent naphtha, ethylbenzene, naphthalene, rosin, octamethylcyclotetrasiloxane (D4), 4-methylpentan-2-one (MIBK) and 4-methylpentan-2-one oxime) and five substances of concern for the environment (octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5), dodecamethylcyclohexasiloxane (D6), MCCP (C14-C17) and zinc oxide) were identified and assessed.

In order to allow for a comparison of risk assessment results for the non-biocidal antifouling products comprised by this study and the risk assessments of biocidal antifouling products conducted by the Danish Environmental Protection Agency, the methodology for assessing biocidal antifouling products was adopted in the risk assessment of this study.

Both the human health and the environmental risk assessment were conservative and based on a worst-case approach. In line with this approach, the highest concentrations from either the safety data sheets or from the results of the chemical analyses were chosen as input for the exposure calculations.

The human health risk assessment focused on consumer uses of the antifouling coatings, i.e. consumers painting their pleasure boats, together with the unintentional exposure of toddlers in contact with the painted boats. Calculated exposure estimates were compared to human health reference values for the general population, resulting in hazard quotients (HQ). It is concluded that five of the 13 assessed non-biocidal antifouling coatings contain hazardous substances for which the health risks, based on the quantitative risk assessment, cannot be regarded as controlled. The coating products, for which a risk was derived, were of different types including one self-polishing coating, two hard coatings, one foul release coating and one tie coat. The two substances causing the potential health risks are 4-methylpentan-2-one

(MIBK) and 4-methylpentan-2-oxime. MIBK, a substance suspected of causing cancer (Carc. Cat 2), is according to the safety data sheets present in four products of different types (two hard coatings, a self-polishing coating and a tie coat). 4-methylpentan-2-oxime is of concern in a foul release coating.

Placing on the market of products with these types of hazardous profiles should be discouraged for consumer health considerations. Additional refinements of the human health risk assessment with substance specific information and more details about the application conditions for the antifouling paints could potentially improve the assessment. Worth noting is that MIBK may very well be used in biocidal antifouling paints, as the substance is a commonly used solvent in paints.

The environmental risk assessment considered the risk for the aquatic environment by estimating exposure with the modelling software MAMPEC, which is developed for the assessment of biocidal antifouling products. Predicted environmental concentrations (PEC) were calculated for freely dissolved substance in the harbour water and adsorbed substance to suspended matter in the harbour water. The PEC values were compared with predicted-no-effect concentrations (PNEC) for the water and sediment compartment, respectively, resulting in PEC/PNEC values. The PEC/PNEC values are used for the risk characterisation. A limitation of the applied method is that it cannot adequately describe the potential risk related to PBT, vPvB and/or endocrine disrupting properties.

The environmental risk from non-biocidal antifouling paints available on the Danish market can be anticipated to be controlled for the harbour water and the sediment compartment based on the simple quantitative risk assessment method applied for the prioritised substances of concern, i.e. D4, D5, D6, MCCP and zinc oxide. The conclusion for MCCP is supported by a qualitative evaluation of environmental exposure, as quantitative data for a realistic refinement of the exposure scenario are not available. The worst-case quantitative risk assessment leads to PEC/PNEC of almost 1 for MCCP, thus indicating a potential risk. The qualitative evaluation of the uncertainties related to the PEC/PNEC calculation leads to the conclusion that, even if MCCP is present, it is unlikely to occur at concentration posing an environmental risk for the marina environment. Nonetheless, it is noted that D4, D5, D6 and MCCP are recognized as PBT/vPvB substances. The use of products potentially leading to releases of the substance to the environment should be discouraged.

Overall, the survey of non-biocidal antifouling coatings and the risk assessment document that non-biocidal antifouling products, which can be regarded as safe for both human health and environment, are available. Health risks related to the use of some non-biocidal antifouling products cannot be excluded. However, one of the identified substances of concern causing the risk may also be present in biocidal coatings and the risk is therefore not specifically related to non-biocidal antifouling coatings.

1. Introduction

In Danish marinas, there are currently more than 57,000 private pleasure boats (Danish EPA, 2023). Private pleasure boats are regularly painted with antifouling paints or coatings to prevent colonisation of aquatic organism on the hull (the fouling), as these increase frictional resistance and thus fuel consumption (Danish EPA, 2023).

Most antifouling paints for private boats contain biocides and are used to prevent fouling in marine environments. When biocidal active substances are released from the hull coatings, they can harm not only the target organisms, but also all non-target organisms that live in the body of water. For this reason, biocides are today regulated under the EU Biocide Regulation (Regulation (EU) No. 528/2012). Currently, only 10 biocides are approved within the product type PR 21 Antifouling products, and the approvals are limited to 9 or 10 years in each case (all end dates in 2025) in order to assess whether there are less environmentally harmful alternatives that can substitute the biocides thereafter.

Following the general authorisation scheme established in the EU under the Biocide Regulation, a biocide is first assessed at EU level and, if it is approved, producers of antifouling products containing this biocide, must submit an application to the national authorities for placing the product on the national market. The Danish Environmental Protection Agency's assessment of the application shall, inter alia, carry out a risk assessment of the specific product and take into account, whether there are suitable functional alternatives that also constitute better alternatives in terms of health and the environment to the biocidal antifouling paints.

Currently, an increasing number of antifouling products without biocides are placed on the market, which could be suitable functional alternatives. Such non-biocidal products do not require an authorisation under the Biocides Regulation before being placed on the market.

The objective of this study is to clarify whether there are functional, non-biocidal alternatives to biocidal antifouling paints and whether these constitute better alternatives regarding health and environment, including whether they can be used without the use of personal protective equipment.

To fulfil this objective, this study comprises a survey of non-biocidal antifouling paints on the Danish market, their functionality, and an environmental and human health risk assessment of selected non-biocidal antifouling paints based on chemical analyses of the selected hazardous components in the non-biocidal antifouling paints.

In order to allow a comparison of the risk assessments of non-biocidal antifouling paints to the risk assessments of biocidal antifouling paints, the same methods as applied in the risk assessments of biocidal antifouling paints are applied here.

2. Survey of non-biocidal paints for pleasure boats

2.1 Methods

The data collection for the survey was based on the following sources

- Literature research of scientific and grey literature
- Review of product information and extraction of TDS and SDS from manufacturer websites
- Review of non-biocidal paints at Danish retailers' websites
- Stakeholder consultation

For the stakeholder consultation, the following organisations have been contacted:

- Industry associations
  - DFL (Danmarks Farve- og Limindustri)
  - EBI (European Boating Industry)
- Six directly contacted manufacturers of paints and coatings
- Additional manufacturers have been contacted through EBI
- Distributor
  - Westing Denmark
- Users' associations
  - FLID (Foreningen af Lystbådehavne I Danmark)
  - Danish Sailing Association (Dansk Sejlunion)
- Media
  - Bådmagasinet ApS

The stakeholders were contacted by phone and/or email, and stakeholder-specific questionnaires were distributed or used for telephone interviews.

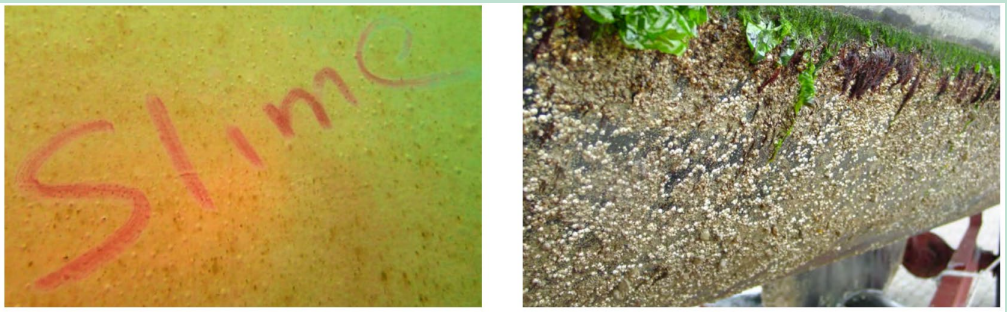
Responses were obtained from 11 stakeholders. Of these, five contributed with filled-in questionnaires, telephone interviews and/or additional material (Westing Denmark, FLID, Danish Sailing Association, Bådmagasinet ApS, one manufacturer). The remaining stakeholders replied that they could not contribute to the investigation. Some manufacturers' responses indicated that the companies did not have available resources to prioritise contribution to this study.

2.2 Definitions

Antifouling paints and coating for pleasure boats may contain different types of biocides. Biocides are approved for different product-types (PT) defined in Annex V of the Biocide Product Regulation (Regulation (EU) No 528/2012, BPR).
The term "antifouling" is used to describe both biocidal and non-biocidal paints with an antifouling effect. The term "biocide-free antifouling paint" could be misleading, as many antifouling paints (especially water-based products) contain pot preservatives (product type 6) to improve durability. Strictly speaking, these products are not completely biocide-free.
Therefore, in this study, the term "**non-biocidal**" paint or coating is principally used for products without any biocides belonging to any biocidal product types, hereunder PT21 (Antifouling products), PT07 (Film preservatives), PT08 (Wood preservatives) and PT09 (Fibre, leather, rubber and polymerised materials preservatives). However, "non-biocidal" paints or coatings may still contain biocides belonging to PT06 (Preservatives for products during storage). Also, if a substance occurs, that is an approved active substance under BPR, but the substance is not added to have a biocidal effect and, at the same time, the substance is unlikely to exert a biocidal effect, the relevant paint may still be regarded as non-biocidal.

When discussing product properties of biocidal or non-biocidal antifouling paints, the term efficacy is used. **Efficacy** denotes the effectiveness or ability of the paint to prevent or reduce the fouling, i.e. the attachment of marine organisms to the hull of the boat.

Fouling is a generic term for the growth and settlement of biological material on hard underwater surfaces such as boat hulls, piers and cooling water piping. Fouling starts with the settlement of bacterial biofilms, microscopic animal larvae or weed (microfouling). These form an adhesive bond to which larger organisms may attach (macrofouling). Fouling may consist of slime, filamentous algae, other algae, mussels, barnacles and hydroids (FIGURE 2-1). The growth of fouling organisms depends on many factors, including water characteristics such as pH, salinity, turbidity, temperature, level of pollution and nutrient availability (Wezenbeek et al., 2018).



Slime layer on the surface of a hull

Macrofouling on a motor vessel

FIGURE 2-1 Examples of fouling (IMO GloFouling Partnerships Project, 2022)**.**

2.3 Types of non-biocidal antifouling products

The International Maritime Organization (IMO) describes “anti-fouling systems” as “a coating, paint, surface treatment, surface or device that is used on a ship to control or prevent attachment of unwanted organisms” (IMO, 2019). The present study focusses on non-biocidal antifouling paints, as these are in their application comparable to biocidal paints, and the objective of the study is to elucidate whether there are functional, non-biocidal alternatives to biocidal antifouling paints. The following sections thus present the different types of antifouling paints. For the sake of completeness, other antifouling systems than paints are shortly mentioned in section 2.3.4.

2.3.1 Hard coatings

Hard coatings represent a diverse category that consists of epoxies, polyesters, vinylesters that often contain more than 50% of volatile organic compounds (VOCs) before application, while having silicon (Si) as a base constituent and sometimes being reinforced with glass flakes (Daehne et al., 2023, Wezenbeek et al., 2018). Their functionality results from their good adhesion to the substrate (the hull), while representing a good barrier that protects the substrate from fouling and corrosion (Pistone et al., 2021). However, the high cross-linking of epoxy resins can result in high stiffness and low impact resistance, which is why they are frequently modified with siloxanes to increase ductility. At the same time, typical silicone surface properties such as hydrophobicity are added, but also adhesion to the substrate is reduced. Therefore, a balancing of different properties is required (Pistone et al., 2021). The siloxanes are chemically bound to the epoxy and do not lead to the release of silicone oils as in the case of foul-release coatings (Watermann & Eklund, 2019).

Advantages of hard coatings are the low amounts of micro-plastic release during the use phase (Daehne et al., 2023), the generally longer service lifetimes, good repairability and the need for fewer coating layers to be applied (Wezenbeek et al., 2018). Resistance to physical wear and tear achieves complementarity to additional antifouling systems that employ the physical removal of fouling, e.g., above and underwater cleaning. According to Wezenbeek et al. (2018), hard coatings typically have no specific antifouling properties and deriving their antifouling function from the easy removal of the fouling[1]. Therefore, hard coatings are designed for multiple cleaning cycles by brushes or hydro-jetting. Depending on the degree of fouling,

1 Still, from a review of commercially available hard coatings, it can be seen that products commonly contain biocides, most predominantly copper.

the forces applied during the cleaning can be adjusted to balance between fouling removal and minimization of abrasion of the coating (Watermann & Eklund, 2019).

During the use phase a potential leakage of bisphenol A and nonylphenol into water is mentioned (Wezenbeek et al., 2018). Nonylphenols have been already included on ECHAs authorization list, which restricts their use, or are included as candidates on the list[2]. Bisphenol A, which is an endocrine disruptor and toxic to reproduction, no publicly available data on consumer uses is registered, but it is mentioned under professional use, with the example of paints and coatings explicitly mentioned[3]. Bisphenols are commonly used in epoxy resins and may be contained or leach from non-biocidal coatings (Wezenbeek et al., 2018).

As further disadvantages of hard coatings it should be stressed that the absence of antifouling properties requires regular cleaning and respective cleaning systems add efforts for the boat owners. While the high durability and adhesion of a hard coating may be an advantage during the use phase, it can be a drawback when the coating needs to be removed. Typically, high-pressure water cleaning or sanding is used to remove hard coatings which can lead to dust emissions (Wezenbeek et al., 2018). Due to the high VOCs content of the coatings, health and environmental risks may be present during the application phase, however, these risks can be minimized by using appropriate personal protection equipment (PPE).

Some manufacturers of hard coatings also market their products as 'thin film' paints (sometimes indicated as TF in the product name). One advantage of TF products is the shorter maintenance time, as less time is needed to remove/sand old, thin layers of paint (personal communication during stakeholder consultation).

2.3.2 Foul release / non-stick coatings

Foul release and non-stick coatings are grouped into one category as it is often difficult to distinguish between coatings that prevent attachment of fouling (i.e. non-stick coatings) and coatings that allow for an easy removal of fouling (i.e. foul release coatings) (Wezenbeek et al., 2018). Most frequently, the coatings are based on silicone elastomers like polydimethylsiloxane (PDMS) (Daehne et al., 2023), but could also be based on fluoropolymers, e.g. perfluoropolyethers (PFPE) or polyethylene glycol (PEG) fluoropolymers, that can be also applied in combination (Wezenbeek et al., 2018). Silicone-based foul release/non-stick coatings may contain siloxanes, which exude from the coating and may support the antifouling effect. In the study by the German EPA (Daehne et al. 2023) cyclic siloxanes such as D4, D5 and D6 have been found to be present as residual monomers in low concentrations. Exuding and thus a release of these substances is therefore not regarded as intended (Daehne et al. 2023).

One key principle of the coatings is based on producing a hydrophobic surface that limits the adhesion of the fouling (Donnelly et al., 2022). However, a draw-back is that the coating requires a combination of coatings layers to be applied. A primer achieves the adhesion to the substrate, while a tie coat provides a connecting layer to ensure the adhesion of the topcoat. Despite the hydrophobicity and smoothness of the topcoat layer not all fouling can be prevented in all situations. Diatom brown slimes can attach to these smooth surfaces, and along with a conditioning film of proteins as well as slime of living and dead bacteria further fouling stages with the settlement of e.g. macroalgae can follow (Nurioglu et al., 2015).

Therefore, some products use a different approach by creating hydrophilic surfaces. In this case, the coating preferentially attracts water molecules over fouling particles that leads to a hydration layer that provides the antifouling property of the coating (Donnelly et al., 2022). Due to the hydration layer some of the coatings are referred to as using 'liquid surface technology' (Wezenbeek et al., 2018). Most frequently foul release coatings are based on PDMS that exude polyethylene glycols during their service life, requiring for a renewal of the coating after 1-2 years (Daehne et al., 2023).

Hydrophobic and hydrophilic characteristics can be also combined in one coating to create an alternating pattern and a more diverse surface, which distorts the proteins that the organisms use to attach to the surface (Donnelly et al., 2022). These more dynamic and complex surfaces that have a higher variability in chemical and mechanical properties are also referred to as 'amphiphilic' coatings (Wezenbeek et al., 2018). Further developments are related to the

2 https://echa.europa.eu/de/substance-information/-/substanceinfo/100.239.148

3 https://echa.europa.eu/de/substance-information/-/substanceinfo/100.001.133

employment of biomimetic approaches as many marine organisms have developed strategies to regulate biofouling (Sánchez-Lozano et al., 2019).

The more complex application of foul release/ non-stick coatings, together with their higher vulnerability to physical forces, may prevent users from choosing such products and inhibit the market uptake despite a potentially superior environmental and health performance.

Further efforts are taken to improve adhesion of the silicone coatings, or develop other coatings, e.g., that are based on polyurethane- and epoxy-silicone. Approaches to improve foul-release coatings aim to improve the mechanical properties and the surface roughness that influences the wettability of the coating (Pistone et al., 2021). In this regard, varying chain lengths and long alkyl chain alkoxysilanes are explored and tested, showing similar hydrophobicity as more traditional fluorinated precursors (Sfameni et al., 2022). Different nano-filling materials have also been proposed, including carbon nanotubes, graphene oxide or titanium dioxide (Daehne et al., 2023), including nano-container based active systems, e.g., for a potential integration of self-healing properties (Shchukina & Shchukin, 2019). Some of the remaining challenges are related to finding the balance between surface mechanical properties, the coating's durability, adhesion strength to the substrate, elasticity, while achieving antifouling performance (Pistone et al., 2021).

2.3.3 Self-polishing coatings

In contrast to traditional self-polishing coatings that derive their antifouling effect mainly from their active substances that are acting on different cellular targets, non-biocidal self-polishing paints employ a combination of processes such as hydrolysis, particle dissolution and surface polishing (Camps et al., 2014; Ielo et al., 2022). For achieving an effective antifouling effect, regular and minimal movement of the boat is necessary to promote the self-polishing functionality of the coating, even though it is also reported that some coatings also function in a stationary state (Daehne et al., 2023).

The general lack of ingredient disclosure for self-polishing coatings can make it difficult to assess the detailed functioning mechanism of the coatings (Wezenbeek et al., 2018). In this context, some authors distinguish between Controlled Depletion Coatings (CDC) that use polyacrylate-based polymers or rosin, and self-polishing coatings (SPC) that are often based on polymethyl acrylates, combined with a variety of functional groups based on fluoropolymers or polycarbohydrates (Daehne et al., 2023). In both systems, that are not further distinguished in the following, the coating depletes over time, thereby losing its antifouling protection. The speed of depletion can be controlled by several coating design characteristics such as the level of polymerization or the ratio of hydrophilic and seawater-hydrolysable groups (Camps et al., 2014; Ielo et al., 2022).

Once the self-polishing coatings is depleted, it needs to be renewed. Time-intervals for renewal are reported to be in the range of 1-2 years, while being well suited for DYI application and repair. However, also for this type of coating removal poses a risk of spreading the paint dust particles as it requires high-pressure cleaning or sanding (Wezenbeek et al., 2018). Further, given the context and increased awareness of microplastic pollution, the environmental impact of self-polishing paints, even without the use of biocides provides room for research and a critical discussion.

2.3.4 Other non-biocidal antifouling systems

Apart from paints, other non-biocidal antifouling systems are available. These systems are shortly mentioned here; however, they are not further investigated in this study as they differ substantially in application and mode of action from antifouling paints. Other non-biocidal antifouling systems are summarized in TABLE 2-1.

TABLE 2-1 Other antifouling systems available and in development (summarized from Wezenbeek et al., 2018).

Antifouling system	Mode of action	Comment
Natural compounds	Fatty acids derived from algae and bacteria with medium to high bioactivity	In the stage of small-scale laboratory testing. May potentially fall under BPR.
Physical defense	Replication of natural hostile and ultrasmooth surfaces of moluscan shells or shark skin, light emitting glow-in-the-dark phosphorus power that inhibits diatom settlement, integration of UV light-emitting diodes into the coating	At different stage of development, but need for further research
Chemical defense	Based on the ability of some organisms to produce antifouling compounds	Biocide Product Regulation (BPR) does not distinguish between naturally or manufactured biocides. . May potentially fall under BPR.
Combined physical and chemical defense	Use of synergetic effects of surface topography and chemical effect by, e.g. replacing 30% copper by 0.1% abamectin, representing a biocide that is produced by a soil bacterium	Abamectin is suspected to be toxic to reproduction and a recognized biocide under BPR
Enzymes	Large variety of mechanisms possible, including the degradation of the adhesives that are produced by microorganisms to attach to the coating	Complex system, e.g., difficult to ensure stability of substrate supply for enzymes. May potentially fall under BPR.
Films and foils	Film with antifouling functionality are glued to the hull, including bio-inspired films, spiky hair layer that vibrates and sways propelled by water movement	Production of drag so that further developments aim to provide applications for fast moving boats
Electro-chemical	Utilization of electro-chemical principles that lead to release of metals (Cu) or adapts the pH-conditions	Biocide release would fall under BPR.
Grease	A layer of grease ('udder cream') is applied, that prevents organisms to settle on the surface	Cheap product that depletes quickly and is forbidden in many marinas as the hull becomes slippery, resulting in a safety issue when lifting the boat, some products contain antibacterial substances
Ultrasound	Transmitter inside the boat's, passing through the hull, creating microscopic vibrations that create cavitation bubbled that implode and kill unicellular organisms	Indication of selectivity to specific microorganisms, requires adaptation of wavelengths and/or combination with coatings, but several thousand systems sold each year, with positive reviews
Mechanical cleaning installations	High-pressure water systems, above- or underwater brushing and cleaning systems, both mobile or stationary, including under water cleaning robots that can collect fouling and paint in a container	Early systems were not taken up by the market, but newer systems seem to have better performance, including drive-in washers, possible limitations regarding size

2.4 Comparison of efficacy of antifouling products

In the following section, a few identified investigations comparing the efficacy of different antifouling paints are reviewed and summarised.

2.4.1 Field efficacy test in the Netherlands by Klijnstra (2020)

Klijnstra, (2020) conducted a study on efficacy of non-biocidal antifouling paints on request of the Netherlands Ministry of Infrastructure and Water Management as the lack of knowledge is recognized as an obstacle in public acceptance of the non-biocidal paints.

Klijnstra, (2020) conducted field tests on real boats at two locations in the Netherlands, one of the tests in a marine location, the other in fresh water. Only the salt water test is considered here. Additionally to the salt water test, a static exposure test with coated panels (the raft test) was conducted. Panels with coatings were mounted onto one of the exposure racks of the raft facility, which was located at a harbour with natural tidal currents occurring between 0 and 2 knots.

Among the 12 antifouling systems tested were three non-biocidal antifouling paints and one biocidal coating (other systems were foils, films, grease and ultrasound systems).
Paints tested were:

A. Non-biocidal, foul release paint
B. Biocidal self-polishing coating
C. Non-biocidal, foul release paint
D. Non-biocidal paint (type not identified)

Field test in salt water
In the saltwater test, 7 small polyester boats and 2 polyester sailing yachts were involved in the test. Paints A, B and C, as well as some of the other antifouling systems, were applied to the small boats, while the sailing yachts were provided with other antifouling systems. The boats were actively sailing during large part of the season. The boats were lifted out from the water and inspected 5 times during the season.
Product A had to be removed in the middle of the season, as the hull was completely covered with different fouling species. The result is attributed to a mistake during application of product A. The biocidal product B, included as a reference, performed well throughout the season, however, at the end of the season a thick slime formed at the aft part of the hull. Product C displayed 35% fouling coverage at the end of the season, however, no barnacles nor algae were attached.

Apart from the degree of fouling developed on the hulls, the ease of cleaning was also evaluated in the field test. Cleaning of silicone-based, foul release paint treated hull (product C) was easy compared to the self-polishing coating (product B).

Raft test
For the raft test, the panels treated with paints as well as untreated PVC panels as blanks were immersed in May 2019 and inspected about once a month until September, where the raft was taken up from the water (FIGURE 2-2). It is noted that the raft test presents a worst-case scenario due to the static conditions, which cause increased fouling.

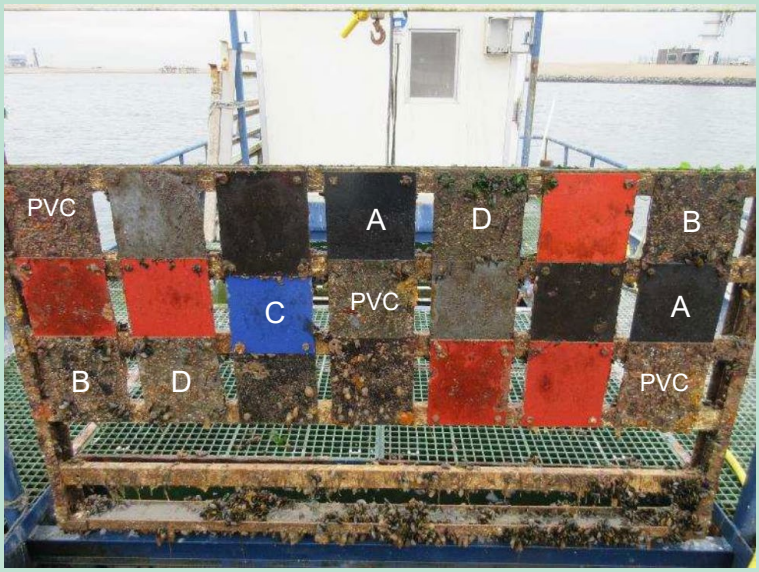


FIGURE 2-2 Panels with antifouling products at final inspection September 2019 (picture modified from Klijnstra, 2020). Panels marked with letters were treated with antifouling paints (see text above).

Among the best performing products was the silicone based, foul release paint C as only thin slime and no macro-fouling formed during the entire exposure period. The other silicone-based, foul release paint A gave slightly less performance with higher rates of macro-fouling later in the season. Panels treated with product D were largely covered with macro-fouling, e.g. barnacles, green and brown algae and colonial tunicates already at the first inspection and the performance was comparable to the PVC blanks. The test of product B is not valid as the supplier recognised that the wrong topcoat was applied.

The raft test thus documents the antifouling effect of two non-biocidal silicone-based foul release paints. A general comparison between performance of non-biocidal vs. biocidal products cannot be made based on the limited number of products and use conditions tested.

Klijnstra, (2020) concludes (amongst others) that the performance of a product depends on the fouling pressure at a given site (higher in salt water) and hull cleaning can be seen as a valuable additional tool to improve coating performance. Also, market acceptance of non-biocidal antifouling products for pleasure boats may increase by stimulating initiatives on development of tools and infrastructure for hull cleaning.

2.4.2 Baadmagasinet

Baadmagasinet is a print and online publication primarily targeting boat owners, touring and racing sailors as well as motorboat and sailing enthusiasts. In the recent years, Baadmagasinet has repeatedly conducted non-scientific tests with antifouling paints.

The 2020 test was carried out with 12 paints, of which one was a non-biocidal, foul release paint. The hull of the boat was divided into 12 test areas (FIGURE 2-3). Each test area was pre-treated before application, i.e. all test areas were hosed with water and brushed with a stiff broom. Last year's fouling was removed and the test areas were sanded. The test boat was launched for seven months and has travelled approx. 200 nautical miles with a period of sway of 30 days. Otherwise, the boat has been in harbour and has been used for weekend trips.

FIGURE 2-3 Test boat with application of different paints (from Rasmussen, 2021).

At the end of the season, the boat was taken out of the water and each test area was inspected for degree and type of fouling. The test results were rated with 1 to 5 stars, where 1 is the lowest achievable and 5 the highest achievable result.

Areas treated with non-biocidal, foul release product (blue colour version) showed macrofouling of hydroids and barnacles, however, re-treated areas only showed slime. The non-biocidal product obtained two stars, and thus received a lower rating than the 11 biocidal products, which were assessed with three - five stars (Rasmussen, 2021).

The test in 2018 was carried out with 31 different antifouling paints, of which one was without biocides, namely the same as used in 2020 (non-biocidal, foul release product). However, three different colours (red, black, blue) were included in the test. The different colours of the non-biocidal, foul release l product got different results in the assessment; black and red only got one star, the blue paint got four stars as it showed only light bryozoan fouling and no algae, unlike the first two (Rasmussen, 2019). There is no information available what could be the cause of this effect.

The database of this test is too small to allow for general conclusions. The variability of results for the same product may be related to deviations in the test methods, subjective rating deviations and/or environmental differences between the test fields.

2.4.3 Other observations from stakeholder consultation

The efficacy and performance of non-biocidal paints compared to biocidal paints was discussed with several stakeholders. Generally, there was agreement between several stakeholders that corresponding antifouling results could not be achieved with non-biocidal paints.

However, the market is also recognised under strong development with new non-biocidal products arriving every year. In the current year (2023), the sailing media Baadmagasin conducts a test exclusively with non-biocidal paints (Øverup, 2023).

During 2001-2010, the Danish Sailing Association has conducted yearly tests with non-biocidal paints by applying the paints on 10-15 boats per season. They observed a large variability in results even for the same paints. Variability could partially be linked to use of the boat (sailing speed and distance), meaning boats that travelled over larger distances usually showed less fouling. Other variables were salinity, but also other conditions at a given harbour (e.g. nutrients in the water, marine biology, currents) as well as light exposure (e.g. increased fouling on the southern facing hull side when the boat is in the harbour) appeared to affect the results

(FLID, 2023). Therefore, it is also difficult to transpose performance results from one location to another scenario.

FLID (2023) remarks that use of non-biocidal paints is desirable from an environmental perspective, but brings along other challenges, hereunder:

- increased requirements to boat cleaning, e.g. cleaning installations
- waste handling of removed fouling
- increased fuel consumption of boats with fouling
- safety issues, e.g. when cooling water intake gets clogged as a result of fouling or difficulties in sailing under challenging weather conditions when the (too) small motors of sailing ships are further burdened due to fouling

Even though hull cleaning can be seen as a valuable additional tool to improve coating performance, it is also recognized that cleaning, especially mid-season, puts increased costs (for lifting the boat out of the water) and work effort on the boat owner. Underwater cleaning installations have earlier been investigated, but not considered as feasible alternatives in Danish marinas (FLID, 2023; Højenvang, 2002).

Several of the contacted stakeholders remark that the use of biocidal paints in the Swedish Baltic Sea is prohibited. The use of biocidal paints is regulated differently at the west, east and north-east coasts of Sweden, with more restrictive requirements for the use of biocidal paints on the east coast and a ban on biocidal paints on the north-east coast. The difference in regulation is explained by differences in fouling pressure. Fouling growth decreases with decreasing salinity, which supports more restrictive regulation in waters with lower salinity.[4]

2.5 Non-biocidal antifouling products

2.5.1 Identified non-biocidal products

Non-biocidal antifouling products have been identified via literature research, searches on manufacturers' and retailers' websites, and information by stakeholders during the stakeholder consultation and in interviews (see chapter 2.1). All available safety and technical data sheets (SDS and TDS) of the identified non-biocidal antifouling products were downloaded and the relevant information such as containing substances, price, efficacy, and the recommendation of the use of PPE were noted in a separate excel sheet.

A total of 65 coating products were identified and reviewed. This group comprises both antifouling paints (topcoats), as well as antifouling paints systems, where a given system comprises several products (e.g. a specific tiecoat, primer or conversion primer has to be used along with the topcoat).

During review, some of the products were identified as less relevant, for the following reasons:

- Only marketed for professional use
- Products only for above waterline-applications, fixed installations or similar limitations
- Contained antifouling biocides of the type PT21, even though they were marketed as eco-friendly
- For a few products identified via literature, limited/no information on manufacturers and/or products were available

In conclusion, 21 antifouling paints and a corresponding number of tie coats, primers and related products for use on private pleasure boats were identified.

2.5.2 Availability of non-biocidal paints on the Danish market

Applications and acceptance of non-biocidal paints by consumers is still in its infancy according to communications with several user associations. According to information from stakeholders, some marinas on the east coast of Sweden require documentation that incoming boats have not been treated with biocidal paints as a consequence of Swedish regulation on biocidal antifouling paints. At Danish marinas, there are no requirements on use of certain types of paints or coatings, e.g., use of non-biocidal paints (Danish Sailing Association, 2023; FLID, 2023; Øverup, 2023).

[4] Swedish Chemicals Agency: Anti-fouling paints (https://www.kemi.se/en/chemicals-in-our-everyday-lives/advice-on-chemicals-in-your-home/anti-fouling-paints)

The notion of low acceptance and use of non-biocidal products communicated by user stakeholders is reflected by the number of different products available at Danish retailers.

The offer of a total of 24 Danish retailers with sailing and boat equipment was screened to obtain an indication of which non-biocidal paints are commonly available for Danish consumers. The number of 24 retailers comprised 14 physical stores in Denmark, which also had a webshop on their homepage (11 special sailing retailers and 3 general DYI warehouses). Additionally, 10 specialised sailing retailers operating exclusively or primarily via webshops were reviewed.

Of the 24 retailers reviewed, 17 offered non-biocidal paint(s). Eight out of these 17 offered only one type of non-biocidal paint. Nine out of the 17 retailers offering non-biocidal products offered two – four types of non-biocidal paints.

According to communication with several stakeholders, the market of antifouling paints (biocidal and non-biocidal) in Denmark is dominated by a few antifouling manufacturers. Products from the mentioned few manufacturers were also the most commonly met brands in the retailer review. A few retailers do also offer other products from other brands/manufacturers than the most commonly met. In principle, Danish consumers can also import paints from other European and non-EU countries. However, according to information from several stakeholders, this does not appear to be common practice among boat owners.

2.5.3 Transition to non-biocidal antifouling paints

The choice of coating system is usually dependent on earlier treatments, as the different types of paints not necessarily are compatible with each other. In certain cases, the boat owner may wish to remove the existing coating systems completely and apply a new system, e.g. if the type of the existing system is not known.

Many boat owners prefer to use the same bottom paint as in the previous year as the easiest, least time-consuming option for preparing the hull for the coming season (Danish Sailing Association, 2023; Hansen, 2022).

The application of a new paint product requires some consideration about the compatibility of the new product in the existing coating system. In some cases, a treatment with a conversion primer after sanding will be sufficient before applying the non-biocidal paint (e.g., when changing from biocidal hard coatings to non-biocidal hard coatings). In other cases, a full sanding is required before a new coating system can be used, e.g., when the old coating is in poor condition or a self-eroding/polishing paints have been used previously (Hansen, 2022).

Among the non-biocidal antifouling paints, silicone-based foul release or non-stick paints appear to be the most prominent alternative to biocidal antifouling paints. The chemistry of silicone-based paints has specifically been developed for non-biocidal paints (i.e., in contrast to hard coatings and self-polishing paints, silicone-based foul release paints are principally without PT21 biocides). Because the chemistry of the silicone-based antifouling paints differs considerably from other paints, special treatment of the hull is required.

The application of a silicon-based paints will initially impose increased costs, as a coating-specific primer (or seal coat) and tie coat are required as well (FLID, 2023; Hansen, 2022). Under favourable use conditions, a non-biocidal, foul release coating may last for two years, saving the cost for one seasonal treatment every second year. However, there are also conventional, biocidal products available with the same advantage (FLID, 2023). The paint manufacturer Hempel states that maintenance costs when using a foul release coating will be above maintenances cost of using a conventional, biocidal product for the first two years, will be at the same level in the third year, and lie below in the consequent years (Hempel, 2023).

The change from using a biocidal paint to using a non-biocidal paint is recognized to be primarily motivated by environmental consciousness of the boat owners. The main drivers for choice of product mentioned by users are, however, price, ease of use and performance. The latter parameter is commonly discussed among boat owners when boats are taken up at the end of the season and differences in fouling become obvious (FLID, 2023).

2.6 Use scenarios of antifouling paints

Different types of boats and different ways of using the boats occur among boat owners, offering diverse fouling conditions. Antifouling systems usually target a certain use scenario and the performance of a product depends on the conditions in a given use scenario.

The degree of fouling is impacted by environmental factors such as salinity of the water, temperature, nutrients and light exposure (Højenvang, 2002; Wezenbeek et al., 2018). Generally, the warmer and more saline the water, as well as the more light, the more fouling occurs. Decisive for the choice of product are the use conditions, i.e. use frequency of the boat, the typical sailing speed, typical sailing distances and cleaning regime. Based on these factors, a decision tree for boat owners is presented in Wezenbeek et al., (2018) and shown in FIGURE 2-4 below.

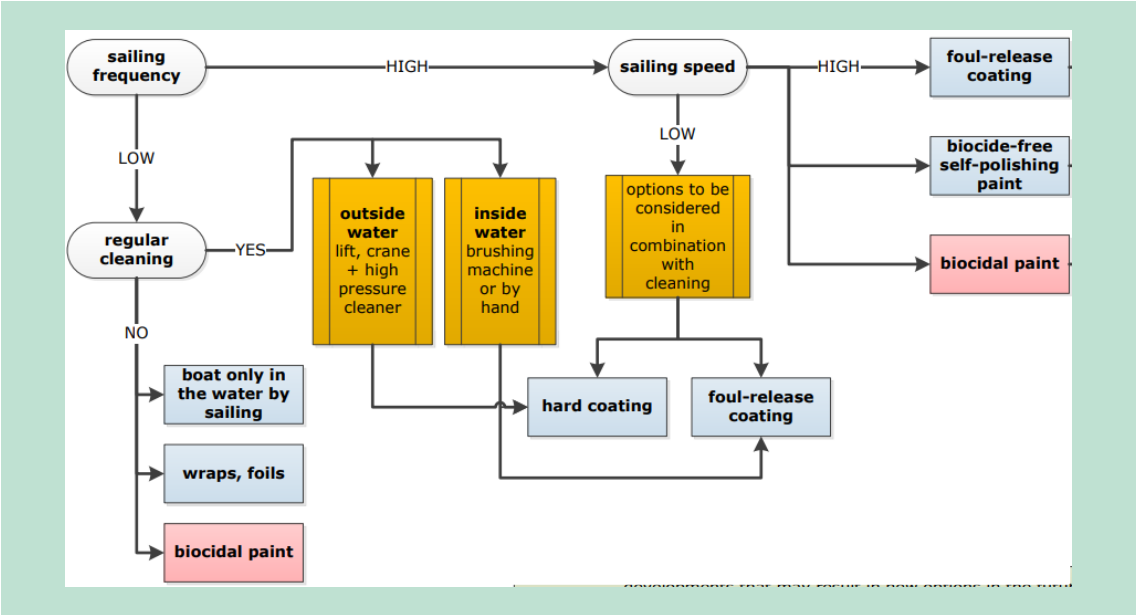


FIGURE 2-4 Decision-tree for boat owners, adapted from Wezenbeek et al., (2018). Note that the figure comprises both biocidal and non-biocidal paints.

The type of hull material can influence the choice of antifouling product, however, this only seems to be relevant for biocidal paints, as certain biocidal ingredients (i.e. copper) are not compatible with aluminium hulls (FLID, 2023).

Due to the differences in mode of antifouling action and differences in product chemistry, use scenarios cannot be defined in the same way for biocidal and non-biocidal paints.

Silicone-based foul release paints (only non-biocidal products) are suitable for all types of boats (slow speed and racing), all substrates (except wood) and all types of water (Hempel, 2023).

Non-biocidal self-polishing paints can principally also be used for all types of boats, however, for boats frequently sailing at high speed, the paint may be depleted quickly, if the self-polishing rate is not adapted to sailing at high speed. As such, self-polishing paints should only be used for high-speed boats if the self-polishing paint is applied in several layers and/or the paint deteriorates at a (low) rate adapted to high speed boats.

Non-biocidal hard coatings can principally also be used for all types of boats. However, as they do not have any actual antifouling mechanism, they may be primarily suited for boats that are used frequently and/or at high speed, in order to “sail off” the fouling. Additionally, boat user(s) should have a cleaning scheme in place, hereunder easy access to harbour facilities allowing for cleaning in or out of water.

Based on the above, a clear attribution between non-biocidal product types and specific use/environmental parameters is not possible. The selection of products relevant for the risk

assessment is therefore based (amongst other criteria) on the representation of different product types, and not on the representation of different use scenarios representation.

Substances of concern in non-biocidal paints
The definition of "substance of concern" for this project is taken from the biocidal products regulation (BPR) (Regulation (EU) No. 528/2012). The wording is as follows:

"substance of concern" means any substance, other than the active substance, which has an inherent capacity to cause an adverse effect, immediately or in the more distant future, on humans, in particular vulnerable groups, animals or the environment and is present or is produced in a biocidal product in sufficient concentration to present risks of such an effect. Such a substance would, unless there are other grounds for concern, normally be:

a substance classified as dangerous or that meets the criteria to be classified as dangerous according to Directive 67/548/EEC, and that is present in the biocidal product at a concentration leading the product to be regarded as dangerous within the meaning of Articles 5, 6 and 7 of Directive 1999/45/EC, or

a substance classified as hazardous or that meets the criteria for classification as hazardous according to Regulation (EC) No 1272/2008, and that is present in the biocidal product at a concentration leading the product to be regarded as hazardous within the meaning of that Regulation,

a substance which meets the criteria for being a persistent organic pollutant (POP) under Regulation (EC) No 850/2004, or which meets the criteria for being persistent, bio-accumulative and toxic (PBT) or very persistent and very bio-accumulative (vPvB) in accordance with Annex XIII to Regulation (EC) No 1907/2006;"

The definition refers to multiple EU laws dealing with the classification and regulation of chemicals.

The first two stated laws Directive 67/548/EEC and Directive 1999/45/EC both regulated the classification, labelling and packaging (CLP) of chemicals and were repealed in 2008 by the CLP Regulation (1272/2008) mentioned in the second bullet point.
The last bullet point refers to a substance being a persistent organic pollutant (POP) as regulated by Regulation (EC) No 850/2004 repealed by Regulation (EU) 2019/1021 on persistent organic pollutants. Additionally, a substance classified as persistent, bio-accumulative and toxic (PBT) or very persistent and very bio-accumulative (vPvB) under the REACH Regulation (EC) No 1907/2006 also falls under the definition of a "substance of concern". Here it should be noted that as of 20.04.2023 the identification of a substance as PBT or vPvB is now regulated under the CLP Regulation (ECHA, 2023b). However, the REACH Annex XIII still contains the criteria for the identification of a substance as PBT or vPvB.

The CLP Regulation classifies a substance (or mixture) as "hazardous" if it fulfils the criteria laid down in Annex I part 2 to 5. The Annex provides criteria for each hazard class, above which the substance (or mixture) is to be classified as such. In case of the human and environmental hazards the Annex also provides concentration limits for the hazardous substances above which a mixture containing the hazardous substance is also classified as hazardous (e.g., a carcinogenic substance with a concentration of 25% is dissolved in ethanol, which results in the solution being classified as carcinogenic, even though the ethanol is not classified as carcinogenic).

All relevant hazard classes as well as corresponding H-codes and concentration limits are presented in Table 0-1 and Table 0-2 in Appendix 1. It should be noted that the mentioned concentration limits are the lowest ones based on all sub-categories and influencing factors for each hazard class. The exact concentration limit and resulting hazard classification depends on the different substances, their concentrations as well as other factors, and as such the limits here should only be seen as guidance values. All substances from the products' SDS were recorded together with their CAS number as well as self-classification as presented in the SDS. In order to compare them to the above definition of "substance of concern" the harmonised classifications under the CLP-Regulation were identified and inserted into the list. Additionally, the POP, PBT and vPvB properties of the substances were researched and extracted, as well as the listing of a substance as an active substance under the BPR.

For the purpose of this project the following hazard classes are considered relevant:

- Germ cell mutagenicity
- Carcinogenicity
- Reproductive toxicity
- Specific target organ toxicity — repeated exposure
- Respiratory or skin sensitisation
- Aspiration hazard
- Hazardous to the aquatic environment

These hazard classes were selected in cooperation with the Danish EPA for prioritising substances for the hazard assessment. Based on the experience with risk assessments from other consumer product surveys, these hazards classes typically comprise the most critical endpoints, and are thus leading to conservative risk assessments.

Additionally, PBT, vPvB and POP properties were considered as well as the listing as an active substance under the BPR. The following TABLE 2-2 summarises the results.

TABLE 2-2: Identified substances of concern in the products' SDS, their harmonised classification, PBT, vPvB properties and listing as an active biocidal ingredient in the BPR

Substance name (times found in products)	CAS Number	Harmonised hazard codes according to project scope	PBT, vPvB, POP	Typical concentration rages [%]. (Exceeding CLP limit?)	Function (if known), additional notes
solvent naphtha (petroleum) (15)	64742-95-6	H340 (Muta. 1B) H350 (Carc. 1B) H304 (Asp. Tox. 1) Note P[1]		10-50 (yes)	solvent
4-methylpentan-2-one (4)	108-10-1	H315 (Carc. 2)		1-15 (yes)	solvent
Silanamine, 1,1,1-trimethyl-N-(trimethylsilyl)-, hydrolysis products with silica (1)	68909-20-6			≥3 - ≤4.6 (no)	thixotrope (modifies rheological properties of the paint). The substances is also an approved biocide under BPR as PT18 (Insecticides, acaricides and products to control other arthropods).[2]
Titanium dioxide (11)	13463-67-7	H351 (Carc. 2, Inhalation) Note W[7] Note 10[8] Note V[9]		5-25 (yes)	White pigment
Bisphenol A epichlorohydrin polymer (5)	25068-38-6	H411 (Aquatic Chronic 2) H317 (Skin Sens. 1)		10-75 (yes)	Binding agent
Ethylbenzene (16)	100-41-4	H373 (STOT RE 2, hearing organs) H304 (Asp. Tox. 1)		1-10 (no)	solvent
Toluene (7)	108-88-3	H361d*** (Repr. 2) H373** (STOT RE 2*) H304 (Asp. Tox. 1)		≤0.3 (no)	solvent

Substance name (times found in products)	CAS Number	Harmonised hazard codes according to project scope	PBT, vPvB, POP	Typical concentration rages [%]. (Exceeding CLP limit?)	Function (if known), additional notes
3,6-diazaoctanethylenediamin (1)	112-24-3	H412 (Aquatic Chronic 3) H317 (Skin Sens. 1)		<1 (no)	
Styrene (2)	100-42-5	H361d (Repr. 2) H372 (STOT RE 1, hearing organs) Note D[6]		≤0.3 (no) 30-40 (yes)	
Hydroquinone (1)	123-31-9	H341 (Muta. 2) H351 (Carc. 2) H317 (Skin Sens. 1) H400 (Aquatic Acute 1)		0.01-0.1 (no)	
4,4'-isopropylidenediphenol (1)	80-05-7	H360F (Repr. 1B) H317 (Skin Sens. 1)		≤0.024 (no)	
Salicylic acid (1)	69-72-7	H361dF (Repr. 2)		≤0.3 (no)	
Octamethylcyclotetrasiloxane (D4) (9)	556-67-2	H361f*** (Repr. 2) H410 (Aquatic Chronic 1)	PBT, vPvB, [3]	≤0.1-0.3 (no)	
Decamethylcyclopentasiloxane (D5) (2)	541-02-6		vPvB, [3]	≤0.3 (no)	
Dodecamethylcyclohexasiloxane (D6) (1)	540-97-6		vPvB, [3]	≤1.0 (no)	
Hydrocarbons, C14-C19, Isoalkanes, cyclics, <2% aromatics (1)	64742-46-7	H350 (Carc. 1B) Note N[4]		≥1.0 - ≤5.0 (yes)	solvent

Substance name (times found in products)	CAS Number	Harmonised hazard codes according to project scope	PBT, vPvB, POP	Typical concentration rages [%]. (Exceeding CLP limit?)	Function (if known), additional notes
Hydrocarbons, C11-C12, isoalkanes, <2% aromatics (1)	64741-65-7	H340 (Muta. 1B) H350 (Carc. 1B) H304 (Asp. Tox. 1) Note P[1]		≥1.0 - ≤5.0 (yes)	solvent
Zinc oxide (1)	1314-13-2	H400 (Aquatic Acute 1) H410 (Aquatic Chronic 1)		25-50 (yes)	dissolution of self-polishing paint, pigment
Butanone oxime (1)	96-29-7	H350 (Carc. 1B) H373 (STOT RE 2, blood system) H317 (Skin Sens. 1)		<0.3 (yes)	by-product of self-catalytic silane, oxime cross linkers
Alkanes, C14-17, chloro (MCCP) (1)[3]	85535-85-9	H400 (Aquatic Acute 1) H410 (Aquatic Chronic 1)	PBT, vPvB	2.5-10 (no)	Plasticiser
3-aminopropyldiethylamine (1)	104-78-9	H317 (Skin Sens. 1)		≤0.3 (yes)	
Trizinc bis(orthophosphate) (1)	7779-90-0	H400 (Aquatic Acute 1) H410 (Aquatic Chronic 1)		≤2.5 (no)	
Ethylenediamine (2)	107-15-3	H334 (Resp. Sens. 1) H317 (Skin Sens. 1)		≤0.3-≤ 1(yes)	
Solvent naphtha (petroleum), medium aliph. (1)	64742-88-7	H372 (STOT RE 1, central nervous system) H304 (Asp. Tox. 1)		≤5 (no)	Solvent
Naphtha (petroleum), hydrotreated heavy (1)	64742-48-9	H340 (Muta. 1B) H350 (Carc. 1B) H304 (Asp. Tox. 1) Note P[1]		<10 (yes)	Solvent

Substance name (times found in products)	CAS Number	Harmonised hazard codes according to project scope	PBT, vPvB, POP	Typical concentration rages [%]. (Exceeding CLP limit?)	Function (if known), additional notes
N-butyl methacrylate (1)	97-88-1	H317 (Skin Sens. 1) Note D[6]		≤0.3 (yes)	
Formaldehyde oligomeric reaction products with 1-chloro-2,3-epoxy-propane and phenol (1)	9003-36-5			2.5 – 10 (no)	
Pyrithione zinc (1)	13463-41-7	H360D (Repr. 1B) H372 (STOT RE 1) H400 (Aquatic Acute 1) H410 (Aquatic Chronic 1)			
Epoxy resin (MW ≤ 700) (3)	1675-54-3	H317 (Skin Sens. 1)		≥10 - ≤50 (yes)	
Distillates (petroleum), hydrotreated light (3)	64742-47-8	H304 (Asp. Tox. 1)		≤0.1 (no)	
Methyl methacrylate (1)	80-62-6	H317 (Skin Sens. 1)		≤0.3 (yes)	
Rosin (1)	8050-09-7	H317 (Skin Sens. 1)		10-25 (yes)	Filler/polymer

[1] Note P: The harmonised classification as a carcinogen or mutagen applies unless it can be shown that the substance contains less than 0,1 % w/w benzene (Einecs No 200-753-7), in which case a classification in accordance with Title II of this Regulation shall be performed also for those hazard classes. Where the substance is not classified as a carcinogen or mutagen, at least the precautionary statements (P102-)P260-P262-P301 + P310-P331 shall apply.

[2] For further information about the substance and how it is dealt with in this survey, please refer to the text below the table.

[3] For D4, D5 and D6, a proposal for listing the substances as POPs under the Stockholm Convention is currently under preparation. For MCCP, a restriction under REACH, restricting the presence of MCCP to ≤ 0.1% w/w in mixtures, is currently under preparation.

[4] Note N: The classification as a carcinogen need not apply if the full refining history is known and it can be shown that the substance from which it is produced is not a carcinogen. This note applies only to certain complex oil-derived substances in Part 3 [of Annex I in the CLP Regulation].

[6] Note D: Certain substances which are susceptible to spontaneous polymerisation or decomposition are generally placed on the market in a stabilised form. It is in this form that they are listed in Part 3. However, such substances are sometimes placed on the market in a non-stabilised form. In this case, the supplier must state on the label the name of the substance followed by the words 'non-stabilised'.

[7] Note W: It has been observed that the carcinogenic hazard of this substance arises when respirable dust is inhaled in quantities leading to significant impairment of particle clearance mechanisms in the lung. This note aims to describe the particular toxicity of the substance; it does not constitute a criterion for classification according to this Regulation.

[8] Note 10: The classification as a carcinogen by inhalation applies only to mixtures in powder form containing 1 % or more of titanium dioxide which is in the form of or incorporated in particles with aerodynamic diameter ≤ 10 µm.

[9] Note V: If the substance is to be placed on the market as fibres (with diameter < 3 µm, length > 5 µm and aspect ratio ≥ 3:1) or particles of the substance fulfilling the WHO fibre criteria or as particles with modified surface chemistry, their hazardous properties must be evaluated in accordance with Title II of this Regulation, to assess whether a higher category (Carc. 1B or 1A) and/or additional routes of exposure (oral or dermal) should be applied.

In total, 28 individual substances were identified as potentially hazardous within the scope of this project, equalling roughly 50% of all identified substances. Most commonly, these are solvents such as light naphtha, toluene and ethylbenzene. Light naphtha and toluene fall under the category of CMR substances and since they are typically used in high concentrations and evaporate during and after application, there is a high risk of exposure to these substances.

One biocide of the product type PT18 was identified. Silanamine, 1,1,1-trimethyl-N-(trimethylsilyl)-, hydrolysis products with silica (CAS: 68909-20-6) is listed as an approved active substance under PT18. PT18 includes insecticides, acaricides and products to control other arthropods. For this substance, only its use against poultry red mites and house dust mites in concentrations up to 1.8% is permitted. The substance can only be applied indoor in homes and hotel rooms or in indoor poultry housing (ECHA, 2023a). The substance was identified in one of the surveyed products (a foul release coating). The manufacturer of the product has been contacted directly to obtain additional information regarding the presence and potential biocidal effect of the substance in the product. According to the manufacturer, the substance is added as a shear thinner and adds strength to the dried paint film. The substance does not leach from the paint film and does not have a biocidal effect according to the manufacturer.

Another chemical that is often used in paints is titanium dioxide, which is typically added as a white pigment agent. It is currently (as of May 2023) still listed as Carc. 2 in the CLP-Regulation, however, the European Court of Justice annulled the harmonised classification as Carc. 2 on 23.11.2022 (EUR-Lex, 2022). This judgement is currently being appealed and suppliers of the substance still need to classify it as Carc. 2 until the entry in the CLP-Regulation is deleted. Additionally, if titanium dioxide is used in liquid mixtures, it does not require a Carc. 2 classification, but if it contains at least 1% of TiO_2 particles with an aerodynamic diameter ≤10 µm, it must be labelled with the supplemental label element '*Hazardous respirable droplets may be formed when sprayed. Do not breathe spray or mist*' (EUH211) (ECHA, 2023a). As paints are available in liquid form when they are applied, none of the products need to be labelled as Carc. 2 even if they contain titanium dioxide.

Many paints contain substances hazardous to the aquatic life, such as zinc compounds, medium chain chlorinated paraffins (MCCP) and polymers such as bisphenol A epichlorohydrin polymers, often in concentrations above 25%, which would lead to the mixture being classified as hazardous to the environment.

Four PBT/vPvB substances were also identified, three of which belong to the group of cyclic siloxanes, all of which are present in concentrations below 1%. The fourth substance are the MCCP, which are typically used as a plasticizer and are added in concentrations up to 10%.

POP substances were not identified in any of the assessed paints.

In summary, it can be said that while the non-biocidal antifouling paints do not contain antifouling biocides (PT21), they still contain other hazardous substances, many of which are CMR substances, especially solvents which are present in high concentration and typically evaporate during or after application. Other biocides of other PT types may also be present.

2.7 Conclusion on non-biocidal antifouling paints as alternatives to biocidal antifouling paints

The objective of survey of non-biocidal antifouling paints was to clarify whether there are functional, non-biocidal alternatives to biocidal antifouling paints.

The review of different non-biocidal paint types revealed that antifouling paints without biocides exist, and that some of the types also have mechanisms of antifouling action (i.e. foul release/non-stick coatings, self-polishing coatings).

A limited number of field tests with non-biocidal paints has been identified. According to information obtained from literature and stakeholders, performance tests of antifouling paints are challenging to conduct and the results are highly dependent not only on the product applied, but also on environmental and use conditions. Even though lab-scale tests of different coatings often show promising results, e.g. in the case of non-biocidal foul release coatings (Sfameni et al., 2022), the field studies under real conditions indicate the full complexity of assessing the efficacy and performance of the coatings. Therefore, a considerable variability in test results is observed and general conclusions on the efficacy of biocidal vs. non-biocidal, or between different non-biocidal products cannot be derived.

Several stakeholders describe that non-biocidal products cannot be used as one-to-one replacements for biocidal paints. Adapted use and mechanical cleaning patterns may function as valuable additional tools to improve non-biocidal coating performance. Stakeholders recognise that the market of non-biocidal antifouling paints is under strong development with new products arriving every year.

The review of available safety data sheets showed that non-biocidal antifouling paints contain hazardous substances, hereunder many CMR substances such as certain solvents, which, however, is common for paints irrespective whether there are non-biocidal or not.

Overall, the survey showed that non-biocidal alternatives are available on the Danish market. Among the non-biocidal antifouling paints, silicone-based foul release or non-stick paints appear to be the most prominent alternative to biocidal antifouling paints. Results on functionality of the non-biocidal paints are varying and the use of non-biocidal paints may require adapted use of the pleasure boat and/or adapted maintenance patterns to achieve a corresponding performance to biocidal paints.

2.8 Selection of relevant products for the risk assessment

For the scope of this project, it has been decided to focus on products and brands that are generally available to Danish consumers via the Danish market, as well as products and brands, that may become relevant as future alternatives.

The following criteria are considered for the selection of products

- products from different manufacturers
- products representing different product types
- products available from Danish or EU retailers, both physical stores and webshops
- products from different price ranges
- products containing substances of concern

Based on the criteria above, the following products as listed in TABLE 2-3 are relevant for the risk assessment. The suggested products comprise products from four different manufacturers with activity in Denmark, products from all three relevant product types, as well as some topcoat-specific tiecoats.

TABLE 2-3 Products relevant for risk assessment

Product ID	Product type	Price example (EUR/L)	Substance(s) of concern (SDS)
38F	Foul release	150	yes
39T	Tiecoat	125	Limited data
40S	Self-polishing	43	yes
02S	Self-polishing	39	yes
07H	Hard coating (thin film)	67	yes
01H	Hard coating	48	yes
03F	Foul release	100	yes
04T	Tiecoat	52	yes
31H	Hard coating	46	yes
28F	Foul release	No data	No data
29T	Tiecoat	No data	No data
32H	Hard coating	35	yes
41H	Hard coating	25	yes

3. Chemical analyses of selected products

3.1 Selection of products for GC-MS screening

The objective of the chemical analyses is to obtain additional data for use in the exposure assessment for the consumer health and environmental risk assessment. Chemical identification of hazardous substances is therefore relevant for products were SDS are missing and/or SDS are less detailed.

In a first step, a gas chromatography–mass spectrometry (GC-MS) screening of the relevant products is conducted to identify any potential substances of concern. Depending on product composition, the identified substance's properties and further analysis parameters, the concentration of the identified substances can be determined semi-quantitatively against an internal standard substance.

Potentially, the GC-MS screening can thus deliver semi-quantitative analytical results for use in the exposure assessment. Semi-quantitatively determined concentrations can also be compared to concentrations of the same substances in corresponding products (i.e. same product type), for which detailed SDS are available. However, high contents of complex solvents (i.e. mixed hydrocarbon fractions as solvent naphtha) in the products may hamper the identification and semi-quantification of substances in the GC-MS screening.

The outcome of the initial GC-MS screening contributed to the choice of target analyses for quantification of specific substances in the products, which were performed as the second step of the chemical analyses (see section 3.3).

Among the products listed in TABLE 2-3, a limited number of products were therefore chosen for a GC-MS screening:

- 40S - Self-polishing coating
- 38F - Foul release coating
- 28F - Foul release coating
- 29T - Tiecoat for foul release

These products were chosen based on their potential for becoming future alternatives on the Danish market and because limited information on chemical composition in the SDS. Indications regarding the products content of complex solvents were also considered, causing preference to products with lower content of complex solvents to increase the possibility of useful analysis results of the GC-MS screening.

3.2 Results and discussion of the GC-MS screening

40S Self-polishing coating

The following substances including their semi-quantitative concentrations were found in the GC-MS screening for the paint 40S. For comparison with the information on chemical substances provided in the SDS, TABLE 3-1 shows the substances mentioned in the SDS.

TABLE 3-1 Found substances in the coating 40S including semi-quantitative concentrations from the GC-MS screening as well as substances mentioned in the SDS. Purple – Substances occur in both SDS and GC-MS screening.

Name	CAS no	Concentration (mg/kg)
Substances listed in SDS		
Reaction mass of ethylbenzene and xylene	-	130,000-180,000
1-Methoxy-2-Propanol	107-98-2	50,000-100,000
Hydrocarbons, C10, aromatics, <1% naphthalene	1189173-42-9	50,000-100,000
Butan-1-ol	71-36-3	10,000-50,000
Alkanes, C14-17, chloro (52%)	85535-85-9	10,000-50,000
Substances identified in GC-MS screening		
Acetic acid, butyl ester	123-86-4	530
Ethylbenzene	100-41-4	56,000
p-xylene	106-42-3	33,000
o-xylene	95-47-6	7,000
Mesitylene	108-67-8	1,500
Benzene, 1,2,3-trimethyl-	526-73-8	960
Benzene, 1,2-diethyl-	135-01-3	450
Benzene, 1-methyl-3-propyl-	1074-43-7	1,700
Benzene, 4-ethyl-1,2-dimethyl-	934-80-5	6,300
Benzene, 1-methyl-4-propyl-	1074-55-1	620
Benzene, 2-ethyl-1,4-dimethyl-	1758-88-9	1,600
o-Cymene	527-84-4	1,700
Benzene, 1-methyl-3-(1-methylethyl)-	535-77-3	610
Benzene, 1-ethyl-2,3-dimethyl-	933-98-2	1,100
Benzene, 1,2,4,5-tetramethyl-	95-93-2	5,900
Benzene, 2-ethenyl-1,4-dimethyl-	2039-89-6	1,100
Benzene, 1-methyl-2-(2-propenyl)-	1587-04-8	1,700

From the GC-Ms screening results it can be seen that only solvents were identified, which is to be expected for paint products. The solvent evaporates after application and only serves to apply the paint to the desired surface. Two solvent groups are also listed in the SDS, namely the reaction mass of ethylbenzene and xylene, and the C10 aromatic hydrocarbons. Furthermore, the SDS mentions 1-methoxy-2-proanol, butane-1-ol and C14-17 chlorinated alkanes (MCCP).

The substances that are mentioned in the SDS and confirmed to be present in the paint via GC-MS are marked in purple in TABLE 3-1. Ethylbenzene and the xylene compounds (p-xylene and o-xylene) stem from the mentioned reaction mass, while the identified alkylated benzene compounds fall under the C10 aromatic hydrocarbons from the SDS. The overall detected concentrations of the ethylbenzene and xylene is 96,000 mg/kg compared to the 130,000-180,000 mg/kg mentioned in the SDS. Similarly, the concentration of the alkylated benzene compounds (25,240 mg/kg) is lower than the concentration in the SDS (50,000-100,000 mg/kg). The concentrations of the solvents in the GC-MS screening are thus below the concentration ranges provided in the SDS. However, it is noted that the GC-MS screening only provides semi-quantitative results and the deviations are therefore not surprising and the information from the GC-MS screening and the SDS are not regarded as contradicting.

1-Methoxy-2-proanol and butane-1-ol could not be identified via the screening. Neither could the MCCP, however as the overall concentration of the substance group is quite low (10,000-50,000 mg/kg or 1-5%), the concentrations of the individual compounds might be too low to be identified via GC-MS screening. Additionally, acetic acid butyl ester was detected at a low concentration of 530 mg/kg in the paint.

From all identified substances, only ethylbenzene is classified with two of the project relevant hazard classes (see chapter 2.6) namely H373 (STOT RE 2, hearing organs) and H304 (Asp. Tox. 1).

38F Foul release coating
The following substances including their semi-quantitative concentrations were found in the GC-MS screening for the paint 38F. TABLE 3-2 also shows the substances mentioned in the SDS:

TABLE 3-2 Found substances in the paint 38F including semi-quantitative concentrations from the GC-MS screening as well as substances mentioned in the SDS. Purple – Substances occur in both SDS and GC-MS screening.

Name	CAS no	Concentration (mg/kg)
Substances listed in SDS		
N-Butyl Acetate	123-86-4	30,000-70,000
3-Aminopropyltriethoxysilane	919-30-2	1,000-5,000
Octamethylcyclotetrasiloxane	556-67-2	1,000-3,000
N-(3-(Trimethoxysilyl)Propyl)Ethylenediamine	1760-24-3	1,000-3,000
Substances found in GC-MS screening		
Acetic acid, butyl ester	123-86-4	11,000
2-Pentanone, 4-methyl-, oxime	105-44-2	17,000
Cyclopentasiloxane, decamethyl- (D5)	541-02-6	770
Cyclohexasiloxane, dodecamethyl- (D6)	540-97-6	820
Hexasiloxane, tetradecamethyl- (L6)	107-52-8	50
Cycloheptasiloxane, tetradecamethyl- (D7)	107-50-6	400
Heptasiloxane, hexadecamethyl- (L7)	541-01-5	60
Cyclooctasiloxane, hexadecamethyl- (D8)	556-68-3	250
Heptasiloxane, hexadecamethyl- (L7)	541-01-5	120
Cyclononasiloxane, octadecamethyl- (D9)	556-71-8	180
2,2,4,6,6,8-Hexamethyl-4,8-diphenylcyclotetrasiloxane	4657-20-9	810
Octasiloxane, 1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15-hexadecamethyl- (L8)	19095-24-0	210
1,1,1,5,7,7,7-Heptamethyl-3,3-bis(trimethylsiloxy)tetrasiloxane	38147-00-1	80
Benzamide, N-[2-(cyclopropylmethyl)-4,5-dimethoxyphenyl]-4-methoxy-	998362-07-3	110
Heptasiloxane, 1,1,3,3,5,5,7,7,9,9,11,11,13,13-tetradecamethyl- (L7)	19095-23-9	60

38F is a foul release coating on silicone basis. In the SDS, the solvent n-butyl acetate is listed with a concentration of 30,000-70,000 mg/kg and its presence was confirmed via the GC-MS screening with a lower concentration of 11,000 mg/kg (marked in purple). The other three mentioned substances were not identified during the screening.

Additionally, the crosslinker by-product 4-methylpentan-2-one oxime was found in the paint at a concentration of 17,000 mg/kg (1.7%). The substance has been found to have a “milder” toxicological profile compared to 2-butanone oxime (C4 oxime), which is also a crosslinker by-product. Crosslinkers with the by-product 2-butanone oxime may therefore be substituted with crosslinkers with other (“larger”) by-products, e.g. 2-pentanone oxime (C5 oxime) or 4-methylpentan-2-one oxime (C6 oxime) (Olsen et al. 2019). The substance 4-methylpentan-2-one oxime has skin and eye irritating properties according to the notified classification in the lead dossier (harmonised classification not available)[5] but does not qualify as a SoC within the current study scope (compare section 2.6).

Several linear and cyclic siloxanes ranging from five (L5 and D5) to nine silicone atoms (D9) were identified, however with concentrations below 1,000 mg/kg. From this substance group, D5 (CAS 541-02-6) and D6 (CAS 540-97-6) are SVHC and classified as vPvB. As D5 and D6 could be identified and D4 is mentioned in the SDS, it can be assumed that D4 is also present in the paint, which is to be investigated via target analysis. However, due to the fact that the paint is silicon-based and the concentrations of the identified silicone compounds are quite low, it is likely that there are not added intentionally to the product but are present as an impurity.

28F Foul release coating
The following substances including their semi-quantitative concentrations displayed in TABLE 3-3 were found in the GC-MS screening for the paint 28F:

[5] https://echa.europa.eu/da/information-on-chemicals/cl-inventory-database/-/discli/details/36496 (Accessed 05-09-2023)

TABLE 3-3: Found substances in the paint 28F including semi-quantitative concentrations from the GC-MS screening. Purple – Substances occur in both SDS and GC-MS screening.

Name	CAS no	Concentration (mg/kg)
Substances listed in SDS		
Hydrocarbons, C9, aromatics (<0.1% cumene)	128601-23-0	200,000-250,000
2-Pentanone, O,O',O''-(ethenylsilylidyne)trioxime	58190-62-8	100,000
Octamethylcyclotetrasiloxan	556-67-2	1,000
Titandioxid	13463-67-7	100,000
Solvent naphtha (petroleum), light aromatic	64742-95-6	200,000-250,000
Substances found in GC-MS screening		
2-Hexanone oxime	5577-48-0	19,000
p-Xylene	106-42-3	560
Benzene, propyl-	103-65-1	2,600
Benzene, 1-ethyl-2-methyl-	611-14-3	25,000
Benzene, 1-ethyl-4-methyl-	622-96-8	7,300
Benzene, 1,2,3-trimethyl-	526-73-8	16,300
Benzene, 1,2,4-trimethyl-	95-63-6	60,000
Benzene, (2-methylpropyl)-	538-93-2	760
p-Cymene	99-87-6	630
Benzene, cyclopropyl-	873-49-4	1,900
Benzene, 2-ethyl-1,4-dimethyl-	1758-88-9	360
Cyclohexasiloxane, dodecamethyl- (D6)	540-97-6	260
Cycloheptasiloxane, tetradecamethyl- (D7)	107-50-6	340
Cyclooctasiloxane, hexadecamethyl- (D8)	556-68-3	280
Cyclononasiloxane, octadecamethyl- (D9)	556-71-8	360

28F is a foul release coating on silicone basis. Like for the other paints, the main components of 28F are solvents mainly comprising of methylated and/or ethylated benzenes (xylene, cymene and others). This is in agreement with the information from the SDS, where both aromatic C9 hydrocarbons and solvent naphtha are listed in concentrations above 200,000 mg/kg (>20%). Both of these solvent mixtures consist mainly of methylated and/or ethylated benzenes.

2-Hexanone oxime has been identified in the product at a concentration of 19,000 mg/kg (1.9%). Most likely this C6 oxime is a by-product of a silane crosslinker (compare discussion on oximes in the previous section) in the paint. No information on classification, health or environmental properties is available from the ECHA database entry for this substance[6]. Based on the structure, 2-hexanone oxime may assumed to have similar properties as the C6 oxime 4-methylpentan-2-one oxime.

The SDS lists 2-pentanone, O,O',O''-(ethenylsilylidyne)trioxime, which is a substance used as crosslinking agent in coatings. During a crosslinking reaction, the oxime group may be released from the crosslinking agent, resulting in the formation of 2-pentanone oxime as leaving group. However, 2-pentanone oxime has not been detected in the analysis, instead 2-hexanone oxime was detected. Based on the analytical method, it is not possible to determine whether there is a substance identification error (i.e. the detected 2-hexanone oxime should have been identified as 2-pentanone oxime), or whether another crosslinking agent was used resulting in the actual release of 2-pentanone oxime.

Additionally, several cyclic siloxanes such as D6, D7, D8 and D9 were found similar to paint 38F (see section above), indicating that the paint has a silicon basis. Due to their low concentrations, it is unlikely that they were intentionally added but are likely to be present as an impurity. D4 is listed as an ingredient on the SDS but was not identified in the GC-MS screening. Still, it can be assumed that D4 is also present in the paint, which is to be investigated via target analysis.

From the identified substances D6 is an SVHC due to it vPvB properties. Additionally, the three solvents propylbenzene (CAS 103-65-1), 1,2,4-trimethylbenzene (CAS 95-63-6) and p-cymene (CAS 99-87-6) are all classified as aquatic chronic 2.

[6] https://echa.europa.eu/da/substance-information/-/substanceinfo/100.024.504 (Accessed 05-09-2023)

Titanium dioxide is listed in the SDS but is not detected in the GC-MS screening as the analytical method is not suitable to detect inorganic substances.

29T Tiecoat

The following substances including their semi-quantitative concentrations displayed in TABLE 3-4 were found in the GC-MS screening for the paint 29T:

TABLE 3-4 Found substances in the paint 29T including semi-quantitative concentrations from the GC-MS screening. Purple – Substances occur in both SDS and GC-MS screening.

Name	CAS no	Concentration (mg/kg)
Substances listed in SDS*		
Reaction mass of ethylbenzene and xylene (part A)	-	200,000-250,000
Titandioxid (part A)	13463-67-7	100,000
Chlorbenzen (part A)	108-90-7	3,000
Octamethylcyclotetrasiloxan (part A)	556-67-2	1,000
Reaction mass of ethylbenzene and xylene (part B)	-	200,000-250,000
2-Pentanone, O,O',O''- (ethenylsilylidyne)trioxime (part B)	58190-62-8	100,000
"N-(3-(trimethoxysilyl)propyl) ethylendiamin (part B)	1760-24-3	30,000
Decamethylcyclopentasiloxan (part B)	541-02-6	3,000
Octamethylcyclotetrasiloxan (part B)	556-67-2	2,500
Substances found in GC-MS screening		
Toluene	108-88-3	460
Octane, 2-methyl-	3221-61-2	230
Benzene, chloro-	108-90-7	320
2-Hexanone oxime	5577-48-0	1,100
Ethylbenzene	100-41-4	25,000
p-Xylene	106-42-3	79,000
Nonane	111-84-2	190
o-Xylene	95-47-6	31,000
Benzene, (1-methylethyl)-	98-82-8	210
Cyclopentasiloxane, decamethyl- (D5)	541-02-6	80
Cyclohexasiloxane, dodecamethyl- (D6)	540-97-6	230
Cycloheptasiloxane, tetradecamethyl- (D7)	107-50-6	270
Cyclooctasiloxane, hexadecamethyl- (D8)	556-68-3	170
Cyclononasiloxane, octadecamethyl- (D9)	556-71-8	300

*29T is a system consisting of part A and part B, and for the substances listed under SDS it is indicated whether they occur in part A or B. The GC-MS screening was done on the mixed coating, corresponding to the way a consumer would use the product.

29T is a two-part tiecoat to be used in combination with 28F.

Similar to 28F and the other paints the main components of 29T are solvents, however the composition of 29T is different from 28F. While 28F is mainly comprised of methylated/ethylated benzenes, this paint also contains aliphatic solvents such as 2-methyl octane and nonane.

Additionally, several cyclic siloxanes such as D5, D6, D7, D8 and D9 were found similar to paint 28F and 38F (see sections above), indicating that the product has a silicon basis. D4 is listed as an ingredient on the SDS but was not identified in the GC-MS screening. Due to their low concentrations, it is unlikely that the cyclosiloxanes were intentionally added.

2-Hexanone oxime occurs also in this product, here at a lower concentration of 1,100 mg/kg. Most likely this C6 oxime is a by-product of a silane crosslinker (compare discussion on oximes in the previous sections) in the tiecoat.

From the identified cyclosiloxanes D5 and D6 are SVHCs due to their vPvB properties. Additionally, toluene (CAS 108-88-3) is classified as reproductive toxic 2 and aspiration toxic for repeated exposure. Similarly, ethylbenzene (CAS 100-41-4) and cumene (benzene, (1-methylethyl)-; CAS 98-82-8) are both also classified as aspiration toxic.

3.3 Selection of substances and products for target analysis

Relevant information developed under project so far as well as the results from the GC MS screening were taken into account for selecting substances for target analyses. More specifically, the following criteria were used to prioritise the substances and products for target analyses:

- Presence of substances of concern (SoC) in the products as extracted from the SDS (excel product list)
- Presence of SoC in high concentrations in the products
- Representation of different paint types with antifouling action (i.e. foul release coatings and self-polishing coatings),
- Common availability of the product on the Danish market in which the substances occurs
- GC-MS screening results from the four screened products
- Availability of analysis methods at two analytical laboratories and costs of analyses

In cooperation with the Danish EPA, the SoC as listed in TABLE 3-5 below were selected for the target analysis. It is noted that analysis methods for substance groups, such as solvent naphtha, do not exist. Instead, analysis of the single constituents of such mixtures can be performed, e.g. alkylated benzenes within VOC analysis and naphthalene within PAH analysis, and the sum of the single constituents can then be applied as expression for the presence of the mixtures.

Three additional non-biocidal products based on availability on the Danish market and specific non-biocidal mode of action were purchased for the target analysis. Non-biocidal hard coatings were not included in the analysis program, because these products typically do not have any antifouling action and their chemical composition typically does not differ from the biocidal versions of the products with the exemption that they are not added a biocide. Additionally, extensive information about the chemical composition of the hard coatings is available from the safety datasheets.

The products selected for the target analysis were thus:

- 40S - Self-polishing coating
- 38F - Foul release coating
- 28F - Foul release coating
- 29T - Tiecoat for foul release coating
- 02S - Self-polishing coating
- 03F - Foul release coating
- 04T - Tiecoat for foul release coating

TABLE 3-5 SoC per product type

Substance			Hazard properties			Typical concentration (SDS)	Substance identified in product type of screened products?		
Name	**CAS no.**	**EC no.**	**Harmonised CLP classification H code**	**Harmonised CLP classification categories**	**PBT/ vPvB**	**% in product**	**Tiecoat (foul release)**	**Foul release coating**	**Self-polishing coating**
octamethylcyclotetrasiloxane (D4)	556-67-2	209-136-7	H361f *** H410	Repr. 2 Aquatic Chronic 1	PBT vPvB	≤0.1-0.3	yes	yes	
Decamethylcyclopentasiloxane (D5)	541-02-6	208-764-9	-		vPvB	≤1.0	yes	yes	
Dodecamethylcyclohexasiloxane (D6)	540-97-6	208-762-8	-		vPvB	≤1.0	yes		
toluene	108-88-3	203-625-9	H225 H361d *** H304 H336 H373 ** H315	Flam. Liq. 2 Repr. 2 Asp. Tox. 1 STOT SE 3 STOT RE 2 * Skin Irrit. 2		≤0.3	yes	yes	
Hydrocarbons, C14-C19, isoalkanes, cyclics, <2% aromatics	64742-46-7	265-148-2	H350	Carc. 1B Note N[4]		≥1.0 - ≤5.0	yes		
ethylbenzene	100-41-4	202-849-4	H225 H332 H304 H373 (hearing organs)	Flam. Liq. 2 Acute Tox. 4 * Asp. Tox. 1 STOT RE 2		≤3 - <20	yes	yes	
Hydrocarbons, C11-C12, isoalkanes, <2% aromatics	64741-65-7	265-067-2	H350 H340 H304	Carc. 1B Muta. 1B Asp. Tox. 1 Note P[1]		≥1.0 - ≤5.0	yes		
solvent naphtha (petroleum)	64742-95-6	265-199-0	H350 H340 H304	Carc. 1B Muta. 1B Asp. Tox. 1 Note P[1]		≥10 - ≤25			yes
zinc oxide	1314-13-2	215-222-5	H400 H410	Aquatic Acute 1 Aquatic Chronic 1		-[a]			yes
Rosin	8050-09-7	232-475-7	H317	Skin Sens. 1		10-25			yes
Alkanes, C14-17, chloro (MCCP)	85535-85-9	287-477-0	H362 H400 H410	Lact. Aquatic Acute 1 Aquatic Chronic 1	PBT vPvB	1-5			yes

[1] Note P: The harmonised classification as a carcinogen or mutagen applies unless it can be shown that the substance contains less than 0,1 % w/w benzene (Einecs No 200-753-7), in which case a classification in accordance with Title II of this Regulation shall be performed also for those hazard classes. Where the substance is not classified as a carcinogen or mutagen, at least the precautionary statements (P102-)P260-P262-P301 + P310-P331 shall apply.
[4] Note N: The classification as a carcinogen need not apply if the full refining history is known and it can be shown that the substance from which it is produced is not a carcinogen. This note applies only to certain complex oil-derived substances in Part 3 [of Annex I in the CLP Regulation].
[a] Information not available from the selected products' SDS.

3.4 Results and discussion of target analyses

Target analyses were done for seven non-biocidal antifouling products in total. For each product, the concentrations were measured by double determinations. The substances/substances groups as displayed in TABLE 3-6 including their reporting limits (similar to limit of quantification) were measured during analysis. For a full list of analytes, please refer to Appendix 2.

TABLE 3-6 Analysed substances in the target analyses

SoC	Note on method	Reporting limit [mg/kg]
Zinc oxide	Speciation analyses were not available and total zinc is analysed in the samples.	1
Polycyclic aromatic hydrocarbons (PAH)	Analysis of 25 PAH with a reporting limit of 0.1 mg/kg for the single substances. Detection of light aromatic hydrocarbons depends on the purity of the used solvent naphtha.	0.1
VOC	'Residual solvents'-analysis. 45 solvents were analysed in the dried samples. The reporting limit varies between 0.1 and 1 for the single substances.	0.1 - 1
Rosin	Analysis of three indicator substances for complex mixture of rosin	1.0
Cyclic siloxanes	Four cyclosiloxanes D3-D6	100
MCCP	Complex mixture of chlorinated paraffins with varying chain length (C14-17) and chlorination degree.	1000

Zinc and PAH were measured in all seven products. Siloxanes were measured in five silicone coatings, rosin in two self-polishing coatings and MCCP in one self-polishing coating.

Furthermore, VOC were measured in all seven products. A method for determining VOC content in wet samples was not available, therefore coatings were analysed for remaining, i.e. residual solvents, after application and drying. The liquid samples (app. 30-50 g) were dried in glassy dishes in the laboratory at room temperature under a laboratory fume hood for five days until they were dried. An aliquot (subsample) of the dried sample material was taken for the headspace analysis.
In general, the concentration of the analysed solvents is in the low mg/kg range, due to the sample being dried before analysis. As such, the measured concentrations are often far below the concentrations mentioned in the SDS. The results on the residual solvents provide information on which substances, are still present even after the coating is dried, and the quantified concentrations are compared with the stated presence of solvents according to the SDS. The results cannot be applied for estimating the exposure a consumer may experience during application of a coating but are still relevant for reflecting environmental exposure or estimating the exposure to dry paint.

All other analytes were determined in the wet products.

In the following only the detected substances for each coating will be discussed and compared to the substances mentioned in the respective SDS and GC-MS screening results.

40S Self-polishing coating
This coating is a black self-polishing coating. The substances displayed in TABLE 3-7 were detected in the target analysis.

TABLE 3-7 Found substances in the paint 40S during target analysis. Ranges denote deviating results from double determinations.

Name	Concentration (mg/kg)
Zinc	9,000-9,380
Acenaphthylene	0.1
Benzo[a]pyrene	0.8
Benzo[b]fluoranthene	0.1-0.2
Benzo[e]pyrene	0.5
Benzo[g,h,i]perylene	2.9
Cyclopenta[c,d]pyrene	8.6-8.8
Fluoranthene	2.3
Indeno[1,2,3-c,d]pyrene	0.6

Name	Concentration (mg/kg)
Naphthalene	170
Phenanthrene	0.5
Pyrene	6.1-6.3
1,2,4-Trimethylbenzene	6.2-7.6
1-Butanol	2,500-2,800
2-Butanol	34-37
2-Propanol	11-12
Acetone	1.1-1.3
Ethanol	43-50
Ethylbenzene	120-150
Methylisobutylketon (MIBK, 4-methylpentan-2-one)	10-12
Xylene	130-160
Abietic acid	74-82.2
Dehydroabietic acid	14.8-16.9

The SDS mentions ethylbenzene, xylene and C10 hydrocarbons as solvents for this coating. These substances could all be detected even after drying. The solvent 1-butanol was found in high concentrations of ~2,600 mg/kg after drying, despite it not being listed in the SDS. Additionally, several PAH could be detected in concentrations <10 mg/kg with the exception of naphthalene which had a concentration of 170 mg/kg, which might be due to the black colour of the paint. PAH are sometimes present in soot/carbon black, which are often used as black pigments.

Zinc was also found in high concentration of around 9,200 mg/kg without being mentioned in the SDS. A likely explanation for this that a zinc compound, e.g. zinc oxide, is used to control the erosion rate of this self-polishing paint. Other functions of zinc oxide are to stabilise wet paint in the can, to modify dry film properties, and as a pigment. Zinc oxide is not used as a biocidal active substance in antifouling paints, and therefore not considered and reviewed as such in the EU approval process of PT21 paints (Wezenbeek et al. 2018). However, both zinc and zinc oxide are recognized as toxic to aquatic organisms and thus considered SoC. Release of zinc from zinc oxide in antifouling paints was demonstrated by Lagerstrøm et al. (2018). Lagerström et al. (2018) also refer to two studies showing that the release of zinc from anti-fouling paints can have toxic effects on aquatic organisms (Karlsson et al.,2010; Ytreberg et al., 2010). Even though zinc may not be added as a biocidal substance, it cannot be ruled out that the substance may have a biocidal effect in the coatings.

Lastly the two rosin components abietic and dehydroabietic acid were both detected at concentrations below 100 mg/kg. Both substances are indicator substances for rosin, which is a complex combination of primarily resin acids derived from wood, especially pine wood. Rosin may cause allergic skin reactions. Because of the complex composition of rosin and variable stability of its components, it is not possible to conclude on the concentration of rosin in the product based on the concentrations of the two indicator substances. However, the presence of rosin in the paint can be interpreted as confirmed by the presence of the indicator substances.

Additionally, the SDS for this coating lists MCCP in a concentration of 1-5% (10,000-50,000 mg/kg). MCCP was not detected in the target analysis. According to communication with the laboratory, it can – for analytical reasons - not entirely be excluded that MCCP are present, even there are not detected. It is also noted that the reporting limit for the substance mixture is quite high (1,000 mg/kg, corresponding to 0.1%).

38F Foul release coating

This coating is a foul release coating on silicon basis. The displayed substances in TABLE 3-8 were detected in the target analysis.

TABLE 3-8 Found substances in the paint 38F during target analysis. Ranges denote deviating results from double determinations.

Name	Concentration (mg/kg)
Naphthalene	0.4
1-Butanol	32-33
Acetone	8.8-9.0
Ethanol	150
Methylisobutylketon (MIBK, 4-methylpentan-2-one)	69-70

Name	Concentration (mg/kg)
Xylene	1.2
Decamethylcyclopentasiloxane (D5)	1,600
Dodecamethylcyclohexasiloxane (D6)	1,600-1,700
Hexamethylcyclotrisiloxane (D3)	160-170
Octamethylcyclotetrasiloxane (D4)	1,500-1,600

The SDS mentions n-butyl acetate as the main solvent in the paint, however as the sample was dried before measuring the solvent the substance could not be detected. Similarly, other detected solvents are present in low concentrations <200 mg/kg in the dried paint.

The SDS also mentions octamethylcyclotetrasiloxane (D4) with a concentration range of 1,000-3,000 mg/kg, which could be confirmed during analysis (~1,500 mg/kg). Additionally, three more cyclic siloxanes D3, D5 and D6 could be detected in similar concentration ranges.

Lastly, the PAH naphthalene was detected with a low concentration of 0.4 mg/kg, and most likely present as an impurity.

28F Foul release coating
This coating is a foul release coating. The displayed substances in TABLE 3-9 were detected in the target analysis.

TABLE 3-9 Found substances in the paint 28F during target analysis. Ranges denote deviating results from double determinations.

Name	Concentration (mg/kg)
Zinc	1.5
Naphthalene	1.9-2.0
1,2,4-Trimethylbenzene	96-100
1,3,5-Trimethylbenzene	18-19
1-Butanol	8.4-9.3
Acetone	1.3-1.8
Heptane	<0.1-0.2
Xylene	1.5-1.6
Decamethylcyclopentasiloxane (D5)	230-260
Dodecamethylcyclohexasiloxane (D6)	630-700
Octamethylcyclotetrasiloxane (D4)	260-290

No SDS could be identified for this coating. However, based on the results of the GC-MS screening (see section on 28F in 3.2) and the results of the target analysis it is likely that the main solvent for this coating is naphtha due to the strong presence of methylated benzene compounds. The presence of zinc could be confirmed, however in low concentrations of 1.5 mg/kg. Additionally, the three cyclic siloxanes D4, D5 and D6 were also found in low concentrations below 700 mg/kg.
Lastly, while the PAH naphthalene was detected the measured concentration of 2 mg/kg is very low, most likely due to the use of naphtha as a solvent, in which naphthalene can be present as an impurity.

29T Tiecoat
This coating is a foul release coating. The substances displayed in TABLE 3-10 were detected in the target analysis:

TABLE 3-10 Found substances in the paint 29T during target analysis. Ranges denote deviating results from double determinations.

Name	Concentration (mg/kg)
Zinc	3.5-4.1
Naphthalene	1.1
Acetone	1.1-1.6
Xylene	1.7-1.9
Decamethylcyclopentasiloxane (D5)	220-260

Name	Concentration (mg/kg)
Zinc	3.5-4.1
Octamethylcyclotetrasiloxane (D4)	260-580
Dodecamethylcyclohexasiloxane (D6)	<100-720
Hexamethylcyclotrisiloxane (D3)	<100-200

This coating is the tie coat for the 28F. For this tie coat no SDS could be identified.
Similar to 28F, this paint also contains zinc in low concentrations as well as the four cyclic siloxanes D3, D4, D5 and D6. Furthermore, the presence of acetone and xylene could be confirmed, however no methylated benzene compound could be detected, indicating that this solvent it not naphtha based.

03F Foul release coating
This coating is a foul release coating on silicone basis. The substances displayed in TABLE 3-11 were detected in the target analysis.

TABLE 3-11 Found substances in the paint 03F during target analysis. Ranges denote deviating results from double determinations.

Name	Concentration (mg/kg)
Zinc	5.7-6.1
1-Butanol	17-21
Acetone	2.2-2.3
Decamethylcyclopentasiloxane (D5)	200-210
Dodecamethylcyclohexasiloxane (D6)	470
Hexamethylcyclotrisiloxane (D3)	120-150
Octamethylcyclotetrasiloxane (D4)	160-180

The SDS mentions n-butyl acetate as main solvent of this coating, however the substance could not be detected, due to the sample being dried before analysis. Two other solvents, 1-butanol and acetone, were detected in the dried sample.

This coating also contains small amount of zinc, which is hazardous to water organisms, but is probably not added intentionally here due to the low concentration. The SDS also mentions D4 in a concentration <1,000 mg/kg, which could be confirmed via analysis (~170 mg/kg). Additionally, the three other cyclic siloxanes D3, D5 and D6 were present in low concentrations above the reporting limit.

04T Tiecoat
This coating is a foul release coating on silicone basis. The substances displayed in TABLE 3-12 were detected in the target analysis.

TABLE 3-12 Found substances in the product 04T during target analysis. Ranges denote deviating results from double determinations.

Name	Concentration (mg/kg)
Zinc	2.5-2.6
1-Butanol	40-41
Acetone	1.0-1.1

This is the tie coat for 03F. The SDS mentions n-butyl acetate as main solvent of this coating, however the substance could not be detected, due to the sample being dried before analysis. Small amounts of zinc, 1-butanol and acetone could be found during analysis, however none of these substances is mentioned in the SDS.
The SDS also mentions D4 in a concentration <1,000 mg/kg, but neither D4 or presence of any of the other cyclosiloxanes could be determined in the analysis.

02S Self-polishing coating
This coating is a white self-polishing coating. The substances displayed in TABLE 3-13 were detected in the target analysis:

TABLE 3-13: Found substances in the product 02S during target analysis. Ranges denote deviating results from double determinations.

Name	Concentration (mg/kg)
Zinc	7,780-7,910
Naphthalane	170-180
1,2,4-Trimethylbenzene	140-150
1,3,5-Trimethylbenzene	39-42
1-Butanol	8.8-9.6
2-Propanol	7.6-8.0
Acetone	19-21
Ethylbenzene	1.7-1.8
Methylisobutylketone (MIBK, 4-methylpentan-2-one)	430-460
Xylene	13-14

The SDS mentions naphtha as main solvent of this coating, which could be confirmed by the presence of several alkylate benzene compounds. Of note for this coating is the high concentration of zinc around 7,800 mg/kg, which might be due to a zinc compound being used a white pigment in this paint.

Furthermore, the solvent MIBK (different name for 4-methylpentan-2-one) was identified in the residual VOC analysis, confirming the presence of the SoC as stated in the SDS for the coating.

3.5 Selection of substances for the risk assessment

From the products most relevant for the project scope (refer to section 2.9), five substances were selected for the environmental hazard assessment, and six substances were selected for the human health effects assessment in cooperation with the Danish EPA. The substances were selected as follows:

a) the substance is recognised as a SoC within the project scope (compare section 2.6)
b) the SoC is present in any of the coating products prioritised for the risk assessment (compare section 2.9)
c) the presence of the SoC in the products is documented by the chemical analyses (GC-MS screening and target analysis) and/or the listing of substances in the products SDS (compare TABLE 2-2, section 3.2 and section 3.4)
d) SoC occurring in high concentrations and/or occurring frequently in the relevant products are prioritised.

An overview of the presence of the substances based on information from the chemical analyses and the SDS is provided in TABLE 3-15.

It is noted that the oxime compounds (4-methylpentan-2-one oxime and 2-hexanone oxime) were semi-quantified in several products during the GC-MS screening. Oxime compounds can occur as leaving groups from silicon crosslinkers, and are not added intentionally to the products, nor are they listed in any SDS. One of the ‘smaller’ oximes, butanone oxime (C4), has a harmonised classification as Carc. 1B, STOT RE 2 and Skin Sens. 1, therefore, crosslinkers releasing this compound have been subject to substitution and instead crosslinkers releasing the ‘larger oximes’ may be used (Olsen et al. 2019). The hazard properties of the mentioned larger oximes (C5, C6 oximes) appear less investigated, meaning that these substances do not qualify as a SoC in this project scope and that a risk assessment for these substances may be impeded by lack of data. Nonetheless, for the above-mentioned reasons, it was decided to investigate 4-methylpentan-2-one oxime in the hazard assessment.

In summary, the substance listed in TABLE 3-14 were chosen for the hazard assessment.

TABLE 3-14 Substances (CAS no.) for the hazard assessment

Human health hazard assessment	Environmental hazard assessment
• Solvent naphtha (incl. ethylbenzene, xylene, toluene, naphthalene) (64742-95-6) • Ethylbenzene • Naphthalene • Rosin (8050-09-7) • Octamethylcyclotetrasiloxane (D4, 556-67-2) • 4-Methylpentan-2-one (108-10-1) • 4-Methylpentan-2-one oxime (105-44-2)	• D4 (556-67-2) • D5 (541-02-6) • D6 (540-97-6) • MCCP (85535-85-9) • Zinc oxide (1314-13-2)

TABLE 3-15 Overview of SoC based on information from the chemical analyses and the SDS

Product ID	Product type	SoC as identified in			Note on other substances
		GC-MS screening	Target analyses	SDS	
38F	Foul release	D5 D6	PAH (only naphthalene) Xylene D4-D6	Octamethylcyclotetrasiloxane (D4)	2-Pentanone, 4-methyl-, oxime detected in GC-MS screening
39T	Tiecoat	-	-	Isobutyl Methyl Ketone (4-methylpentan-2-one) Bis-[4-(2,3-Epoxipropoxi)Phenyl]Propane	
40S	Self-polishing	hydrocarbons, C10, aromatics (solvent naphtha) ethylbenzene	Zinc PAH (several compounds, 2-6 rings) Rosin (indicator substances) Ethylbenzene Xylene	hydrocarbons, C10, aromatics ethylbenzene, xylene MCCP C14-17 (52%)	
02S	Self-polishing	-	Zinc Solvent naphtha (several alkylated benzenes, ethylbenzene, xylene) 4-methylpentan-2-one (different name for methylisobutylketone)	solvent naphtha (petroleum) 4-methylpentan-2-one titanium dioxide	
07H	Hard coating (thin film)	-	-	Solvent naphtha (petroleum), light arom. titanium dioxide styrene n-butyl methacrylate methyl methacrylate toluene	
03F	Foul release	-	Zinc D4-D6	octamethylcyclotetrasiloxane (D4)	
04T	Tiecoat	-	Zinc	titanium dioxide octamethylcyclotetrasiloxane (D4)	
31H	Hard coating	-	-	Solvent naphtha (petroleum), light arom.	

Product ID	Product type	SoC as identified in			Note on other substances
28F	Foul release	Hydrocarbons, C10, aromatics (solvent naphtha) D6	Zinc PAH (only naphthalene) Xylene D4-D6 Solvent naphtha (several alkylated benzenes, xylene)	Octamethylcyclotetrasiloxan titanium dioxide Solvent naphtha (petroleum), light arom.	2-Hexanone oxime detected in GC-MS screening
29T	Tiecoat	toluene ethylbenzene xylenes cumene	Zinc PAH (only naphthalene) Xylene D4-D6	titanium dioxide Chlorobenzene Octamethylcyclotetrasiloxan 2-Pentanone, O,O',O''-(ethenylsilylidyne)trioxime N-(3-(trimethoxysilyl)propyl)ethylendiamine Octamethylcyclotetrasiloxane	2-Hexanone oxime detected in GC-MS screening
33C	Hard coating	-	-	Reaction product: bisphenol-A-(epichlorhydrin) and epoxy resin, 700 <mol weight < 1000 Solvent naphtha (petroleum), light arom. ethylbenzene	
41H	Hard coating	-	-	4-methylpentan-2-one Solvent naphtha (petroleum), light arom. Titanium dioxide	

4. Human health risk assessment

4.1 Human health hazard assessment

As described in chapter 3.4., solvent naphtha (petroleum), light aromatic, ethylbenzene, naphthalene, rosin, octamethylcyclotetrasiloxane (D4), 4-methylpentan-2-one as well as 4-methylpentan-2-one oxime, were chosen to be included in the human health risk assessment. In the hazard assessment, the substances' inherited properties of concern have been addressed. To identify the most critical effects and tolerable exposure levels (in the REACH terminology indicated as DNEL values) for the identified SoCs in the selected antifouling products, the main data source were disseminated REACH dossiers available on ECHA's substance information webpage. REACH stipulates all substances, mixtures or articles placed on the EU market, have to be safe for humans to use. The responsibility for this resides with the company placing the substance, mixture or article on the EU market. The companies have to assess the hazard and potential risks presented by the substance for each of its intended use. This information has to be communicated to ECHA through a registration dossier. The REACH data is therefore also used as the main source of information for the human hazard assessment in this project as the antifouling paints evaluated in this project are available on the Danish market. In cases where the disseminated data was limited, additional data sources were checked such as the risk assessment reports for existing chemical substances in the EU (EU RAR), Monographs of the International Agency for Research on Cancer (IARC), Toxicological Profiles of the Agency for Toxic Substances and Disease Registry (ATSDR) and the US EPA. A literature search was performed using both PubMed and Google using relevant search terms such as chemical name, CAS number etc. The collected data was subsequently used in the risk assessment of the SoCs, as the calculated exposure levels from relevant scenarios were compared with the tolerable exposure levels outlined in this chapter.

The substance-specific data below includes, when available, general population DNEL values for inhalation, dermal as well as oral exposure. As the consumer use of antifouling paint is in focus of this project, relevant reference values for general population were collected. If no such value was available, the DNEL for workers was used applying an additional assessment factor of 2 in order to consider intraspecies variability for more vulnerable sub-populations like children and elderly people, as described in the ECHA guidance R.8 (ECHA, 2012).

The lowest DNEL values available from the dossiers were evaluated and, if applicable, used for each route of exposure in this risk assessment. For most substances and exposure scenarios the $DNEL_{long\text{-}term}$ will be sufficient for controlling risks also for uses covering short term handling of the substance. The reason for this is that often the tolerated doses in toxicity studies decrease with increasing exposure duration. A DNEL based on a chronic toxicity study will generally be lower than a DNEL derived from a sub-chronic, sub-acute or acute toxicity study. The $DNEL_{long\text{-}term}$ may be used in the Tier 1 risk assessment and only if it is significantly exceeded by actual peak exposure levels a $DNEL_{acute}$ should be derived (ECHA, 2012). For biocidal substances, the methodology describes that the acceptable exposure levels should be derived independently of the route of exposure, generating a systemic value. Such reference values represent the internal (absorbed) doses available for systemic distribution from any route of exposure and are expressed as internal levels (mg/kg bw/day) (ECHA, 2017b). This is a different approach compared to how the DNEL values are derived for industrial chemicals under REACH, where DNELs should generally be expressed as external values. Thus, for substances with inhalation as the single or major route of exposure, external values are preferred as they are more easily interpreted in compliance assessment of use conditions when mostly only external exposure estimates are available (ECHA, 2012). The DNEL values for inhalation derived under REACH and presented in mg/m^3 are therefore used only as reference values for the local inhalation concentration. The oral DNEL values are used for risk assessing the systemic exposure also via the inhalation route. This is in line with the ECHA guidance document describing that systemic acceptable exposure levels are usually set based on data from oral studies. Where dermal and/or inhalation studies are available the doses must be converted to systemic doses (ECHA, 2017b).

However, it is not possible to derive DNEL values where there is no quantifiable information, or where no toxic effect is seen in the available substance specific studies. Additionally, it is not possible to derive any DNEL values for substances with sensitizing or (genotoxic) carcinogenic properties. Instead a qualitative approach should be taken, in line with the ECHA guidance R.8 (ECHA, 2012).

4.1.1 Solvent naphtha (petroleum), light aromatic (CAS no. 64742-95-6)

Classification

Solvent naphtha (petroleum), light aromatic, further on referred to as solvent naphtha, is a REACH registered petroleum product consisting of a combination of different hydrocarbons predominantly in the range of C8 through C10 and is thus recognized as a UVCB (substance of unknown or variable composition, complex reaction products or of biological materials). The substance has a harmonized classification under CLP and may cause cancer (Carc. 1B

H350, Note P), may cause genetic effects (Muta. 1B H340) and may be fatal, if swallowed and enters airways (Asp. Tox. 1 H 304). Additionally, based on the read-across data presented in the ECHA disseminated dossier the substance fulfils the requirement for classification as a skin irritant category 2 (Skin Irrit. 2 H315). Likewise, the substance has several notifications as skin irritant cat 2 in the ECHA list of notified classification and labelling.

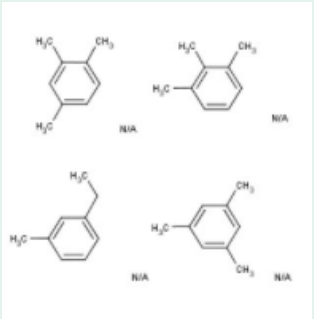
The aspiration toxicity classification of solvent naphtha is based on the kinematic viscosity of the substance, according to the CLP regulation. The basis for this is that some hydrocarbons (petroleum distillates) and certain chlorinated hydrocarbons have been shown to pose an aspiration hazard in humans. The pure solvent naphtha fulfils the classification criteria of a kinematic viscosity of 20,5 mm^2/s or less. For formulated products as paints containing solvent naphtha, the viscosity of the paint product is typically considerably higher than the classification limit according to information in their SDS. Aspiration hazard is therefore not considered a hazard for paint products such as the antifouling paints evaluated in this project.

All the available human toxicological information in the substance's registration dossier is based on read-across where data from gasoline or similar naphtha blending stocks have been used. Based on the *in vivo* and *in vitro* genetic toxicity studies available in the registrant's registration dossier on ECHA's webpage, the registrant concludes that the read-across substances gasoline and various forms of naphtha are not genotoxic. The composition of the tested substances is not clearly presented in the publicly available data and it has therefore not been possible to verify the suitability of the read-across. Despite the absence of genotoxic effects in the available data, there is a regulatory requirement to classify the product, if it contains ≥0.1% benzene in accordance with the CLP regulation. According to the SDSs of the antifouling paints evaluated in the project, none of the solvent naphtha used in the paint products contained benzene in concentrations above the classification threshold of ≥0.1%. This is in line with the restriction of benzene under REACH. As stipulated by Regulation (EC) No.1907/2006 Annex XVII, entry 5, benzene shall not be used in concentrations ≥ 0.1% in substances or preparations placed on the market. This together with the more general restriction on substances classified as Carc Cat 1A or 1B in substances, constituents or mixtures for general public (Regulation (EC) No.1907/2006 Annex XVII, entry 28) should ensure that the general population is protected from certain hazardous substances and mixtures. Following these EU regulations, the highest allowable concentration of benzene in the solvent naphtha is therefore <0.1% and the solvent naphtha is not considered carcinogenic in this report.

To clarify the composition of the substance as well as evaluating the basis for classification, a literature search was performed using ECHA webpage, PubMed and Google using search terms such as "solvent naphtha", "solvent naphtha (petroleum), light aromatic ", "64742-95-6" as well as "composition", "carcinogenicity" and "benzene" in the search. Limited data was found in the search, for example it was not possible to retrieve the CLH dossier on solvent naphtha or any background information for the harmonized classification, but the European Medicines Agency report with available data on solvent naphtha was identified (EMA, 2018).

Substance identity and physicochemical properties
The physical and chemical properties of solvent naphtha, light aromatic are described in TABLE 4-1.

TABLE 4-1 Solvent naphtha (petroleum), light aromatic, identification and physicochemical properties.

Parameter	Description	Source
CAS	64742-95-6	ECHA Substance Info-card
Structure		ECHA Substance Info-card
Chemical group	Aromatic hydrocarbons	
Vapour pressure (interpretation)	Not applicable since it is an UVCB substance. Indicative vapour pressure values for the category is 4 to 240 kPa at 37,8 °C.	REACH Registration Dossier
Molecular weight	115.174 g/mol	REACH Registration Dossier
LogPow	1.54 at 20.0 °C.	REACH Registration Dossier
CLP classification	Asp Tox.1 – H304 Muta. 1b – H340 Carc 1b – H350 Note P[1]	ECHA C&L inventory

[1] Note P: The harmonised classification as a carcinogen or mutagen applies unless it can be shown that the substance contains less than 0,1 % w/w benzene (Einecs No 200-753-7), in which case a classification in accordance with Title II of this Regulation shall be performed also for those hazard classes. Where the substance is not classified as a carcinogen or mutagen, at least the precautionary statements (P102-)P260-P262-P301 + P310-P331 shall apply.

Substance toxicity

The toxicity of comparable substances to solvent naphtha, light aromatic has been tested in numerous animal studies. In the REACH registration dossier (ECHA, Solvent naphtha (petroleum), light arom.), it is simply stated that a read-across has been conducted based on grouping of substances (i.e., category approach), although no justifications for the various read-across approaches are provided. Human evidence has shown that prolonged exposure to high levels of solvent naphtha vapor can cause central nervous system depression and can cause severe injury if it enters the lungs as a liquid.

A number of carcinogenicities read-across studies are available in the REACH registration dossier. In the key inhalation study conducted in similarity to OECD Test Guideline 451 (analytical concentrations of 0, 322, 1402, and 9869 mg/m^3) findings of renal neoplasms and renal carcinomas in male rats and liver tumours in female mice were observed. The study concluded on a NOEL of 1400 mg/m^3 (Kitched D., 1984, cited in the REACH registration dossier). In the registration dossier the toxicological relevance of the findings has been discussed as several reports have described that the mice strain B6C3F1, in particular, has a high spontaneous tumour rate (Doull et.al, 1983 and Drinkwater NR., 1986, cited in the REACH registration dossier). The registrant conclude that the kidney incidences are consistent with alpha-2u-globulin mediated nephropathy in male rats and not relevant for humans. This is supported by a review paper concluding that the induction of alpha-2u-globulin nephropathy is a mechanism specific for male rats and suggest that it is unlikely to pose a carcinogenic risk in humans (Swenberg, 1993). Regarding the key dermal carcinogenicity study, performed in similarity to OECD Test Guideline 451 (dose 0.05 ml), no carcinogenetic properties were observed and the NOEL was 0.5 ml/animal via dermal application (unnamed study report in the REACH registration dossier, 1983). In another supporting read-across study equivalent to OECD Test Guideline 453 (dose 50 µl), findings of skin tumours were observed in mice as well as dermal irritation at the treatment sites in all groups. It is described that the skin tumours are considered to be non-genotoxic and developed as a consequence of repeated irritation and skin injury. Hence, it is argued that solvent naphtha, light aromatic, is not expected to cause skin tumours in the absence of repeated skin injury (unnamed study report in the REACH registration dossier, 1989).

Several supporting read-across *in vivo* and *in vitro* skin irritation/corrosion studies are available in the REACH registration dossier, although the majority of them do not meet the EU OECD testing criteria necessary for classification. The key skin irritation/corrosion study is a Test Guideline 404, conducted on the read-across substance unleaded gasoline (CAS: 86290-81-5) with a dose of 0.5 ml, which showed results of moderate to severe erythema in rabbits but fully reversible within 14 days (unnamed study report in the REACH registration dossier, 1995). No dermal and oral DNEL values have been derived in the REACH Registration Dossier for solvent naphtha with the hazard assessment conclusion "No hazard identified".

Lastly, the human toxicological data in the REACH registration dossier is entirely based on read-across where it is not well described and justified how the substances are selected to be analogues and it is difficult to follow how available DNEL values have been derived. Therefore, additional information on the substance was sought. European Medicines Agency has published a report where available data on solvent naphtha is summarized (EMA, 2018). In the report data of cognitive neurobehavioral testing in rats were identified as point of departure for short-term exposure. A NOEC value of 200 mg/m^3 was defined in the study where rats were exposed by inhalation (0, 200, 1000 and 5000 mg/m^3 for 8 hours/day for 3 days).

The critical effect and derivation of DNEL
The report from the European Medicines Agency on solvent naphtha was used to derive DNELs for solvent naphtha, light aromatic (EMA, 2018). The NOEC value of 200 mg/m^3 from the neurobehavioral inhalation study was adjusted according to the ECHA conversion equation based on breathing volume of rats (ECHA, 2012), deriving the oral NOEL of 76 mg/kg bw (200 mg/m^3 x 0.38 m^3/kg bw). An overall assessment factor of 100, following ECHA standards, was applied: assessment factor of 4 for allometric scaling from rat to humans, 2.5 for interspecies differences, 10 for intraspecies differences, 1 for differences in duration of exposure and 1 for dose-response relationship. The application of an overall assessment factor of 100 resulted in a short-term DNEL of 0.76 mg/kg bw (European Medicines Agency (EMA), 2018). A chronic DNEL can also be derived based on chronic data from the same report. Relevant repeated dose data is a 12-month rat chronic repeat dose inhalation toxicity study (0, 450, 900 or 1800 mg/m^3 for 6 hours/day, 5 days/week for up to 12 months) using a mixture of two qualities of high aromatic naphtha products. A NOEC of 900 mg/m^3 corresponding to a NOEL of 109 mg/kg bw/day was derived when adjusted for exposure time (5/7 as exposure is only 5 days a week in the rat study) and using strain-specific breathing volumes of rats used in the study (0.17 m^3/kg bw for Wistar rats compared to the ECHA default value of 0.29 m^3/kg bw). The relevant assessment factors identified were 4 for allometric scaling from rat to humans, 2.5 for interspecies differences, 10 for intraspecies differences, 1 for differences in duration of exposure and 1 for dose response relationship. Applying the overall assessment factor of 100 generated a chronic DNEL of 1.09 mg/kg bw (European Medicines Agency (EMA), 2018). As the short-term DNEL (0.76 mg/kg bw/day) is lower than the chronic DNEL (1.09 mg/kg bw/day), it is used as the overall oral DNEL for general consumers in this report.

The same point of departure (NOAEC value of 200 mg/m^3) was used to calculate the inhalation DNELs for the general population within this project. In order to derive the inhalation DNEL for this project, the ECHA guidance is applied on the NOAEC value of 200 mg/m^3. An overall assessment factor of 25, following ECHA standards, was applied. An assessment factor of 1 for allometric scaling was applied as air concentrations for animal and human exposure are generally compared directly (ECHA, 2012). Additional assessment factors are 2.5 for interspecies differences, 10 for intraspecies differences, 1 for differences in duration of exposure and 1 for dose response relationship, resulting in an overall assessment factor of 25. The short-term inhalation DNEL for general population is 8 mg/m^3 (200 mg/m^3 /25).

The critical effect for solvent naphtha, light aromatic is neurotoxicity. TABLE 4-2 summarizes DNELs used in the human risk assessment.

TABLE 4-2 Identified DNELs for solvent naphtha, light aromatic.

DNEL-values General population	Inhalation Systemic effects, short term: **8 mg/m^3** NOAEC: 200 mg/m^3 AF= 25 Most sensitive endpoint: neurotoxic effects No information about test guideline	EMA MRL report (2018)
	Dermal Local effects, skin irritant: data not sufficient to derive DNEL	REACH Registration Dossier
	Oral Systemic effects, short term: **0.76 mg/kg bw** NOAEC: 200 mg/m^3 AF= 100 Systemic effects, long term: **1.09 mg/kg bw** NOAEC: 900 mg/m^3 AF= 100 Most sensitive endpoint: neurotoxic effects No information about test guideline	EMA MRL report (2018)

4.1.2 Ethylbenzene (CAS no. 100-41-4)

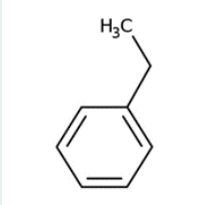
Classification

Ethylbenzene is a REACH registered mono-constituent substance. According to the harmonized classification and labelling, ethylbenzene is an acute toxicant (Acute Tox. 4 H332), aspiration toxicant (Asp. Tox. 1 H304) and may cause damage to organs through prolonged or repeated exposure (STOT RE 2 H373, hearing organs).

Substance identity and physicochemical properties

The physical and chemical properties of ethylbenzene is described in TABLE 4-3.

TABLE 4-3 Ethylbenzene overview identification and physicochemical properties.

Parameter	Description	Source
CAS	100-41-4	ECHA Substance Infocard
Structure		ECHA Substance Infocard
Chemical group	Aromatic hydrocarbon	
Vapour pressure	952 Pa at 20 °C	REACH Registration Dossier
Molecular weight	106.165 g/mol	REACH Registration Dossier
LogPow	3.6 at 20.0 °C.	REACH Registration Dossier
CLP classification	Asp Tox.1 – H304 Acute tox. 4 – H332 STOT RE 2 – H373 (hearing organ)	ECHA C&L inventory

Substance toxicity

In the REACH registration dossier for ethylbenzene, it is described that ethylbenzene may cause ototoxicity and inhalation studies suggest that it is the most critical effect of ethylbenzene exposure. Damage to the hearing organs were observed in an OECD Test Guideline 424 inhalation study, where rats were exposed to ethylbenzene 6 hours/day, 6

days/week for 13 weeks at doses of 0, 200, 400, 600 and 800 ppm. Irreversible ototoxic effects were observed at 200 ppm with hearing loss and damage of the sensory cells in the ear (Ggnaire, 2007, cited in the REACH registration dossier). The NOAEC was extrapolated to 114 ppm (500 mg/m^3). In the REACH registration dossier it is argued that the effects are considered relevant to humans, which is supported by human evidence from workers exposed to different solvents (e.g., xylene, toluene, ethylbenzene and styrene) in concentrations in the proximity of their occupational exposure limits. In the dossier no substance specific concentrations are provided (Sulkowski et al., 2002, cited in the REACH registration dossier). Furthermore, simultaneous exposure to ethylbenzene and noise have indicated synergistic effects in rats. In a rat study, two test doses of ethylbenzene (300 and 400 ppm) caused a greater loss of the hair cells of the outer ear at a noise level of 105 dB, compared to the sum of losses of ethylbenzene and noise, respectively (Cappaert, 2001). Another study showed that ethylbenzene (660 ppm) alone did not cause impaired hearing or loss of hair cells, whereas in combination with a noise exposure of 93 dB caused a loss in auditory function and hair cell loss (Fechter, 2007).

One 90-day oral gavage toxicity study in rats, conducted according to OECD Test Guideline 408 (0, 75, 250 and 750 mg/kg/bw/day) resulted in a NOAEL of 75 mg/kg bw/day. The NOAEL is based on haematological changes, indicative of a mild regenerative anaemia, increased liver weights and hepatocellular hypertrophy (Mellert et al., 2007, cited in the REACH registration dossier).

Regarding developmental toxicity, several studies are available. In a prenatal developmental toxicity study conducted according to OECD Test Guideline 414 in rats (0, 100, 500, 1000 and 2000 ppm) there were indications of foetal toxicity as the foetal body weight was reduced and some skeletal variations were observed at 1000 ppm and 2000 ppm, although in presence with maternal toxicity and limited to the time after weaning. The NOAEL for teratogenicity was 2000 ppm, 500 ppm for maternal toxicity and developmental toxicity (Saillenfait et al., 2003, cited in the REACH registration dossier). In another study following OECD Test Guideline 415 in rats, the animals were dosed at 0, 100, 500 and 1000 ppm. The NOEC for fetotoxicity and maternal toxicity was 100 ppm, as reduced body weight in the parental generation and reduced pup survival and reduced pup weight were seen at 500 ppm and above (unnamed study report in the REACH registration dossier, 2003). The effects from the OECD Test Guideline 415 study were not reproducible in an OECD Test Guideline 416 Two generation toxicity study and no adverse reproductive and developmental effects were observed at the tested doses: 0, 25, 100 and 500 ppm (Faber et al., 2006, cited in the REACH registration dossier).

ECHAs' risk assessment committee (RAC) have evaluated the toxicological data on ethylbenzene and concluded that it should not be classified as a skin irritant (RAC, 2012).

The critical effect and derivation of DNEL

According to the REACH registration dossier the most critical effect from long-term repeated exposure to ethylbenzene is ototoxicity. The human data is not detailed enough to derive a DNEL. For general population, the long-term inhalation DNEL for ototoxicity is based on a repeated dose toxicity study in rats with an extrapolated NOAEC of 114 ppm for ototoxicity. In the REACH dossier, the NOAEC has been adjusted for rat absorption rate of 45%, human absorption after inhalation 65%, experimental inhalation duration (6 h/day, 6 days/week) and environmental exposure conditions (24 h/day, 7 days/week). Thus, the adjusted starting point is 114 x 0.45/0.65 x 6/24 x 6/7 = 17 ppm. An overall assessment factor of 5 has been used for intraspecies differences, corresponding to the DNEL of 3.4 ppm (15 mg/m^3). According to the registration dossier, the endpoint-specific DNEL for ototoxic effects results in the lowest DNEL for inhalation (15.4 mg/m^3) which is therefore used in the risk assessment. The assessment factors used in the registration dossier do not follow the ECHA Guidance, thus revised assessment factors have been used in this report. An overall assessment factor of 50 has been applied on the adjusted NOAEC of 17 ppm: 2.5 for interspecies differences, 10 for intraspecies differences and 2 for sub-chronic to chronic, 1 for dose response and 1 for the quality of the database resulting in a DNEL of 0.34 ppm (1.5 mg/m^3).

The long-term oral DNEL for the general population presented in the REACH dossier is 1.6 mg/kg/day, based on a 90-day oral repeated dose toxicity study in rats. The NOAEL of 75 mg/kg bw/day has been adjusted for 84% oral absorption in rats and 100 % in humans (75 mg/kg bw/day x 0.84), thus the point of departure is 63 mg/kg bw/day. In the REACH dossier an assessment factor of 4 is applied for interspecies differences, 5 for intraspecies, 2 for differences in duration of exposure, 1 for dose response and 1 for the quality of the database. This leads to the DNEL of 1.6 mg/kg bw/day by oral exposure. In the same way as for the inhalation DNEL, appropriate assessment factors have not been used in the registration dossier. Therefore, revised assessment factors of 50 are used in this assessment: 2.5 for interspecies differences, 10 for intraspecies differences and 2 for sub-chronic to chronic extrapolation. The DNEL used in this report is 1.3 mg/kg bw/day.

No DNEL values have been derived for acute/short term exposure, and the available long term DNEL values will be used in the risk assessment in accordance with ECHA guidance R8 (ECHA, 2012). Regarding dermal effects, no DNEL values have been derived in the REACH registration dossier for this route of exposure. Considering the poten-

tial systemic effect of dermal exposure to ethylbenzene, it is considered relevant to derive a long-term dermal systemic DNEL value in the same way as the oral DNEL value is derived. The dermal DNEL is set to 1.3 mg/kg bw/day in this report.

The identified DNEL are summarized in TABLE 4-4.

TABLE 4-4 Identified DNELs for ethylbenzene.

DNEL-values General population	Inhalation Systemic effects, long term exposure: **1.5 mg/m^3** NOAEC: 114 ppm Assessment factors: 50 Study conducted according to OECD Test Guideline 424 Most sensitive endpoint: Ototoxicity Acute/short term exposure: low hazard (no threshold derived) Local effects: no hazard identified Dermal Systemic effects, long term exposure: **1.3 mg/kg bw/day** NOAEL: 75 mg/kg/bw/day Assessment factors: 50 Study according to OECD Test Guideline 408 Most sensitive endpoint: Haematology, clinical chemistry parameters, increased liver weight and hepatocellular hypertrophy Local effects: no hazard identified Oral Systemic effects long term exposure: **1.3 mg/kg bw/day** NOAEL: 75 mg/kg/bw/day Assessment factors: 50 Study according to OECD Test Guideline 408 Most sensitive endpoint: Haematology, clinical chemistry parameters, increased liver weight and hepatocellular hypertrophy Acute/short term exposure: no hazard identified	REACH Registration Dossier

4.1.3 Naphthalene (CAS no. 91-20-3)

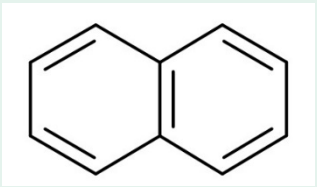
Classification

Naphthalene is a REACH registered mono-constituent substance. Naphthalene has a harmonized classification under CLP as an acute toxicant (Acute Tox. 4 H302), and is suspected of causing cancer (Carc. 2 H351).

Substance identity and physicochemical properties

The physical and chemical properties of naphthalene is described in TABLE 4-5.

TABLE 4-5 Naphthalene overview identification and physicochemical properties.

Parameter	Description	Source
CAS	91-20-3	ECHA Substance Infocard
Structural formula		ECHA Substance Infocard
Chemical group	Aromatic hydrocarbon	
Vapour pressure	10.5 Pa at 25°C	REACH Registration Dossier
Molecular weight	128.171 g/mol	REACH Registration Dossier
LogPow	3.7 at 25.0 °C	REACH Registration Dossier

CLP classification	Acute Tox. 4 – H302	ECHA C&L inventory
	Carc. 2 – H351	
	Aquatic Acute 1 – H400	
	Aquatic Chronic – H410	

Substance toxicity
In the REACH registration dossier it is described that exposure to naphthalene can cause haemolytic anaemia, nasal lesions and carcinogenicity of the nasal epithelium (ECHA, Naphthalene). At least 30 cases of exposure to naphthalene causing haemolytic anaemia in humans have been reported, following dermal and oral exposure. The haemolytic anaemia can be fatal, especially for neonates (ECB, 2013, cited in the REACH registration dossier).

In an EPA OPP 81-3 4 week inhalation study in rats, a local NOAEL could not be identified as signs of proliferative repairs in the nasal olfactory epithelium were observed in all dose groups (1, 3, 10, 29, 71 ppm) with effects observed at the lowest test concentration 1 ppm or 5.24 mg/m^3 (unnamed study report in the REACH registration dossier, 1993). However, the anatomy of the upper respiratory tract in rats and humans differs and it is argued in the dossier that the species differences make it uncertain how relevant the effects seen in rats are to humans.

Naphthalene is suspected to be carcinogenic based on animal data. Respiratory epithelial adenomas and olfactory epithelial neuroblastomas were seen in a two-year carcinogenicity inhalation study in rats dosed 6 h/day, 5 days/week at concentrations of 0,10, 30 and 60 ppm (not conducted according to any test guideline) (NTP, 2000, cited in the REACH registration dossier). Another 2-year inhalation study in mice dosed 0, 10, 30 ppm 6 h/day, 5 days/week also showed evidence of carcinogenicity, as incidences of pulmonary alveolar/bronchiolar adenomas were increased in female mice (NTP, 1992). The tumours were only developed where non-neoplastic inflammatory changes also took place; therefore, the tumours are believed to be caused by chronic tissue injury and the mode of action is concluded to be via a non-genotoxic mechanism. (ECHA, 2018 (CoRAP)).

There is no human evidence of naphthalene induced carcinogenicity (Rhomberg et al., 2010, cited in the REACH registration dossier). In the dossier it is concluded that there is an unlikely risk for workers that naphthalene would cause tumours following respiratory irritation.

The mode of action and the relevance to humans of these effects have been evaluated, both in the International Agency for Research on Cancer (IARC) monograph on naphthalene (IARC, IARC Monographs volume 82. Naphthalene (Group 2B)., 2002) as well as in the CoRAP report on naphthalene (ECHA, 2018). In the International Agency for Research on Cancer (IARC) monograph on naphthalene it is reported that the lung tumours observed in mice are dose dependent and specific to Clara cells (IARC, 2002). This is supported by another study showing that exposure to naphthalene causes negative effects on the bronchiolar epithelium in mice, more precisely the Clara cells and ciliated cells, whereas rats and hamsters are insensitive to this effect upon exposure to naphthalene (Plopper, 1992). The proposed mechanism for the carcinogenic effect is that mice have a higher rate of metabolism of naphthalene, consequently causing a higher cell turnover and tumours. No lung tumours have been observed in rats, which is consistent with the proposed mechanism. In humans, the maximal rate of metabolism in lung microsomes is about 10-100 lower than in mice.(IARC, 2002).. In the CoRAP report on naphthalene it is concluded that the lung tumours found in mice are not considered to be of relevance for humans. The Category 2 Carcinogen classification is based on the findings in rats, which are likely to have arisen via a non-genotoxic mechanism (ECHA, 2018).

One 90-day dermal repeated dose toxicity study in rats conducted according to OECD Test Guideline 411 is available in the REACH registration dossier. Naphthalene showed no effects on rats treated dermally for 5 days/week, 13 weeks at doses 0, 100, 300 and 1000 mg/kg day and the NOAEL was 1000 mg/kg bw/day (unnamed study report in the REACH registration dossier, 1986).

The critical effect and derivation of DNEL
The critical effect for naphthalene is nasal and olfactory epithelial damage, consequently causing carcinogenicity via a non-genotoxic mechanism. The suggested DNELs are therefore considered to be sufficient to protect against the identified hazards. No official DNEL values are available in the REACH dossier for the general population. Regarding workers, DNEL values have been derived for inhalation and for dermal exposure. Since no NOAEC could be derived from the rat inhalation study described above, the available DNEL value for inhalation is based on the current EU-wide Indicative Occupational Exposure Limit Value (IOELV) of 50 mg/m^3 (8-hr TWA), which is used in Denmark and several other European countries. This is in accordance with ECHA REACH Guidance R.8, an IOELV may be used as a DNEL for the same exposure route and duration (ECHA, 2012). Historically, the occupational exposure levels are assumed to have been higher than 50 mg/m^3 and there are no reports that naphthalene has induced olfactory epithelium damage in workers. For risk assessment in this report, DNEL values for the general population were derived based on the dataset used for worker DNELs. An additional assessment factor of 2 has been applied to account

for inter-species variation in human sub-populations, as described in regulatory guidance documents (ECHA, 2012). However, the data used to derive the IOELV are not properly described in the dossier and the relevance and quality of the data can therefore not be assessed. Nevertheless, the IOELV is used instead of available NOAEL in the dossier as it results in a lower DNEL. As the worker inhalation DNEL is based on the IOELV, no additional assessment factor is used for dose-response relationship, differences in duration of exposure, interspecies, intraspecies and for the quality of the whole database. To compensate for remaining uncertainties an assessment factor of 2 is added, resulting in a worker DNEL of 25 mg/m^3. This is in line with the conclusions in the CoRAP report which concludes that the current IOELV should be revised (ECHA, 2018). The value of 25 mg/m^3 (5 ppm) is by the registrant considered sufficient to protect workers for haemolytic anaemia, nasal and olfactory epithelium damage, and consequently non-genotoxic carcinogenicity following inhalation. Using the same data for deriving the general population DNEL by adding an additional assessment factor of 2, resulting in an overall assessment factor of 4, gives a general population inhalation DNEL of 12.5 mg/m^3.

In the REACH dossier, two dermal DNEL values for workers have been calculated, the lowest one is based on the inhalation ILV of 50 mg/m^3, resulting in a DNEL of 3.57 mg/kg bw/day. This is not in line with the ECHA Guidance R.8, where IOELV are allowed to replace DNELs for the same route of exposure only. Even though such an approach generates a lower DNEL, the concept is not fully acceptable and derivation of dermal general population DNEL in the current assessment is following the ECHA default methodology. The other DNEL value calculated in the dossier was based on an OECD Test Guideline 411 rat study (0, 100, 300, 1000 mg/kg) with a NOAEL of 1000 mg/kg/day (unnamed study report in the REACH registration dossier, 1986). By applying assessment factors of 4 for allometric scaling from rat to humans, 2.5 for interspecies differences, 5 for intraspecies differences, 2 for differences in duration of exposure and 1 for dose response relationship, the overall assessment factor is 100 and a DNEL value of 10 mg/kg is derived. However, in the dossier, it is described that it is uncertain whether the DNEL is sufficient to protect against haemolytic anaemia. In order to compensate for uncertainties in the dataset, ECHA Guidance R.8 recommends an additional assessment factor to be applied on a case-by-case basis. This was not done in the naphthalene REACH dossier, but in this project an additional assessment factor of 2 to take into account the uncertainties related to haemolytic anaemia. The assessment factors applied are 4 for allometric scaling from rat to humans, 2.5 for interspecies differences, 10 for intraspecies differences, 2 for differences in duration of exposure, 1 for dose response relationship and 2 for additional uncertainties. The overall assessment factor is 400 and a DNEL value of 2.5 mg/kg bw/day is derived.

Since no oral DNEL for the general population is available from the registrant, the study result from the dermal OECD Test Guideline 411 study with a NOAEL of 1000 mg/kg/day has been used to derive a DNEL for this report. The assessment factors applied are 4 for allometric scaling from rat to humans, 2.5 for interspecies differences, 10 for intraspecies differences, 2 for differences in duration of exposure, 1 for dose response relationship and an additional factor of 2 for additional uncertainties. The overall assessment factor is 400 and a DNEL value of 2.5 mg/kg bw/day is generated.

The identified DNELs are summarized in TABLE 4-6.

TABLE 4-6 Identified DNELs for naphthalene.

DNEL-values General population	Inhalation Systemic and local long term exposure: **12.5 mg/m^3** Indicative limit value': 50 mg/m^3 Assessment factors: 4 DNEL derived from national IOELV (EU and USA), based on human experience Most sensitive endpoint: carcinogenicity Acute/short exposure: low hazard (no threshold derived) Dermal Systemic long term exposure: **2.5 mg/kg bw/day** Most sensitive endpoint: no critical effects identified NOAEL: 1000 mg/kg/bw Assessment factors: 400 Study according to OECD Test Guideline 411 Acute/short term exposure: low hazard (no threshold derived) Most sensitive endpoint: acute toxicity Local effects: Long term exposure: no hazard identified Most sensitive endpoint: sensitisation Acute/short term exposure: no hazard identified Most sensitive endpoint: skin irritation/corrosion Oral Systemic and local long term exposure**: 2.5 mg/kg bw/day** Most sensitive endpoint: DNEL derived from dermal NOAEL, no critical effects NOAEL: 1000 mg/m^3 Assessment factors: 400 Study according to OECD Test Guideline 411	REACH Registration Dossier

4.1.4 Rosin (CAS no. 8050-09-7)

Classification

Rosin is a UVCB, a complex combination derived from wood, especially pine wood and is composed primarily of resin acids and modified resin acids such as dimers and decarboxylated resin acids. It has a harmonized classification under CLP as a skin sensitizer (Skin Sens. 1 H317). It has not been possible to retrieve the data on which the CLH registration was done, or any decision from the process via the ECHA website or the RAC home page. According to Karlberg et al. (1999) the harmonized classification of the substance was decided in 1993, but no more details were given (Karlberg et al.,1999). A literature search was performed to identify data relevant to skin sensitization, using both PubMed and Google using search terms such as “rosins”, "colophony", “8050-09-7” as well as “skin sensitization” in the search, but additional information was not identified.

Substance identity and physicochemical properties

The physical and chemical properties of rosin is described in TABLE 4-7.

TABLE 4-7 Rosin overview identification and physicochemical properties

Parameter	Description	Source
CAS	8050-09-7	ECHA Substance Infocard
Structural formula	Not available	ECHA Substance Infocard
Chemical group	Resin	
Vapour pressure	0.006 kPa at 25 °C	ECHA Substance Infocard, REACH Registration Dossier
Molecular weight	ca. 302 g/mol	REACH Registration Dossier
LogPow	3.0 to 6.2 in unbuffered media and 1.9 to 7.7 in media adjusted to pH 2	REACH Registration Dossier
CLP classification	Skin sens. 1 – H317	ECHA C&L inventory

Substance toxicity
In the REACH registration dossier, several *in vivo* skin sensitisation tests are available both for rosin and hydrogenated rosin and its salts, all concluding that the substance has a low potential of causing skin sensitisation (ECHA, Rosin). One of the key local lymph node assays (OECD Test Guideline 429) in mouse demonstrated sensitization upon exposure to a mixture of resin acids, rosin acids, hydrogenated, potassium salts at concentrations of 5, 10 and 25%. The highest test concentration, 25% resulted in a stimulation index ≥3, thus the mixture is considered to be a sensitizer (unnamed study report in the REACH registration dossier, 2005). However, several other skin sensitisation studies on the mixture and analogues of the category have demonstrated negative results. Therefore, the registrant doubts the reliability of the positive finding. In the REACH disseminated dossier, it is argued that the skin sensitising properties are assigned to oxidation products and not to rosin itself. This is also supported by published literature (Karlberg et al., 1999). A NICNAS (2016) report published by the Australian authority also concludes that the skin sensitisation potential is related to oxidation products of rosins. In this report, the rosin is therefore regarded as not skin sensitizing in line with these arguments.

Acute oral and dermal toxicity studies did not show any acute toxic effects and the LD50 was >2000 mg/kg/bw, for both routes of exposure (unnamed study report in the REACH registration dossier, 2010 and 2009). No acute inhalation toxicity studies are available. The vapor pressure of rosin is 0.006 kPa at 25 °C which, based on the definition in the EU Industrial Emissions Directive[7], is regarded as non-volatile. Inhalation exposure of rosin is therefore considered unlikely.

The critical effect and derivation of DNEL
Due to limited available data of the substance and no defined point of departure, a DNEL for the current risk assessment could not be derived (TABLE 4-8). Data was searched for in both the disseminated information from the REACH registration dossier, in publicly available articles as well as information from national authorities, but no relevant data could be retrieved.

TABLE 4-8 Identified DNELs for rosin.

DNEL-values General population	Inhalation The hazard is unknown but assessed as not necessary as no exposure is expected. Dermal Systemic: no hazard identified Local: no hazard if skin sensitising effect is attributed to oxidised product only Oral Systemic/local: no hazard identified	REACH Registration Dossier

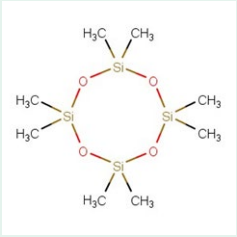
4.1.5 Octamethylcyclotetrasiloxane (D4) (CAS no. 556-67-2)

Classification
D4 is a cyclic volatile methyl siloxane with four siloxane groups. It is a high production volume chemical within EU having several applications such as monomers to produce silicone polymers or in products used by the general population and professionals, such as cosmetic products, medicinal products and household cleaning products (ECHA, 2023d). D4 has a harmonized classification under CLP for “suspected of damaging fertility” (Repr. 2 H361f).

Substance identity and physicochemical properties
The physical and chemical properties of D4 is described in TABLE 4-9.

[7] https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX%3A32010L0075

TABLE 4-9 D4 overview identification and physicochemical properties.

Parameter	Description	Source
CAS	556-67-2	ECHA Substance Infocard
Structural formula		ECHA Substance Infocard
Chemical group	Organosilicon	
Vapour pressure	0.132 kPa at 25 °C	REACH Registration Dossier
Molecular weight	296.616 g/mol	REACH Registration Dossier
LogPow	6.98 at 21.7 °C	REACH Registration Dossier
CLP classification	Repr. 2 – H361f Aquatic chronic 1 – H410	ECHA C&L inventory

Substance toxicity
In the REACH registration dossier several studies addressing reproductive effects are available for D4 (ECHA, Octamethylcyclotetrasiloxane). In the key two-generation reproductive toxicity inhalation study, conducted according to EPA OPPTS 870.3800 Guideline (comparable to OECD Test Guideline 416), rats were dosed 6 h/day, 7 days/week at 0, 70, 300, 500, and 700 ppm. The NOAEC for reproductive toxicity and general toxicity was 300 ppm, based on reduced fertility indices, reduced mean live litter sizes, and reduced body weight gain (Siddiquie et al., 2007 and WIL Research Laboratories Inc, 2001, cited in the REACH registration dossier). Other studies have shown that the effect on fertility is associated with exposure surrounding the ovulatory phase, more precisely that D4 exposure increases the incidence of delayed/suppressed pre-ovulatory LH surge and ovulation (Dow Corning Corporation, 2002 and WIL Research Laboratories Inc, 1998, cited in the REACH registration dossier). The registrant argue that these effects may not be considered relevant to humans. Regardless, the effects observed are limited to females and specifically during the ovulatory phase.

D4 is considered to be an endocrine disruptor according to the CeHoS (Danish Centre on Endocrine Disrupters), based on a study screening for endocrine disrupting properties where it was concluded that D4 has strong evidence for estrogenic activity and adverse effects linked to endocrine disruption (Hass, 2017).

Adverse effects have been observed in one 24-month combined repeated dose toxicity and carcinogenicity inhalation study in rats, conducted according to EPA OPPTS 870.4300 Guideline (comparable to OECD Test Guideline 453). Rats were treated 6 h/day, 5 days/week at 0, 10, 30, 150 and 700 ppm. Exposure to the highest test dose 700 ppm caused an increase of endometrial adenomas and an increase of endometrial hyperplasia in the uterus. For carcinogenic effects the NOAEC was 150 ppm in females and ≥700 ppm in males. The NOAEC for general toxicity and local respiratory effects was 150 ppm or 1820 mg/m^3, based on findings of chronic nephropathy and effects in the nasal cavity (unnamed study report in the REACH registration dossier, 2004).

The critical effect and derivation of DNEL
The most critical systemic effect is repeated dose toxicity and respiratory tract irritation. Respiratory tract irritation following repeated exposure gives the lowest DNEL, therefore it is regarded as the most critical effect for risk characterisation.

The inhalation long-term DNEL is 13 mg/m^3, based on the 24 months repeated dose toxicity and carcinogenicity study in rats. The inhalation NOAEC of 1820 mg/m^3 was modified to correct for the experimental exposure duration (from 6 h/day to 24 h/day) and dosing frequency (from 5 days to 7 days), resulting in a NOAEC of 325 mg/m^3. The DNEL is derived according to the ECHA REACH Guidance where an overall assessment factor of 25 has been applied to the modified NOAEC. An assessment factor of 2.5 was applied to adjust for interspecies differences and 10 for intraspecies differences.

The DNEL for the oral route is 3.7 mg/kg bw/day, based on route-to-route extrapolation from the inhalation 24 months repeated dose toxicity and carcinogenicity study. The inhalation NOAEC of 1820 mg/m^3 was adjusted for dosing frequency (5 days to 7 days) and respiratory volume in rat (24 hour: 1.15 mg/kg bw). The adjusted NOAEC for the oral route is therefore 373.75 mg/kg bw/day. To derive the DNEL, an overall assessment factor of 100 is used; 4 for interspecies differences (allometric scaling), 2.5 for other interspecies differences and 10 for intraspecies differences.

For acute/short-term effects, no hazards have been identified.

It was not considered relevant to determine a dermal DNEL value as the dermal absorption of D4 is less than 1% and no hazardous effects have been identified in the dermal studies.

The identified DNELs are summarized in TABLE 4-10.

TABLE 4-10 Identified DNELs for D4.

DNEL-values General population	Inhalation Systemic and local effects long term effects: **13 mg/m^3** Most sensitive endpoint: respiratory tract irritation NOAEC: 1820 mg/m^3, modified to 325 mg/m^3 Assessment factors: 25 DNEL derived from inhalation chronic toxicity and carcinogenicity study conducted in similarity to OECD Test Guideline 453 Acute/short exposure: no hazard identified Dermal No hazard identified Oral Systemic long term effects: **3.7 mg/kg bw/day** NOAEC: 1820 mg/m^3 (extrapolation from the inhalation study), modified to 373.75 mg/kg bw/day Assessment factors: 100 DNEL derived from inhalation chronic toxicity and carcinogenicity study conducted in similarity to OECD Test Guideline 453 Most sensitive endpoint: respiratory tract irritation Acute/short term exposure: no hazard identified	REACH Registration Dossier

4.1.6 4-Methylpentan-2-one, MIBK (CAS no. 108-10-1)

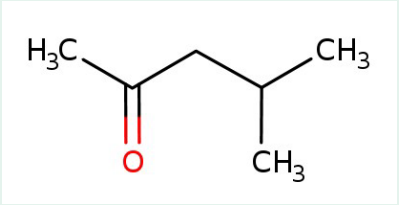
Classification

4-methylpentan-2-one (MIBK) is a mono-constituent substance. MIBK has a harmonized classification under CLP and is suspected of causing cancer (Carc. 2 H351), may cause drowsiness or dizziness (STOT SE 3 H336), causes serious eye irritation (Eye Irrit. 2 H319) and is harmful if inhaled (Acute Tox. 4 H332).

Substance identity and physicochemical properties

The physical and chemical properties of MIBK is described in TABLE 4-11.

TABLE 4-11 4-metylpentan-2-one overview identification and physicochemical properties.

Parameter	Description	Source
CAS	108-10-1	ECHA Substance Infocard
Structural formula		ECHA Substance Infocard
Chemical group	Ketone	
Vapour pressure	2.64 kPa at 25 °C	REACH Registration Dossier
Molecular weight	100.159 g/mol	REACH Registration Dossier
LogPow	1.9 at pH 6.7 (temperature not provided)	REACH Registration Dossier
CLP classification	Carc. 2 – H351 Eye Irrit. 2 – H319 Acute Tox. 4 – H332 STOT SE 3 – H336	ECHA C&L inventory

Substance toxicity
A literature search was performed to identify data relevant to carcinogenicity, using both PubMed and Google using search terms such as “4-methylpentan-2-one”, “Methyl isobutyl ketone”, “MIBK” or “108-10-1” in the search.

Two 2-year inhalation carcinogenicity and chronic toxicity studies in rats and mice are available in the REACH registration dossier. The studies were conducted according to OECD Test Guideline 451 and the rats and mice were administered MIBK at concentrations of 0, 450, 900 and 1800 ppm 6h/day, 5 days/week for two years. In the rat study neoplastic and non-neoplastic lesions were observed in the kidneys at doses of 900 and 1800 ppm. Whereas in mice hepatocellular adenomas and carcinomas were observed at 900 and 1800 ppm. A NOAEC of 1840 mg/m^3 for the rat study and 1843 mg/m^3 for the mice study was derived, for neoplastic and non-neoplastic lesions (Stout et al., 2008, cited in the REACH registration dossier). Based on the available data from these studies, there is no evidence of genotoxic effects for MIBK. Human relevance of the findings in rats and mice could not be ruled out and in the IARC report it was concluded that MIBK is possibly carcinogenic to humans (IARC, 2013). The ECHA Committee for Risk Assessment (RAC) published in September 2019 an opinion proposing the harmonised classification of MIBK as Carcinogen Category 2. Different modes of action were investigated, and some were not of relevance for humans, while others could be. Based on the available data, the RAC concluded 4-methylpentan-2-one is probably not genotoxic but should be classified as suspected of causing cancer (Carc Cat 2).

There are some studies available on human volunteers and workers. Workers exposed to MIBK have complained about headache, stomachache, nausea and vomiting after exposure up to 500 ppm for 20-30 min/day (Linari et al., 1964 and Armeli et al., 1968, cited in the REACH registration dossier). Three studies on human volunteers are available. In one of the studies, people exposed to the highest test dose (200 mg/m^3) for two hours showed symptoms of fatigue and effects on the central nervous system (Iregren et al., 1993, cited in the REACH registration dossier).

The critical effect and derivation of DNEL
The most critical effect for exposure to MIBK is carcinogenicity, which is most probably acting via a non-genotoxic mode of action. In this report, the DNELs protecting against kidney effects are therefore considered to also safeguard against cancer. In the REACH registration dossier, different points of departure for the same route of exposure are presented using both an IOEL value and a NOAEL value as starting point. For simplicity and to focus on the data generating the lowest DNEL values in this report, the kidney effects seen in the OECD 451 data is used as point of departure.

The inhalation DNEL is derived from the NOAEC of 1840 mg/m^3 in the OECD Test Guideline 451 study in rats (0, 1840 mg/m^3, 2680 mg/m^3 and 7360 mg/m^3 for 2 years, 6 hours/day, 5 days/week). By adjusting for duration of exposure for the general population (6 h/24 h, 5 d/7 d) the adjusted NOAEC is 328 mg/m^3. The assessment factors used

in the registration dossier do not follow the ECHA Guidance, thus revised assessment factors have been used in this report. By applying a revised overall assessment factor of 25 to the NOAEC of 328 mg/m^3, an inhalation DNEL of 13 mg/m^3 is derived. The assessment factors used are: 1 for allometric scaling from rat to humans, 2.5 for remaining interspecies differences, 10 for intraspecies differences and 1 for differences in duration of exposure and 1 for dose response relationship. This DNEL is more protective than the registrant's calculated DNEL and is therefore used in the risk assessment in this project.

The point of departure for both the dermal and oral DNEL calculations is the adjusted NOAEC of 328 mg/m^3 from the OECD Test Guidance No 451 chronic inhalation study in rats. Using the ECHA conversion equation based on breathing volume of rats (ECHA, 2012), the oral NOEL of 95 mg/kg bw was derived (328 mg/m^3 x 0.29 m^3/kg bw). An overall assessment factor of 100, following ECHA standards was applied: assessment factors of 4 for allometric scaling from rat to humans, 2.5 for interspecies differences, 10 for intraspecies differences, 1 for differences in duration of exposure and 1 for dose response relationship. The overall assessment factor is 100 which resulted in both a dermal and an oral DNEL of 0.95 mg/kg bw.

The identified DNEL are summarized in TABLE 4-12.

TABLE 4-12 Identified DNELs for 4-metylpentan-2-one.

DNEL-values General population	Inhalation Systemic and local long term effects: **13 mg/m^3** NOAEC: 328 mg/m^3 Assessment factors: 25 DNEL derived from studies conducted according to OECD Test Guideline 451 Most sensitive endpoint: carcinogenicity Acute/short exposure: 155.2 mg/m^3 Dermal Systemic long term effects: **0.95 mg/kg bw/day** NOAEC: 328 mg/m^3 Assessment factors: 100 DNEL derived from studies conducted according to OECD Test Guideline 451 Acute/short term exposure: no hazard identified Local effects long term exposure: hazard unknown Acute/short term exposure: no hazard identified Oral Systemic long term effects: **0.95 mg/kg bw/day** NOAEC: 328 mg/m^3 Assessment factors: 100 DNEL derived from studies conducted according to OECD Test Guideline 451 Most sensitive endpoint: carcinogenicity Acute/short term exposure: no hazard identified	REACH Registration Dossier

4.1.7 4-Methylpentan-2-one oxime (CAS no. 105-44-2)

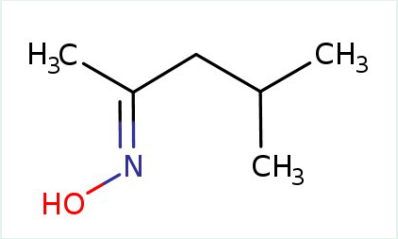
Classification

4-methylpentan-2-one oxime is a mono-constituent substance and has a notified classification and labelling according to the CLP criteria. Different classifications have been notified in the Classification and Labelling inventory. Companies manufacturing and/or importing the substance have notified that it is harmful if swallowed (Acute Tox. 4 H302), causes skin irritation (Skin Irrit. 2 H315) and eye irritation (Eye Irrit. 2 H319).

Substance identity and physicochemical properties

The physical and chemical properties of 4-methylpentan-2-one oxime is described in TABLE 4-13.

TABLE 4-13 4-methylpentan-2-one oxime overview and toxicity data.

Parameter	Description	Source
CAS	105-44-2	ECHA Substance Infocard
Structural formula		ECHA Substance Infocard
Chemical group	Oxime	
Vapour pressure	80 Pa at 20 °C 113 Pa at 25 °C	REACH Registration Dossier
Molecular weight	115.17 g/mol	REACH Registration Dossier
LogPow	1.54 at 20.0 °C	REACH Registration Dossier
Notified CLP classification	Acute Tox. 4 – H302 Skin Irrit. 2 – H315 Eye Irrit. 2 – H319	ECHA C&L inventory

Substance toxicity
In the REACH registration dossier for 4-methylpentan-2-one oxime, it is described that an acute oral toxicity study in rats performed similar to OECD Test Guideline 402 resulted in a LD50 ≥1.5 mL/kg bw, corresponding to 1333.5 mg/kg bw based on the substance density of 889 kg/m^3 (unnamed study report in the REACH registration dossier, 1991). Anaemia was observed in the medium and high dosed males (0.75 and 1.5 mL/kg) and in some female rats, which is supported by microscopic changes of the spleen and reticulocytosis. The NOEL for female rats was 0.15 mL/kg (134 mg/kg bw), the lowest dose group, whereas no NOEL could be established for male rats. It is described that the substance is classified as an acute oral toxicant category 4, as a precautionary approach.

A skin irritation study on six rabbits performed in similarity to OECD Test Guideline 404 showed that the applied dose of 0.5 mL 4-methylpentan-2-one oxime caused irritant effects on treated animals. For one animal the erythema was not reversible within 14 days and the mean primary dermal irritation index was calculated to be 3.6 (unnamed study report in the REACH registration dossier, 1990). The substance does not meet the criteria stated for skin irritant classification under the CLP regulation, as the criteria that at least 2 out of 3 test animals should have a mean score of ≥2,3 - ≤4.0 is not fulfilled. Regarding eye irritation, the substance met the criteria for classification of eye irritation category 2 according to CLP, based on an *in vivo* eye irritation/corrosion study in rabbit.

One reproductive toxicity study (0, 10, 30 and 100 mg/kg bw/day) in rats, equivalent to OECD Test Guideline 415 is available in the dossier (unnamed study report in the REACH registration dossier, 2009). No reproductive effects where seen, neither in reproductive organs of parental animals nor in their reproductive performance. There were also no results of reproductive toxicity or adverse effects in the F1 generation, but it is important to note that only low doses were tested. Parental toxicity such as histopathological findings in the spleens and hemosiderosis in the highest dose group (100 mg/kg bw) were considered to be treatment related.

The critical effect and derivation of DNEL
No DNEL values are derived in the REACH dossier of the substance. For this report, the histopathological findings in the OECD Test Guideline 415 study are therefore used as point of departure and the DNEL values are derived based on the NOAEL level of 30 mg/kg bw/day.

The inhalational DNEL value is derived in accordance with the ECHA guideline (ECHA, 2012) using the NOAEL of 30 mg/kg bw/day as starting point. The overall assessment factor used is 44.41 which is based on the allometric scaling factor (1/0.38*6.7/10) and remaining differences (2.5) and a factor of 10 for intraspecies variations in the consumer group. The derived inhalation DNEL for consumers is therefore 0.68 mg/m^3.

For the oral and dermal DNEL values, the overall assessment factor used in this report is 100: 10 for interspecies differences (4 for allometric scaling rat to humans and 2.5 for remaining differences) and 10 for intraspecies in general population, 1 for differences in duration of exposure, 1 for dose response and 1 for the quality of the database. The oral DNEL is 0.3 mg/kg bw/day following the ECHA guideline (ECHA, 2012).

It is worth to note that the classification of the 4-methylpentan-2-one oxime substance is based on limited available information. As one of the 'smaller' oximes, butanone oxime (CAS no. 96-29-7), has a harmonised classification as Carc. 1B, STOT RE 2 and Skin Sens. 1, there may be a risk that also larger oximes have a similar hazardous profile. Because the only genetic toxicity study available is an *in vitro* gene mutation study in bacteria ("Ames test") and no long-term carcinogenicity study is available, this endpoint cannot be fully evaluated. Based on the limited information, a read-across to structurally related substances could be an option, although it is not possible within the scope of this project.

The identified DNELs are summarized in TABLE 4-14.

TABLE 4-14 Identified DNELs for 4-metylpentan-2-one oxime.

DNEL-values General population and workers	Inhalation Systemic long term effects: **0.68 mg/m^3** NOAEL: 30 mg/kg bw/day Assessment factors: 44.41 DNEL derived from study similar to OECD Test Guideline 415 Most sensitive endpoint: histopathological changes Dermal Systemic long term effects: 0.3 mg/kg bw/day NOAEL: 30 mg/kg bw/day Assessment factors: 100 DNEL derived from study similar to OECD Test Guideline 415 Local effects, skin irritant: data not sufficient to derive DNEL Oral Systemic long term effects: **0.3 mg/kg bw/day** NOAEL: 30 mg/kg/bw Assessment factors: 100 DNEL derived from studies similar to OECD Test Guideline 415 Most sensitive endpoint: histopathological changes	REACH Registration Dossier

4.2 Human health exposure assessment

When consumers, i.e., non-professional users, are using antifouling paints on their pleasure boats, it is relevant to consider several different activities where potential exposure to hazardous substances within the coating may occur. Those activities, or scenarios, cover application, post-application, and disposal or removal of the paint.

As described in the ECHA guidance document on human health exposure methodology for biocides (ECHA, 2017b) harmonized assessment approaches have been developed for many applications of biocidal products. The methodology document contains technical details towards the harmonized approach to exposure assessments and is based on the Technical Notes for Guidance on Exposure that were developed in the past technical implementation of the Biocidal Products Directive (BPD 98/8/EC) (ECHA, 2015). In this assessment, it was agreed with the Danish EPA to apply the same methodology for exposure assessment as is used for evaluating biocides. The available guideline documents on biocidal antifouling paint were therefore used as basis for this exposure assessment, as the non-biocidal antifouling paints were to be risk assessed applying the same exposure scenarios used for antifouling paints containing active biocide ingredients.

In general, the following parameters are important to consider in order to estimate human exposure:

1) Composition of the product
2) Intended use of the product
3) What is the pattern of use – who is the user; how much – how often – which equipment is used
4) Which tasks are to be covered – application – post-application
5) Who else may be exposed – during use – after use – duration
6) Exposure route – on/through skin – inhalation – ingestion
7) Quantity of exposure – route and uptake

An overview of the workflow for the exposure assessment for biocidal products is shown in FIGURE 4-1.

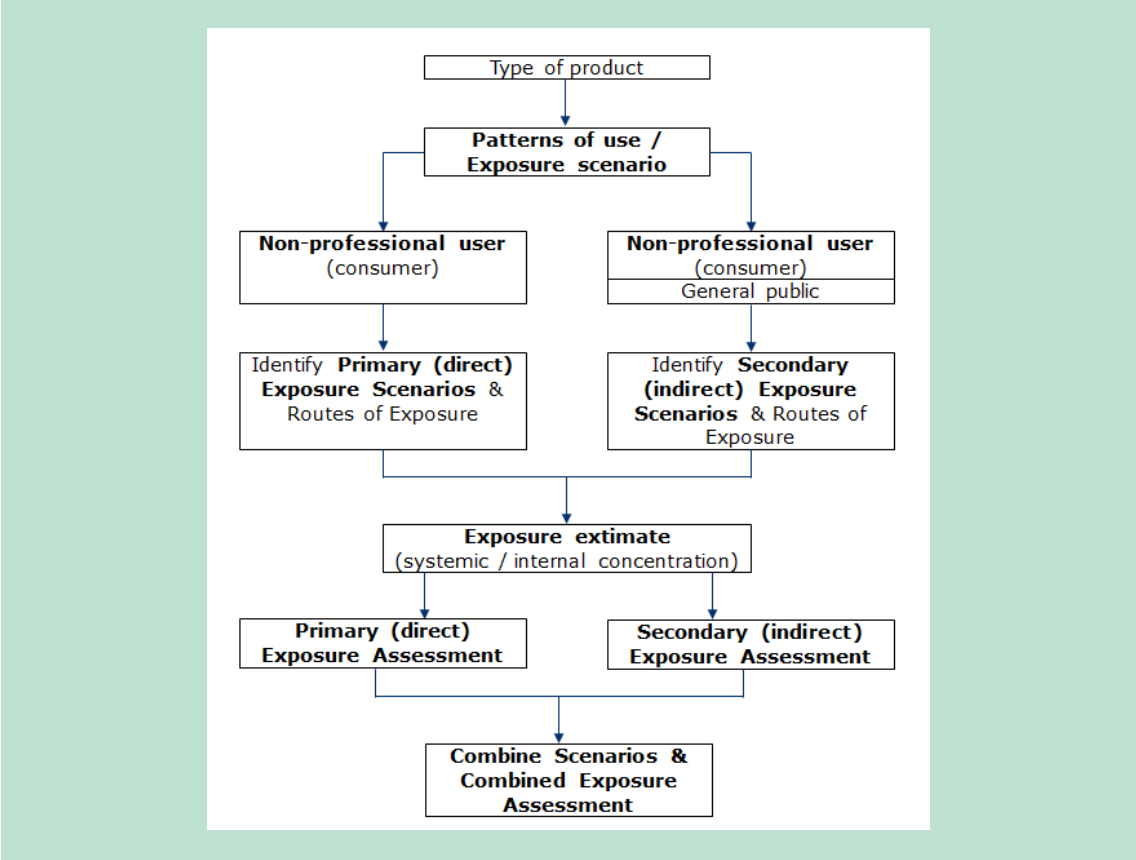


FIGURE 4-1 An overview of the general workflow for the exposure assessment described for biocidal products, also applied in this risk assessment, picture re-worked from ECHA (2017b).

All these parameters may be evaluated using a tiered approach. The exposure assessment can therefore be refined using higher tier methodologies where appropriate.

For many biocidal products, harmonized assessment approaches have been agreed upon and presented in the ECHA document “Biocides human health exposure methodology” (ECHA, 2015), one of which is the use of antifouling paints. In this project the exposure assessment of non-biocidal antifouling paints for the general population follows the pre-defined scenarios available for biocidal products. The main user in scope is a consumer performing yearly maintenance of a pleasure boat. Toddlers unintentionally getting in contact with the paint when playing on the site are also considered. In this project the standard scenarios for general population uses were followed. Tier 1 assessment provides the worst-case assessment for each identified exposure. For the consumer use of antifouling paints, it is assumed that no PPE are worn, and the worst-case duration has been used, following the recommendations published by ECHA Biocidal Products Committee Ad hoc Working Group on Human Exposure.

4.2.1 Routes of exposure

In general, three main potential routes of exposure are relevant for humans following use of paints and coatings, and these are: dermal contact, inhalation, and ingestion.

Dermal exposure

Dermal exposure is a significant exposure pathway for paints and coatings, especially because consumers are not regularly using appropriate PPE, when they are handling the paint (ECHA, 2015).

When dermal exposure to paint occurs, the absorption of the substance in the paint is highly dependent of the physico-chemical properties, such as molecular weight and lipophilicity. In the tier 1 assessment, 100% uptake is used as a worst case. If refinements are needed in the tier 2 assessment, substance specific data or cut off points at a molecular weight of 500 and log P values < -1 or > 4 may be used to set a general value of 10% cutaneous absorption as a conservative default absorption factor (ECHA, 2017b).

Inhalation exposure

Depending on the use, the inhalation exposure may in some cases become the predominant route of exposure for volatile substances or dusts. It is therefore relevant to consider the physico-chemical properties of the substances

selected for risk assessment. Volatile substances can generate potential exposure, while for non-volatile chemicals the inhalational route may be waived. Depending on the nature of the airways, especially the delicate structure of alveoli responsible for the blood-air gas exchange, up to 100% of the inhaled substance may be bioavailable. As a default worst case scenario 100 % absorption is estimated for inhalation route for the exposure assessment in this project. For inhalation of dust, it is important to have some insight in the particle size distribution of the generated dust as coarser particles are deposited in the upper airways and swallowed (ECHA, 2017b). If no such data is available, a worst case scenario of 100% exposure to dust is considered.

Oral exposure – ingestion
This exposure route covers the amount of the substance entering the mouth from other activities than being inhaled, for example hand-to-mouth activities. For the risk assessment of the antifouling products in this project, the oral exposure is not considered a significant way of exposure for adults, but for toddlers playing close to the painted boats. In the toddler exposure assessment toddlers touch painted boats and transfers paint from two fingers totally covered with paint into the mouth (ECHA, 2015). The model furthermore assumes that 100 % of the ingested paint is absorbed, as a worst case scenario (ECHA, 2017b).

4.2.2 Exposure scenarios

The biocidal product committee under ECHA has developed recommendations on how to model several uses of biocidal products. This is described in the ECHA document “Biocides human health exposure methodology” (ECHA, 2015). These exposure scenarios are used for exposure assessment of biocidal products and are therefore relevant to apply also in the current assessment of non-biocidal products in order to allow for a comparison of the risks from these two types of products. The main paths of human exposure to substances from the use of the selected non-biocidal antifouling products are given in the TABLE 4-15 below:

TABLE 4-15 Summary table over relevant exposure paths of human exposure.

Exposure path	Primary (direct) exposure		Secondary (indirect) exposure	
	Professional use*	Consumer use	Professional use*	General¤ public
Inhalation	n/a	Yes	n/a	No
Dermal	n/a	Yes	n/a	Yes
Oral	n/a	No	n/a	Yes

* As the anti-fouling paint products are for consumer use, professional use is not part of the assessment
¤ Includes people other than those directly handling the product. Worst case is applied as toddlers are one of the most sensitive subpopulations in the general public.

Four relevant human exposure scenarios have been identified within the scope of this project focusing on the use of antifouling paint for pleasure boats. The scenarios are pre-set and described in guidance documents, see TABLE 4-16 below for references.

TABLE 4-16 Overview of exposure scenarios relevant for antifouling paints.

Exposure scenario no.	Scenario name	Reference
1	Brushing and roller painting of antifouling paint on underside of small boats, outdoor	(ECHA, 2016)
2	Washing out of a brush which has been used to apply paint	(HEEG, 2010)
3	Removal of exhausted surface coatings from hulls before re-painting	(ECHA, 2002)
4	Toddler exposure	(ECHA, 2015)

The tiered approach for exposure presented in the ECHA biocide guidance (ECHA, 2017b) will be applied and the more generic settings will be used in the first step. The ECHA Ad hoc Working Group on Human Exposure has compiled default human factor values for use in exposure assessment of biocidal products (ECHA, 2017a). These default values are presented in TABLE 4-17 and used in the exposure assessment calculations in this project.

TABLE 4-17 Default values for body weight, hand areas and inhalation

	Toddler (1 to < 2 years old) irrespective of gender	Adult irrespective of gender
Body weight	10 kg	60 kg
Hands (palms and backs of both hands)	230.4 cm^3	820 cm^2
Inhalation	1.26 m^3/h	1.25 m^3/h

The maximum concentration of each substance of concern, as described in chapter 3 above, is also used as input data for the different exposure scenarios. In most cases the information from the SDS is the main source, see typical

concentrations in TABLE 3-1 to TABLE 3-4. However, for example naphthalene is not an intentionally added ingredient but considered to be a part of hydrocarbons, C10, aromatics, <1% naphthalene (CAS 1189173-42-9). According to the relevant SDS, the paint contains maximum 5-10% of the hydrocarbon substance with CAS 1189173-42-9; hence maximum 1% of the constituent present at a concentration of up to 10% of the paint product is naphthalene. The maximum content of naphthalene in the paint product is therefore 0.1%.

Primary human exposure
The primary human exposure scenario of non-biocidal antifouling paints for pleasure boats describes the consumer, actively handling the paint product. The intended use of the consumer product is in focus, but also other reasonably foreseeable uses should be covered in separate scenarios. There are three main scenarios that are relevant to human primary exposure:

1) Application of the paint by brush or roller
2) Post-application activities such as cleaning and maintaining process of equipment and tools
3) Removal of 'old' surface coatings before re-painting

Consumer exposure scenarios do not assume that the consumers read or follow the instructions for use. Therefore, application of formal PPE is not anticipated and should not be assumed even in the Tier 2 refinement step for the general population (ECHA, 2015). On the other hand, the frequency and/or duration of use for the consumer is expected to be much lower compared to professionals.

Exposure scenario 1: Brushing and roller painting of antifouling paint on underside of small boats, outdoor
One of the main activities when using antifouling paints on a pleasure boat is the application of the paint on the bottom of the boat. This activity includes a potential high risk of direct contact with the paint as it is handled directly from the can or a paint tray and applied by using a brush or roller. The Biocides Human Health Exposure Methodology Document (ECHA, 2016) contains technical details towards a harmonised approach to exposure assessments and gives generic values for in-use antifouling paints of densities ranging from 1.25 to 2 g/ml (ECHA, 2015). In this project, some of the paints have a lower density compared to the reference value from the biocide methodology document. The model is nevertheless considered valid to use for indication of exposure values in the tier 1 assessment. However, depending on the application, the generic values may be underestimating or overestimating the exposure as lower-density products may have a tendency to form droplets when painting, while higher density paints may have a higher tendency to drip from the brush or roller when painting overhead.

The relevant routes of exposures for the consumer are via the dermal and inhalational routes through handling and during application. This scenario covers the duration of painting the pleasure boat, including the preparation, i.e., stirring the product and if painting is done by roller, decanting it into a paint tray as well as the time it takes to cleaning up the scene. The required time varies depending on the size of the boat but following the standard scenario derived for biocides, it is assumed that it takes 120 minutes to paint the bottom of the boat. Taking the cleaning time into account, the total duration is expected to be 132 minutes (ECHA, 2015a). The basis for the scenario is outdoors, where the consumer is not wearing any PPE such as chemical resistant gloves. In the standard scenario, the setting is outdoors which would be representative for most of the cases. No standardized scenario is describing indoor use. The indicative exposure values published in the ECHA methodology document are therefore applied in the exposure assessment (TABLE 4-18). It is noted that the uncertainty is high for hand exposure, while the uncertainty for body and inhalation exposure is moderate (HEEG, 2008). The maximum concentration of each substance of concern, as reported in chapter 3, is used in the exposure assessment.

Depending on the position of the user, the dermal exposure will vary. For painting overhead, the paint may drip on the hands during application. The tendency of the paint to drip is depending on the viscosity and density of the antifouling product. Cleaning or wiping of hands is not considered in the first-tier assessment.

TABLE 4-18 Input data used for exposure scenario (ES) 1

	Parameter	Value	Unit
Exposure parameters specific for ES 1	Indicative dermal exposure of hands	76.6	mg/min
	Indicative dermal exposure of body	30.7	mg/min
	Total indicative dermal exposure	107.3	mg/min
	Inhalation exposure of paint	0.05	mg/m^3
	Duration of scenario	132	min/day
	Dermal absorption (Tier 1 worst case)	100	%
General exposure parameters	Body weight	60	kg
	Inhalation rate	0.021	m^3/min

Tier 1 exposure assessment for the dermal and inhalation routes is calculated as follows:

1) Systemic exposure via dermal route, expressed in the unit of mg/kg bw/day:

$$Dermal\ exposure = \frac{(Total\ indicative\ dermal\ exposure * SoC\ concentration\ in\ paint * Dermal\ absorption) * Duration\ of\ scenario}{Body\ weight}$$

2) Systemic exposure via inhalation route, expressed in the unit of mg/kg bw/day:

$$Inhalation\ exposure = \frac{(Inhalation\ exposure\ of\ paint * SoC\ concentration\ in\ paint) * Inhalation\ rate * Duration\ of\ scenario}{Body\ weight}$$

3) Local inhalation exposure, expressed in the unit of mg/m^3 is the value presented in TABLE 4-18.

If the risk assessment shows that the risk cannot be controlled refinements of the exposure scenario is required in a tier 2 assessment. Either substance specific data on dermal absorption can be used to refine the exposure assessment, or higher tier exposure assessment tools such as RISKOFDERM, or similar tools available from ECHA[8] can be used for refinement of exposure estimation.

An overview of the results from the exposure calculations for all the SoC in this project is summarized in TABLE 4-19 below.

[8] https://echa.europa.eu/documents/10162/19680902/calculator_riskofderm_enl.xls/9e0c3fa8-4764-4a18-95f9-8fbccf3acf2a

TABLE 4-19 Results from the tier 1 exposure calculations for ES 1 Brushing and roller painting of antifouling paint on the underside of small boats, outdoor

Substance	Concentration of SoC in coating*	Exposure route	Tier 1 exposure assessment	Unit
Solvent naphtha	50%	Dermal, short term	118.03	mg/kg bw/day
		Inhalation, short term local	0.025	mg/m^3
		Inhalation, short term systemic	0.001	mg/kg bw/day
		Oral	Not relevant	
Ethylbenzene	5%	Dermal, short term	11.80	mg/kg bw/day
		Inhalation, short term local	0.003	mg/m^3
		Inhalation, short term systemic	0.0001	mg/kg bw/day
		Oral, short term	Not relevant	
Naphthalene	0.1%	Dermal, systemic	0.24	mg/kg bw/day
		Inhalation, short term local	0.00005	mg/m^3
		Inhalation, short term systemic	0.000002	mg/kg bw/day
		Oral, short term	Not relevant	
Rosin	25%	Dermal, local	59.02	mg/kg bw/day
		Inhalation, short term local	0.01	mg/m^3
		Inhalation, short term systemic	0.001	mg/kg bw/day
		Oral, short term	Not relevant	
Octamehtylcyclotetrasiloxane	0.3%	Dermal, systemic	0.71	mg/kg bw/day
		Inhalation, short term local	0.0002	mg/m^3
		Inhalation, short term systemic	0.000007	mg/kg bw/day
		Oral, short term	Not relevant	
4-methylpentan-2-one (MIBK)	15%	Dermal, systemic	35.41	mg/kg bw/day
		Inhalation, short term local	0.008	mg/m^3
		Inhalation, short term systemic	0.0003	mg/kg bw/day
		Oral, short term	Not relevant	
4-methylpentan-2-one oxime	2%	Dermal, systemic	4.72	mg/kg bw/day
		Inhalation, short term local	0.001	mg/m^3
		Inhalation, short term systemic	0.00005	mg/kg bw/day
		Oral, short term	Not relevant	

* Mainly based on information in the SDS on the antifouling paint products, see information in Chapter 2. For 4-methylpentan-2-one oxime, a rounded value was used based on the GC-MS screening analyses results for 38F (1.7% 4-methylpentan-2-one oxime) and 28F (1.9% for 2-hexanone oxime).

Exposure scenario 2: Washing out of a brush which has been used to apply paint

HEEG has developed a scenario to estimate the potential exposure to the skin of hands during cleaning of the brush used for painting, as illustrated in TABLE 4-20. Worst case scenario was applied covering non-water-based paints, assuming the paint has a density of 1 g/ml (ECHA, 2015). For water-based paints, the equipment is usually cleaned under running water from a tap. The running water is then cleaning both the equipment and any paint contaminating the hands of the user.

When cleaning a brush used for non-water based paint, the exposure model assumes that a large size brush (10 x 10 x 2 cm) is used, corresponding to a volume of 200 ml. After use, it is assumed that one eighth (1/8) of the brush volume is paint, i.e., 25 ml. One way of cleaning a brush is by dipping and swirling it in a container with solvent. The cleaning is assumed to be done in three steps, each time using fresh solvent of at least 400 ml resulting in 10-fold dilution of the residues in the brush. After each step the person cleaning the brush is assumed to squeeze it by the hand to remove as much solvent as possible, resulting in 50 % of the contaminated solvent is potentially covering the hand. However, it is further assumed that the brush is wrapped using a cleaning rag or piece of paper before it is squeezed by hand. This results in 90% of the contaminated solvent is absorbed by the rag. This process is assumed to be repeated maximum three times. The maximum concentration of each substance of concern is also taken into account in the exposure assessment (HEEG, 2010).

This dermal exposure scenario is built on a worst-case assuming all contamination remains on the hands at the end of the activity, thus is available for dermal absorption. The input data used for exposure scenario 2 is presented in TABLE 4-20 (HEEG, 2010).

TABLE 4-20 Input data used for exposure scenario 2.

	Parameter	Value	Unit
Exposure parameters specific for ES 2	Volume of brush	200	ml
	Volume of paint remaining in brush after painting (1/8 of 200 ml = 25 ml)	25	ml
	Density of paint (worst case)	1500	mg/ml
	Weight of paint remaining in brush after painting = volume of paint remaining on brush after painting (ml) x density of paint (mg/ml)	37500	mg
	Minimum volume of each washing solution	400	ml
	Percentage of SoC remaining in brush after each cleaning step	10	%
	Percentage of SoC squeezed from brush into cloth	50	%
	Amount of SoC absorbed in cloth	90	%
	Amount of SoC contaminating hands from cloth	10	%
General exposure parameters	Dermal absorption (worst case)	100	%
	Body weight	60	kg

Tier 1 systemic dermal exposure for washing out of brushes is calculated in several steps, taking dilution of SoC through three cleaning rounds into consideration. In the HEEG document an excel based calculator for systemic exposure is available (HEEG, 2010). An example showing an extraction from the calculator applied on solvent naphtha is available in Appendix 3.

The results from the exposure calculations for all the SoC in this project are summarized in TABLE 4-21 below.

TABLE 4-21 Results from the tier 1 exposure calculations for exposure scenario 2 Washing out a brush which has been used to apply a paint.

Substance	Concentration of SoC in coating*	Exposure route	Tier 1 exposure asssessment	Unit
Solvent naphtha	50%	Dermal, short term	1.64	mg/kg bw/day
Ethylbenzene	5%	Dermal, short term	0.16	mg/kg bw/day
Naphthalene	0.1%	Dermal, short term	0.003	mg/kg bw/day
Rosin	25%	Dermal, short term	0.8	mg/kg bw/day
Octamehtylcyclotetrasiloxane	0.3%	Dermal, short term	0.01	mg/kg bw/day
4-methylpentan-2-one (MIBK)	15%	Dermal, short term	0.5	mg/kg bw/day
4-methylpentan-2-one oxime	2%	Dermal, short term	0.1	mg/kg bw/day

*Mainly based on information in the SDS on the antifouling paint products, see information in Chapter 2.

Exposure scenario 3: Removal of exhausted surface coatings from hulls before re-painting
In the 2002 version of Technical Notes for Guidance (ECHA, 2002), an example on exposure scenario covering consumers removing exhausted antifouling paints from hulls before re-painting is given, summarized in TABLE 4-22. In this example the following assumptions are made to assess the exposure from removal of exhausted coatings using

hand-held or powered tool. No personal protective equipment was anticipated for the task with an estimated duration of two hours for one day per year. The exposure model is only covering inhalation of dust, as it states dermal exposure to dust is considered as dust is not dermally absorbed. The input data used for exposure scenario 3 is presented in TABLE 4-22 (ECHA, 2002). The estimated exposure of dust is 10 mg/m^3, where the concentration of the SoC in the dried paint product should be considered. As the paint dries, solvents will evaporate from the wet paint resulting in higher concentration of the non-volatile SoC in the dried paint, compared to the wet paint. Concentration of SoC in dry paint was estimated in different ways depending on if the SoC was considered to be a volatile substance or not. For solvents like ethylbenzene and solvent naphtha, the target analysis indicates only very low residue levels left in the dried paint. For ethylbenzene and xylene, which is a trace substance for solvent naphtha, the analytical results show only minimal concentrations < 0.02% in the dried paint. For non-VOC substances, such as rosins and 4-methylpentan-2-one oxime the SoC concentrations presented in the SDS documents were recalculated based on the information on VOC content of each specific paint according to their SDS.

TABLE 4-22 Input data used for exposure scenario 3.

	Parameter	Value	Unit
Exposure parameters specific for ES 3	Exposure by inhalation	10	mg/m^3
	Duration of scenario	2	h
	Inhalation rate	1.26	m^3/h
	Percentage of SoC absorbed when inhaled (worst case)	100	%
General exposure parameters	Body weight	60	kg

Tier 1 exposure assessment for the inhalation route is calculated as follows:

Systemic exposure via inhalation route, expressed in the unit of mg/kg bw/day

$$= \frac{(Inhalation\ exposure\ of\ paint * SoC\ concentration\ in\ paint) * Inhalation\ rate * Duration\ of\ scenario}{Body\ weight}$$

An overview of the results from the exposure calculations for all the SoC in this project is presented in TABLE 4-23 below.

TABLE 4-23 Results from the tier 1 exposure calculations for exposure scenario 3 Removal of exhausted surface coatings from hulls before re-painting.

Substance	Concentration of SoC in dry coating*	Exposure route	Tier 1 exposure assessment	Unit
Solvent naphtha	0.06%	Inhalation, short term local	0.01	mg/m^3
		Inhalation, short term systemic	0.0002	mg/kg bw/day
Ethylbenzene	0.02%	Inhalation, short term local	0.002	mg/m^3
		Inhalation, short term systemic	0.0001	mg/kg bw/day
Naphthalene	0.02%	Inhalation, short term local	0.002	mg/m^3
		Inhalation, short term systemic	0.001	mg/kg bw/day
Rosin	36%	Inhalation, short term local	3.6	mg/m^3
		Inhalation, short term systemic	0.2	mg/kg bw/day
Octamethylcyclotetrasiloxane (D4)	0.2%	Inhalation, short term local	0.02	mg/m^3
		Inhalation, short term systemic	0.001	mg/kg bw/day
4-methylpentan-2-one (MIBK)	0.05%	Inhalation, short term local	0.005	mg/m^3
		Inhalation, short term systemic	0.0002	mg/kg bw/day
4-methylpentan-2-one oxime	2%	Inhalation, short term local	0.2	mg/m^3
		Inhalation, short term systemic	0.008	mg/kg bw/day

*Mainly based on information in the SDS on the antifouling paint products (Chapter 2) or analyses of residual VOC in dried paint (Chapter 3).

Secondary human exposure
Persons may also be exposed without deliberately using the products themselves, hence the general public may be unintendedly affected by chemicals both during or after their actual use. Such inadvertently exposed persons may include adults, infants as well as children depending on the scenario. Experience indicates that post application exposure of children may be the most important exposure to a biocidal substance. This is because children are a sensitive subgroup (ECHA, 2017b). The secondary exposure of a toddler to antifouling paint is therefore taken into consideration in the risk assessment of anti-fouling paints.

Exposure scenario 4: Toddler exposure
As children may come in contact with antifouling paint when playing on the site where pleasure boats are painted and kept, a scenario to cover this potential exposure was published by ECHA in 2015 (ECHA, 2015), shown in TABLE 4-24. The scenario is modelled using a toddler as the exposed individual covering exposure via both dermal and oral (hand-to-mouth) routes. The scenario covers two sub-scenarios:

1) Exposure to wet paint
    a. Dermal exposure
    b. Oral exposure through hand-to-mouth transfer
    c. Combined exposure
2) Exposure to dried paint
    a. Dermal exposure
    b. Oral exposure through hand-to-mouth transfer
    c. Combined exposure

The wet paint exposure assessment is based on the amount of paint used to paint the boat, the density of the paint and the concentration of the hazardous substances in the paint. The input data used for exposure scenario 4:1 and 4:2 are presented in TABLE 4-24 and TABLE 4-26 (ECHA, 2015).

TABLE 4-24 Input data used for exposure scenario 4:1 Wet paint

	Parameter	Value	Unit
Exposure parameters specific for ES 4:1	Application rate for wet paint	0.013	ml paint/cm^2
	Density of paint (worst case)	1.5	g/ml
	Transfer coefficient of wet paint from treated surface to hand	50	%
	Total area of toddler hands in contact with the removed wet paint (100% palms of both hands)	115.2	cm^2
	Dermal absorption (worst case)	100	%
	Transferable fraction of paint from hand to mouth (for wet paint) = two fingers	10	%
	Oral absorption (worst case)	100	%
General exposure parameters	Toddler body weight	10	kg

An example showing how the exposure assessment of wet paint is done is available in Appendix 4. The results from the wet paint exposure calculations for all the SoC in this project is summarized in TABLE 4-25 below.

TABLE 4-25 Results from the tier 1 exposure calculations for exposure scenario 4:1 Toddler exposure to wet paint.

Substance	Concentration of SoC in coating*	Exposure route	Tier 1 exposure	Unit
Solvent naphtha	50%	Dermal, short term	0.06	mg/kg bw/day
		Oral, short term	0.006	mg/kg bw/day
Ethylbenzene	5%	Dermal, short term	0.01	mg/kg bw/day
		Oral, short term	0.001	mg/kg bw/day
Naphthalene	0.1%	Dermal, short term	0.0001	mg/kg bw/day
		Oral, short term	0.00001	mg/kg bw/day
Rosin	25%	Dermal, short term	0.03	mg/kg bw/day

		Oral, short term	0.003	mg/kg bw/day
Octamehtylcyclotetra-siloxane	0.3%	Dermal, short term	0.00003	mg/kg bw/day
		Oral, short term	0.00003	mg/kg bw/day
4-methylpentan-2-one (MIBK)	15%	Dermal, short term	0.02	mg/kg bw/day
		Oral, short term	0.002	mg/kg bw/day
4-methylpentan-2-one oxime	2%	Dermal, short term	0.002	mg/kg bw/day
		Oral, short term	0.0002	mg/kg bw/day

*Mainly based on information in the SDS on the antifouling paint products, see information in Chapter 2.

For the second sub-scenario of the toddler exposure scenario, exposure via dried paint is considered, as summarized in TABLE 4-26. The dry paint exposure assessment is based on the amount of paint used to paint the boat, the density of the paint and the concentration of the hazardous substances in the dry paint. The concentration of substances of concern in dry paint is estimated in the same way as described in exposure scenario 3.

TABLE 4-26 Input data used for exposure scenario 4:2 Dry paint

	Parameter	Value	Unit
Exposure parameters specific for ES 4:2	Application rate for wet paint	0.013	ml paint/cm^2
	Density of paint (worst case)	1.5	g/ml
	Transfer coefficient of dry paint from treated surface to hand	3	%
	Total area of toddler hands in contact with the removed dry paint (40% of palms of both hands)	46.08	cm^2
	Dermal absorption (worst case)	100	%
	Transferable fraction of paint from hand to mouth (for dry paint)	50	%
	Oral absorption (worst case)	100	%
General exposure parameters	Toddler body weight	10	kg

An example showing how the exposure assessment of wet paint is done is available in Appendix 5. The results from the wet paint exposure calculations for all the SoC in this project is summarized in TABLE 4-27 below.

TABLE 4-27 Results from the tier 1 exposure calculations for exposure scenario 4:2 Toddler exposure to dry paint.

Substance	Concentration of SoC in dry paint	Exposure route	Tier 1 exposure	Unit
Solvent naphtha	0.06%	Dermal, short term	0.000001	mg/kg bw/day
		Oral, short term	0.0001	mg/kg bw/day
Ethylbenzene	0.02%	Dermal, short term	0.0000004	mg/kg bw/day
		Oral, short term	0.0002	mg/kg bw/day
Naphthalene	0.02%	Dermal, short term	0.0000005	mg/kg bw/day
		Oral, short term	0.00002	mg/kg bw/day
Rosin	36%	Dermal, short term	0.001	mg/kg bw/day
		Oral, short term	0.05	mg/kg bw/day
Octamehtylcyclotetra-siloxane	0.2%	Dermal, short term	0.000004	mg/kg bw/day
		Oral, short term	0.0002	mg/kg bw/day
4-methylpentan-2-one (MIBK)	0.05%	Dermal, short term	0.000001	mg/kg bw/day
		Oral, short term	0.0001	mg/kg bw/day
4-methylpentan-2-one oxime	2%	Dermal, short term	0.0001	mg/kg bw/day
		Oral, short term	0.003	mg/kg bw/day

4.3 Risk assessment for consumers

The basis for conducting human health risk characterization is to compare the derived reference values (such as DNEL values) for the critical toxicity endpoints of that substance with the exposure levels of the identified use scenarios of the same substance. For biocidal products this ratio is called Hazard Quotient (HQ), which is comparable with the Risk Characterization Ratio (RCR) used for risk assessment of chemicals under REACH. If the HQ (exposure level/DNEL) is 1 or above, the risk is considered unacceptable and further refinement is needed with respect to exposure and/or hazard assessment including risk mitigation measures. Where a quantitative risk assessment cannot be made, a qualitative assessment shall be conducted. For biocidal products, a tiered approach for human health risk characterization of biocides has to be followed and is therefore also applied in this project. In a tiered approach, if the estimated exposure is lower than the reference value, there is no cause for concern and no further refinement is needed (ECHA, 2017b). In situations where the same person is potentially exposed to the same substance in the same setting via different routes of entry into the body or from different products containing the same substance, exposure scenarios reflecting these concomitant exposures should be assessed in the exposure estimation. These scenarios – typically related to workplaces and aggregated exposure for consumers need specific attention in the risk characterization step (ECHA, 2016).

The outcome from the risk characterization for consumers handling antifouling paint is presented in TABLE 4-28. The HQ values for each substance of concern are presented for the identified scenarios, as well as the total exposure of paint from all the contributing uses. A general conclusion that can be drawn is that most of the non-biocidal antifouling paints are considered to be safe to use, provided consumers are following the intended uses. This is the case even though no specific risk management measures, nor personal equipment have been accounted for. For the unintended exposure of children who may come into contact with painted boats and in such way be exposed to the antifouling paints, the risk assessment presented in this report indicates no risk of adverse health effects.

TABLE 4-29 presents the results from the risk assessment for the secondary exposure scenarios focusing on toddlers.

TABLE 4-28 Results from the risk assessment for each of the exposure scenarios with primary exposure, and total highest exposure from all the contributing scenarios.

	Exposure scenarios – primary exposure						Total exposure for consumer handling antifouling paint
	ES–1 – Brushing and roller painting (Dermal + inhalation exposure)		ES–2 – Washing out a brush (Dermal exposure only)		ES–3 – Removal of old paint (Dermal + inhalation exposure)		
Substance	**Combined HQ**	**Comment**	**Combined HQ**	**Comment**	**Combined HQ**	**Comment**	**Total HQ**
Solvent naphtha	0.005	No refinement needed	-	No defined dermal AEL[º]	0.007	No refinement needed	0.04
Ethylbenzene	Tier 1: **9.1**[*] Tier 2: 0.36	Refinement after tier 1 required	0.13	No refinement needed	0.0001	No refinement needed	Tier 1: **9.2**[*] Tier 2: 0.5
Naphthalene	0.09	No refinement needed	0.001		0.0001	No refinement needed	0.10
Rosin	No hazard identified; no risk assessment needed.						No risk
Octamehtylcyclotetrasiloxane (D4)	0.00001	No refinement needed	-	No defined dermal AEL[º]	0.001	No refinement needed	0,001
4-methylpentan-2-one (MIBK)	Tier 1: **37.3**[*] Tier 2: **22.3**[*¤]	Not acceptable risk due to dermal exposure	0.52	No refinement needed	0.0006	No refinement needed	Tier 1: **37.7**[*] Tier 2: **22.8**[*¤]
4-methylpentan-2-one oxime	Tier 1: **15.7**[*] Tier 2: **9.4**[*¤]	Refinement required Data lacking for Tier 2 assessment	0.22	No refinement needed	0.32	No refinement needed	Tier 1: **16.3**[*] Tier 2: **9.9**[*¤]

[*] HQ value >1, health risks not under control. In ES 1, it is dermal exposure which drives the risk. HQ for inhalation is <<1.
[#]Tier 2 risk assessment based on substance specific dermal absorption data (4% for Ethylbenzene (ECHA, Ethylbenzene, [cited 2023]))
[¤] Tier 2 risk assessment based on RISKOFDERM calculations as no substance specific information on dermal adsorption is available.
[º] AEL – Adverse effect level

TABLE 4-29 Results from the risk assessment for each of the exposure scenarios with secondary exposure, toddlers being exposed to wet and dry paint.

Exposure scenarios – secondary exposure		
	ES4–1 – Toddler wet paint	ES4–2 – Toddler dry paint
Substance	**Combined HQ**	**Combined HQ**
Solvent naphtha	0.01	0.0001
Ethylbenzene	0.005	0.00002
Naphthalene	0.00005	0.0000002
Rosin	No hazard identified, no risk assessment needed	No hazard identified, no risk assessment needed
Octamehtylcyclotetra-siloxane (D4)	0.00001	0.0001
4-methylpentan-2-one (MIBK)	0.02	0.00007
4-methylpentan-2-one oxime	0.01	0.01

In general, it is the direct contact with wet paint in ES-1 which generates the highest potential exposure of any of the investigated scenarios. Intuitively, this is in line with expectations, as the paint scenario covers both direct handling and has the longest duration of any of the evaluated scenarios. In the human health risk assessment, it is sufficient for most of the substances to perform a tier 1 assessment in order to evaluate and conclude acceptable risks from using the paint, i.e., the HQ values are <1. For three of the substances of concern in this report; ethylbenzene, 4-methylpentan-2-one (MIBK) and 4-methylpentan-2-one oxime, the tier 1 risk assessment cannot show safe use for the brushing and roller painting scenario (ES-1). For all these three substances it is the dermal route giving rise to an unacceptable exposure using the tier 1 input data.

In order to refine the risk assessments, substance specific information on dermal absorption was sought, following the recommendations in the ECHA guidance document (ECHA, 2017b). For ethylbenzene such information was available in the REACH dossier, indicating the dermal absorption of the substance is 4% of the applied dose as the highest (ECHA, Ethylbenzene, [cited 2023]). For 4-methylpentan-2-one (MIBK) several sources indicate dermal exposure is close to 100% (ECHA, 4-methylpentan-2-one, [cited 2023]) (IARC, 2013). Available information on 4-methylpentan-2-one oxime was limited and no information on dermal absorption was possible to retrieve. Instead, the ECHA recommended tool for higher tier assessments, RISKOFDERM[9], was used to refine the exposure for those two substances. The input data used in RISKOFDERM model for the brushing and roller painting exposure scenario was 2,5 L as the amount of paint, the duration of exposure was 132 minutes, and the viscosity of the paint was considered similar to oil.

The outcome of the tier 2 risk assessments shows that only for ethylbenzene, where substance specific data indicate low dermal absorption, the risk is adequately controlled. After the refinement, the HQ value is reduced to 0.36. For 4-methylpentan-2-one (MIBK) and 4-methylpentan-2-one oxime the HQ is still well above 1.

The combined HQ for MIBK, a widely used solvent not only specific for non-biocidal antifouling paints, is 22.8 after refinement of the exposure assessment. This HQ value is derived based on the highest MIBK concentration in any of the evaluated products. MIBK is listed in the SDS of four coating products included in this risk assessment, representing different types of coatings: one hard coating, one self-polishing coating and one tie coat. All these products have a concentration of MIBK that generates a too high HQ. The tie coat has the highest concentration ranging up to 15%. The hard coating and the self-polishing coating contain 1-3% of MIBK according to SDS, which generates a HQ of 4.5. Additionally, MIBK was detected as a residual VOC in two coatings in the chemical analyses (one self-polishing coating and one foul release coating).

The refined risk assessment of 4-methylpentan-2-one oxime generates a combined HQ of 9.9. This substance, which is related to the silicone-based foul release coatings and thus specific for non-biocidal antifouling paints, is identified in only one of the products evaluated within this project, a foul release coating.

[9] RISKOFDERM tool available from ECHA: https://echa.europa.eu/documents/10162/19680902/calculator_riskofderm_enl.xls/9e0c3fa8-4764-4a18-95f9-8fbccf3acf2a

Risk management measures for the consumer products containing substances of concern are limited. The actual implementation of technical controls and PPE is usually difficult to achieve in practice.

4.4 Discussion and conclusion on consumer risk

The risk assessment methodology for biocides is applied on the non-biocidal antifouling paints evaluated in this project to allow a comparison of the outcome of the risk assessments of non-biocidal paints with biocidal antifouling paints. The types of non-biocidal antifouling coatings included in this project were foul release coatings, tie coats for foul release coatings, self-polishing and hard coatings. Substances of concern for human health were unevenly distributed within the different products and product types. A summary of the human health risk assessment of the antifouling coatings is provided in TABLE 4-30.

The following substances were included in the human health risk assessment of non-biocidal antifouling coatings; solvent naphtha, ethylbenzene, naphthalene, rosin, octamethylcyclotetrasiloxane (D4), 4-methylpentan-2-one (MIBK) and 4-methylpentan-2-one oxime. For solvent naphtha, naphthalene and octamethylcyclotetrasiloxane (D4), it is sufficient to perform a tier 1 assessment to evaluate and conclude acceptable risks from using the paint, i.e., the HQ values are <1. For rosin, no hazard was identified in the hazard assessment, and therefore no risk estimate was calculated. The tier 1 risk assessment cannot show safe use for ethylbenzene, 4-methylpentan-2-one (MIBK) and 4-methylpentan-2-oxime in the non-biocidal antifouling paints. For ethylbenzene, the tier 2 assessment showed an acceptable risk. For 4-methylpentan-2-one (MIBK) and 4-methylpentan-2-oxime, the tier 2 assessment showed that risk is not controlled due to high dermal exposure from the painting scenario. Specific risk management measures are not considered as the general population handling the products are assessed.

MIBK is, according to the safety data sheets, present in four different types of coatings evaluated in this study: two hard coatings, one self-polishing coating and one tie coat. All the products have a concentration of MIBK that is of concern, but the tie coat has the highest concentration ranging up to 15%. Additionally, residual concentrations of MIBK were detected during target analyses in two more coatings. The presence of MIBK in six out of 13 non-biocidal antifouling coatings included in the risk assessment indicates the common use of this solvent.

4-methylpentan-2-oxime is the second substance where the risk is not considered to be under control. The substance dataset is rather limited and additional data would be needed to fully risk assess the substance. 4-methylpentan-2-oxime was found in one of the antifouling paints evaluated in this project, a foul release coating product. It is noted that 4-methylpentan-2-oxime was not listed in the safety data sheet of the product but detected in the GC-MS screening in a concentration of 1.7%. A similar substance, 2-hexanone oxime, was also detected in the GC-MS screening in two foul release coatings. The substances are most likely not added to the coatings but occur as crosslinking by-products from silane crosslinkers. Worth to note is the structural similarity to ‘smaller’ oximes such as butanone oxime (C4, Cas no. 96-29-7), which has a more severe hazardous profile having a harmonized classification as Carc. 1B, STOT RE 2 and Skin Sens. 1.

Out of the 13 non-biocidal antifouling coatings evaluated in this project, five contain hazardous substances for which health risks cannot be excluded. Placing on the market of anti-fouling paint products containing hazardous substances, for which safe use cannot be ensured, should be discouraged for consumer health considerations. However, it is noted that there may be other considerations (e.g. applicability, durability or lack of better alternatives) that are outside the scope of the project, but which may favour the marketing of such products. Further, it is noted that one of those components, MIBK, may very well be used in antifouling paints containing active biocides, as it is a commonly used solvent used by in the paint industry. Comparing health effects of non-biocidal and biocidal antifouling paints was not in the scope of this project.

TABLE 4-30 Summary of the human health risk assessment of anti-fouling coatings

Product	Risk during use, dermal	Risk during use, inhalation	Substances giving rise to risk and combined HQ*
02S – Self-polishing coating	Yes Systemic effects Potentially increased cancer risk	No	4-methylpentan-2-one (MIBK) Combined HQ = 4.6
40S – Self-polishing coating	No	No	-
01H – Hard coating	Yes Systemic effects Potentially increased cancer risk	Uncertain Potentially increased cancer risk	4-methylpentan-2-one (MIBK) Combined HQ = 4.6
41H – Hard coating	Yes Systemic effects Potentially increased cancer risk	No	4-methylpentan-2-one (MIBK) Combined HQ = 4.6
31H – Hard coating	No	No	-
33C – Hard coating	No	No	-
07H – Hard coating	No	No	-
38F – Foul release	Yes Systemic effects Organotoxicity: Spleen and kidney	No	4-methylpentan-2-oxime Combined HQ = 9.9
03F – Foul release	No	No	-
28F – Foul release	No	No	-
39T – Tie coat	Yes Systemic effects Potentially increased cancer risk	No	4-methylpentan-2-one (MIBK) Combined HQ = 22.8
04T – Tie coat	No	No	-
29T – Tie coat	No	No	-

* Combined HQ from all primary exposure scenarios accounting for the product-specific concentration of the substance in the product.

5. Environmental risk assessment

5.1 Environmental hazard assessment

As described in chapter 3.4., five substances, namely octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5), dodecamethylcyclohexasiloxane (D6), MCCP (C14-C17) and zinc oxide, were chosen for the environmental risk assessment. These five substances are either classified as being toxic to the aquatic environment (Aquatic Acute and/or Aquatic Chronic 1) or recognized as PBT or vPvB substances (TABLE 2-2).

Predicted-no-effect-concentrations (PNECs) were collected from the registration dossiers and compared with hazard data from other review reports to the extent available, e.g. EU risk assessment reports and the Danish environmental quality standards for surface water. Generally, the lowest available PNEC values were chosen for this risk assessment. It is noted, that the derivation of PNEC values and applied assessment factors is not always fully transparent from the data provided in the registration dossiers, adding some uncertainty to the used values. With regard to the environmental compartments relevant for this project, PNECs for marine water and marine sediment were selected. In all cases, the values from the registration dossiers were the lowest PNEC-values available and were thus chosen for a conservative approach. The PNECs are displayed in TABLE 5-1. An applicable PNEC value for water for dodecamethylcyclohexasiloxane (D6) was not identified. D6 has a very low solubility of 5.13 µg/L and a high log K_{OW} of 8.87, making the toxicity testing of the test organisms exposed via water difficult. Therefore, PNEC values from aquatic toxicity tests could not be found and no value was thus used in this assessment.

TABLE 5-1 PNEC values for marine water and marine sediment.

PNECs	Octamethylcyclotetrasiloxane D4	Decamethylcyclopentasiloxane D5	Dodecamethylcyclohexasiloxane D6	Alkanes, C14-C17, chlorinated MCCP	Zinc oxide
Marine water [µg/L]	0.15[a]	0.12[b]	-[c]	0.2[d]	3.4[e]
Sediment (marine water) [mg/kg dw]	0.3[a]	1.1[b]	1.35[f]	2.6[d]	49[e]

[a] Retrieved from the ECHA REACH D4 Dossier (accessed 26.10.2023)
[b] Retrieved from the ECHA REACH D5 Dossier (accessed 26.10.2023)
[c] No value identified. In the ECHA REACH D6 Dossier it is stated that there are no effects on aquatic organisms at the limit of solubility of the substance in water. It is noted that the solubility of D6 is very low.
[d] Retrieved from the ECHA REACH MCCP Dossier (accessed 26.10.2023)
[e] Retrieved from the JRC Risk assessment report for zinc metal, and the assumption that zinc will occur as zinc oxide (accessed 23.11.2023)
[f] Retrieved from the ECHA REACH D6 Dossier (accessed 26.10.2023)

5.2 Environmental exposure assessment

5.2.1 Method for the exposure and risk assessment

In alignment with the environmental risk assessment of biocides and according to communication with the Danish EPA, the freely available modelling software MAMPEC (version 3.1.0.5) was used for estimating the environmental exposure in/from a representative European marina (OECD EU marina scenario). For the modelling using the MAMPEC software, different input data was needed, such as environmental scenario data, substance-specific data and emission-related data. The data retrieved and used in this assessment were chosen on a worst-case basis and reflect the worst possible outcome from the exposure of the substances to the environment.

For the scenario data, the pre-set data for the OECD-EU marina was used (see FIGURE 0-1 in Appendix 6). Substance-specific properties such as water solubility, octanol-water partitioning and degradation rates were retrieved from literature (see Appendix 6 for data and sources).

In order to estimate the emission of substance from the coatings, leaching rates were calculated based on information from the suppliers' SDS or TDS of the corresponding coatings and additional information (see Appendix 6 for input data and calculation the leaching rate). Additional information needed to calculate leaching rates were the specific substance concentration in the coating. In line with the worst-case approach, the highest concentration as stated in either the SDS, or quantified during chemical analysis, was chosen as input value. The concentrations of the substances used

were for all, but zinc oxide, derived from the SDS supplied. The concentration of zinc oxide was taken from analysis reports performed during this project.
For the calculation also some assumptions were made for some endpoints to be true for all substances. As such the percentage of substance that is released during the lifetime was set to 90%, in line with corresponding assessments for biocides. The lifetime of the paint was set to 6 months, as the sailing season usually lasts about 6 months, thus being the time frame, in which leaching to the water is possible.
Using these assumptions and substance-specific properties, the leaching rates for the substances were calculated (TABLE 5-2).

TABLE 5-2 Input concentrations and leaching rates calculated from substance and coating-specific properties.

Substance	Octamethylcyclo-tetrasiloxane D4	Demathylcyclo-pentasilocane D5	Dodecamethylcyclo-hexasiloxane D6	Chlorinated par-rafins MCCP	Zinc oxide
Concentration in weight-%	0.3[a]	0.3[b]	1[c]	5[d]	1.16[e]
Leaching rate [µg/(cm² d)]	0.15	0.13	0.94	2.31	0.54

[a] This information was taken from the safety data sheet for the paint obtained from the supplier.
[b] This information was taken from the safety data sheet for the paint obtained from the supplier.
[c] This information was taken from the safety data sheet for the paint obtained from the supplier.
[d] This information was taken from the safety data sheet for the paint obtained from the supplier.
[e] This information was taken from the analysis reports obtained during this project. Calculated based on zinc measurements in 40S self polishing coating (9,380 mg/kg; section 3.4), based on assumption that all zinc occurs as zinc oxide.

The comparably higher leaching rates for D6 and MCCP result from a higher concentration in the coatings, a lower volume solids content and a higher dry film thickness of the coatings in which the substances are present.

In addition to the leaching rates, emission scenarios have to be defined in the software. The emission scenarios are described in the EC (2004) report on environmental emission of antifouling products in OECD countries. Based on the scenario descriptions in this report and in agreement with the Danish EPA, emission scenarios were defined for the sailing season, when the boats are in the water (scenario service life), and during winter, when the boats are taken up from the water for maintenance (scenario paint removal). One difference that was made with regard to the scenarios described in the EC (2004) report was that as a worst-case assumption, the application factor in the service-life scenario was set to 100 instead of 90. This reflects that 100 % of the boats in the marina are using the same paint.

The parameters comprise, amongst others, assumptions about number of boats releasing the substances, size of boat, emission period and amount of coating applied to the boat. All parameters are listed in Appendix 6, Table 0-5 and Table 0-6.

5.2.2 Results of the environmental exposure assessment – PEC values

Environmental exposure, i.e. predicted environmental concentrations (PECs) using MAMPEC was calculated based on the aforementioned data. From the results obtained, average concentrations of harbour water “freely dissolved” was used for comparison with the PNEC values for marine water, and average concentration of harbour water “suspended matter” was used for comparison with PNEC values for sediment, according to the methodology applied for environmental risk assessment of biocides by the Danish EPA. The calculated PECs resulting from emissions from both service life and maintenance are displayed in TABLE 5-3. PECs obtained from the single scenarios of either the service-life or maintenance can be found in the Appendix 6, Table 0-7 and Table 0-9.

TABLE 5-3 PECs obtained from MAMPEC modelling considering a scenario including service life and maintenance.

PEC values	Octamethyl-cyclotetra-siloxane (D4)	Decamethyl-cyclopenta-siloxane (D5)	Dodecame-thylcyclo-hexa-siloxane (D6)	Alkanes, C14-C17, chloro (MCCP)	Zinc oxide (ZnO)
Harbour "freely dissolved" (average concentration) [µg/L]	0.02	0.01	0.05	0.15	0.01
Harbour "suspended matter" (average concentration) [mg/kg dw]	0.01	0.05	1.12	2.53	1.40

5.3 Environmental risk assessment

5.3.1 Environmental risk of SoC in non-biocidal antifouling coatings

A hazard quotient was calculated as the ratio of PEC and PNEC values (PEC/PNEC). The calculated PEC/PNEC are shown in TABLE 5-4. PEC/PNEC ratios obtained from the single scenarios service-life or maintenance can be found in the appendix, in Table 0-8 and Table 0-10.)

TABLE 5-4 PEC/PNEC calculated for the harbour environment as described in chapter 5.1 and 5.2**.**

PEC/PNEC values	Octamethyl-cyclotetra-siloxane (D4)	Decamethyl-cyclopenta-siloxane (D5)	Dodecame-thylcyclo-hexa-siloxane (D6)	Alkanes, C14-C17, chloro (MCCP)	Zinc oxide (ZnO)
Harbour water "freely dissolved" (average concentration)	0.10	0.10	-[a]	0.75	0.004
Harbour "suspended matter" (average concentration)]	0.02	0.05	0.83	0.97	0.03

[a] A value could not be determined, as not PNEC value was available.

Except for one substance (MCCP), all substances show a PEC/PNEC value well below 1 for the average concentrations in the compartment harbour water "freely dissolved", and harbour water "suspended matter". As such the environmental risk from coatings containing the substances D4, D5, D6 and zinc oxide can be regarded as controlled in the specific compartments.

MCCP shows a PEC/PNEC value of 0.72 and 0.97 for the water and sediment compartment, respectively. Both values are relatively close to the threshold of 1, above which an environmental risk is indicated.

The uncertainty related to the results is discussed in section 5.4.

5.3.2 Environmental risk of non-biocidal antifouling coatings

The PEC/PNEC values in TABLE 5-4 above characterize the risk from the single substances potentially present in a coating product. In order to account for simultaneous exposure from several ingredients within one coating product, the BPR guidance (ECHA, 2017c) describes a tiered approach for estimating the risk of product containing several biocides/SoC. The first tier suggests simple addition of PEC/PNEC ratios of the single SoC ingredients present within one product.

Most SDS for foul release coatings list D4 as the only cyclosiloxanes potentially present in the products, however, a single product´s SDS lists all three cyclosiloxanes. The addition of the PEC/PNEC ratios of D4, D5 and D6 can therefore be justified. The $PEC/PNEC_{product\ (D4,\ D5,\ D6)}$ is < 1 for both compartments, therefore no risk is indicated from a product containing all three cyclosiloxanes.

The SDS for one of the self-polishing coatings lists MCCP, additionally, zinc was determined in the chemical analyses in the same product. The addition of the PEC/PNEC ratios of MCCP and zinc oxide can therefore be justified. The $PEC/PNEC_{product\ (MCCP,\ ZnO)}$ is ≤ 1 for both compartments. According to the BPR regulation, no further information for the risk characterisation is necessary, as long as the PEC/PNEC does not exceed 1.[10]

The uncertainty related to the results is discussed in section 5.4.

[10] BPR Regulation No 528/2012, Annex XI e), 66.

5.4 Discussion and conclusion on environmental risk

The risk assessment is based on a methodology developed for biocides and on a worst-case approach. Therefore, the following uncertainties are included within the assessment:

a) Leaching of the substances – The method assumes that the substances actually leach from the coating. However, for the substances assessed, leaching behaviour is not known. Environmental exposure to substances present in self-polishing coatings (e.g. zinc oxide, MCCP) can be assumed, as the functionality of the coating is based on the degradation/depletion of the coatings. Cyclic siloxanes such as D4, D5 and/or D6 may or may not leach out of the coating, depending on the chemistry of the coating (compare section 2.3.1 and 2.3.2).

b) The worst-case approach assumes that all boats within a marina are painted with the same coating, i.e. a specific substance is released from all boats within a marina. This is quite unlikely considering the number of different coatings and their applicability for different use scenarios. Reducing the number of boats releasing a specific substance causes a direct proportional reduction in the level of PEC/PNEC.

c) The worst-case approach also assumes that the entire amount of coating removed during winter maintenance is released into the harbour water. This is an overestimation, as many marinas have (at least some) measures in place to collect particles from high pressure cleaning or dust from sanding. Even if not collected, the environmental release of removed paint will be distributed between the soil compartment, sewage treatment plant and surface water. Data on realistic distribution of releases has not been identified in this assessment.

d) Mixture toxicity, i.e. assessing the combined effects of the substances, has not been included in this assessment. The BPR Guidance on environmental risk assessment mentions some generic options for assessing mixture toxicity. The option of using a component-based approach (CBA) is highlighted in the guidance. This approach requires knowledge about effects, mode of action and toxicity potency of the substances that are to be assessed in combination. A review of these properties has not been possible within the scope of this assessment.

e) PNEC values – most of the applied PNEC values originate from the registration dossiers. Which original studies, effect concentrations and applied assessment factors were used for the PNECs, is in some cases not transparent. In other cases, the use of (too) low assessment factors (e.g. 50 instead of 100) in the calculation of the PNEC based on a NOEC becomes apparent, compared to the European methodology for developing environmental safe exposure levels[11]. Furthermore, the studies have not been subject to independent reliability assessment. Therefore, it cannot be excluded that for some of the PNECs, lower values should be used. This would typically lead to increase of PNEC/PEC values by a factor of two to ten.

f) Secondary poisoning (i.e. effects on biota and/or humans via consumption of contaminated food items) is not included in the risk assessment according to the outlined methodology (the MAMPEC modelling does not estimate biota concentrations).

It is emphasized that point a) – c) generally lead to an overestimation of the risk, while point d) -f) may or may not reveal an underestimation of the risk.

Additionally, it is noted that the PEC/PNEC presented here apply to the water in the harbour. PEC values for the surrounding environment (outside the harbour) were usually one to three magnitudes lower, meaning that PEC/PNEC for the surrounding environment are also one to three magnitudes lower (data not shown). The water inside the marina is chosen as the relevant compartment in line with the approach under the BPR, and taking into account that the water inside the marina a relevant compartment as it is used as nursery by several marine species.

The cyclic siloxanes D4, D5, and D6 as well as zinc oxide all present a PEC/PNEC of ≤0.1 in all compartments, meaning that environmental risks from the coatings containing these substances can be regarded as controlled in these compartments, also under consideration of uncertainty related to the applied PNEC values.

For D4 and D5 in the harbour water freely dissolved compartment, slightly elevated PEC/PNEC between 0.1 and 0.09 were calculated. However, this does not lead to direct concern also considering the potential underestimation of uncertainties, for the following reasons:

- For the PEC/PNEC for water for D4 (PEC/PNEC = 0.1), another PNEC derived from a lower NOEC available from the registration dossier could be used (PNEC = 0.044 µg/L based on a NOEC of ≥ 4.4 µg/L for early-life stage effect on *O. mykiss* and assessment factor of 100) instead of the here applied one of 0.15

[11] The size of assessment factor depends on data availability and reliability of studies as outlined in European Commission, Technical guidance for Deriving Environmental Quality Standards 2018.

µg/L. This would result in a PEC/PNEC of 0.35 for the water in the marina, and thus still presents a controlled risk.

- Cumulative exposure and additive effects of D4, D5 and D6 cannot be excluded. Considering cumulative exposure via suspended matter of D4, D5, and D6 (resulting in a sum $PEC_{D4, D5, D6}$ of 1.2 mg/kg dw) may be assumed. The $PEC_{D4, D5, D6}$, corresponds to (for D5 and D6) or exceeds (for D4) the PNECs for the sediment compartment, which would result in a PEC/PNEC ≥ 1. However, as knowledge about potency, potential synergism and mode of action is lacking, it is not concluded on cumulative exposure in this assessment. Additionally, actual exposures can be anticipated to be lower (see reasoning below)
- Scenarios were designed as worst-case scenarios and a refinement (bullet a)- c) in the above list) would further reduce the PEC/PNEC

The presence of cyclosiloxanes (D4, D5, D6) is documented (either in SDS and/or in target analysis) in five out of the 13 products relevant for the current risk assessment, comprising three different foul release coating as well as two tie coats to be used in combination with the foul release coatings. The cyclosiloxanes occur as impurities in the silicone-based foul release products. It is thus unlikely that the substances may occur at higher concentrations as anticipated in the exposure scenarios calculated here. The chemical analyses of the cyclosiloxanes in the selected foul release paints (results from target analyses presented in Chapter 3.4, sections “38F Foul release coating”, “28F Foul release coating” and “03F Foul release coating”) documented maximum concentrations of ≤0.17% (≤1700 mg/kg) for a single compound, thus being lower than the concentrations provided in the SDS and applied in the exposure modelling (0.3% -1%). It is noted that a proposal for listing D4, D5 and D6 under the POP regulation is under preparation due to their PBT/vPvB properties.

MCCP shows PEC/PNEC values close to 1 (0.72 water, freely dissolved, and 0.97, suspended matter/sediment) in both compartments, thus indicating a potential risk from coatings containing MCCP. Also for MCCP, the assessment was made based on a worst-case scenario regarding the concentrations of the substances in the coatings. MCCP was listed in the SDS of a single product, as ingredient present in concentrations of 1-5% by weight. In the target analysis performed, the substance was not found in the paint (analytical reporting limit 0.1%). According to the laboratory, the presence of MCCP could not be completely ruled out, however, if present at all, a lower concentration could be expected. Using a concentration of 1% MCCP as input for the leaching rate, reduces the PEC/PNEC based on the average concentration PEC in the freely dissolved compartment to a level <0.2 and in the suspended matter compartment to a level of <0.3 (data not shown). Additionally, it is noted, that MCCP was listed in only one of the SDS out of five self-polishing coating product SDS reviewed. The substance is therefore not expected to have essential function for the performance mechanism of the products, and other products of the self-polishing type without MCCP are available. Regarding the uncertainty about the presence of the substance and the lack of applicable data for a refinement of the risk assessment (e.g. realistic number of boats treated with coatings containing MCCP, leaching behaviour of MCCP, disposal of removed coatings containing MCCP), further quantitative refinement of the risk assessment was not performed. It is noted that MCCP is proposed to be listed as a POP under the Stockholm Convention[12] as well as proposed to be restricted under REACH[13], either measure expectedly leading to a ban/restriction of the substance in products such as antifouling coatings.

A limitation of the simple quantitative risk assessment method applied is that it cannot adequately describe the potential risk related to PBT, vPvB and/or endocrine disrupting properties, which are relevant effects for D4, D5, D6 and MCCP.

Overall, the risk from non-biocidal antifouling paints available on the Danish market can be anticipated to be controlled for the harbour water and the sediment compartment based on the risk assessment method applied for the prioritised SoC, i.e. D4, D5, D6, MCCP and zinc oxide. The conclusion for MCCP is supported by a qualitative evaluation of environmental exposure, as quantitative data for a realistic refinement of the exposure scenario are not available. The worst-case quantitative risk assessment leads to PEC/PNEC of almost 1, thus indicating a potential risk. The qualitative evaluation of the uncertainties related to the PEC/PNEC calculation leads to the conclusion that, even if MCCP is present, it is unlikely to occur at concentration posing an environmental risk for the marina environment.

[12] UNEP/POPS/POPRC.17/6

[13] https://echa.europa.eu/de/registry-of-restriction-intentions/-/dislist/details/0b0236e18682f8e1

6. Overall conclusion

An increasing number of antifouling products without biocides are placed on the market as environmentally better alternatives to biocidal antifouling products for protecting pleasure boats against fouling. Even though the non-biocidal coatings may not contain biocides, they may contain other substances with intrinsic hazardous properties both for the human health and the environment. The objective of this study is to clarify whether there are functional, non-biocidal alternatives to biocidal antifouling paints and to gain knowledge about the environmental and health risks associated with the use of non-biocidal antifouling coatings, including whether they can be used without the use of personal protective equipment.

Within the project, 65 coating products marketed as non-biocidal products were reviewed. Functionality of the non-biocidal antifouling coatings depends on the type of antifouling coating as well as on a variety of environmental and use parameters. A general conclusion on the performance of non-biocidal antifouling coatings compared to biocidal coatings is therefore not possible. However, adapted use and mechanical cleaning patterns are recognized as valuable additional tools to improve non-biocidal coating performance.

Of the 65 coating products reviewed, 13 non-biocidal antifouling coatings were evaluated as relevant for the Danish market and for inclusion in the risk assessment. Based on information from the SDS and chemical analyses of selected products, seven substances of concern for human health and five substances of concern for the environment were identified and assessed.

The human health risk assessment focused on consumer uses of the antifouling coatings, i.e. consumers painting their pleasure boats, together with the unintentional exposure of toddlers in contact with the painted boats.

Following the human health risk assessment method on the selected substances of concern (solvent naphtha, ethylbenzene, naphthalene, rosin, octamethylcyclotetrasiloxane (D4), 4-methylpentan-2-one (MIBK) and 4-methylpentan-2-one oxime), it is concluded that five of the 13 antifouling products contain hazardous substances for which the health risks cannot be regarded as controlled. These five paint products were of different types including one self-polishing coatings, two hard coatings, one foul release coating and one tie coat. The two substances causing the potential health risks are 4-methylpentan-2-one (MIBK) and 4-methylpentan-2-one oxime. MIBK, a solvent and a potential carcinogenic substance, is present in four different products. 4-methylpentan-2-one oxime, which most likely is a byproduct from silane crosslinkers and for which limited health data are available, is of concern in one foul release coating.
Placing on the market of products with these types of hazardous profiles should be discouraged for consumer health considerations. Additional refinements of the human health risk assessment with substance specific information and more details about the application conditions for the antifouling paints could potentially improve the assessment. Worth noting is that MIBK may very well be used in biocidal antifouling paints, as the substance is a commonly used solvent in paints.

For the remaining eight out of the 13 selected antifouling products, no risks from consumers exposure were identified in the evaluated exposure scenarios. Comparing health effects of non-biocidal and biocidal antifouling paints was not in the scope of this project. Depending on the hazardous profile of the active biocidal substance, there may be health benefits from replacing a biocidal antifouling paint with a non-biocidal antifouling paint.

The environmental risk assessment considered the risk for the aquatic environment within the harbour, i.e. the water and sediment compartment following the risk assessment method developed for biocides in antifouling products. A limitation of the applied risk assessment method is that it cannot adequately describe the potential risk related to PBT, vPvB and/or endocrine disrupting properties, which are relevant effects for D4, D5, D6 and MCCP.
The environmental risk from non-biocidal antifouling paints available on the Danish market can be anticipated to be controlled for the harbour water and the sediment compartment based on the risk assessment method applied for the prioritised SoC, i.e. D4, D5, D6, MCCP and zinc oxide. For D4, D5, D6 and zinc oxide, PEC/PNEC values were ≤0.1. For MCCP in the harbour water compartment, the applied methodology and worst-case approach leads to PEC/PNEC close to 1, thus indicating a potential risk. Quantitative data for a realistic refinement of the exposure scenario were not available. A qualitative evaluation of the uncertainties related to the PEC/PNEC calculation leads to the conclusion that, even if MCCP is present in any of the coatings, it is unlikely to occur at a concentration posing an environmental risk for the marina environment. Nonetheless, it is noted that D4, D5, D6 and MCCP are recognized as PBT/vPvB substances and the use of products potentially leading to releases of the substance to the environment should be discouraged.

Overall, the survey of non-biocidal antifouling coatings and risk assessment document that non-biocidal antifouling products, which can be regarded as safe for both human health and environment, are available. Health risks related to the use of some non-biocidal antifouling products cannot be excluded. Partly, these risks are a result of use of a solvent that may also be present in biocidal coatings and are therefore not related specifically to non-biocidal antifouling coatings.

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Appendix 1. Lists of H-codes

Table 0-1: Hazard classes and H-codes relating to physical hazards. Taken from Annex I of the CLP Regulation

Explosive	Flam-amable	Aerosols	Oxidising gases	Gas un-der pres-sure	Flammable liquids and solids	Self-reactive substances	Pyrophoric liquids and solids	Self heating sub-stances	Substances and mixtures which in contact with water emit flammable gases	Oxidising liquids and solids	Organic peroxides	Corrosive to metals	Desensitised explosives
H200 H201 H202 H203 H204 H205	H220 H221 H230 H231 H232	H222 H223 H229	H270	H280 H281	H224 H225 H226 H228	H240 H241 H242	H250	H251 H252	H260 H261	H271 H272	H240 H241 H242	H206 H207 H208	H270

Table 0-2: Hazard classes and H-codes relating to health and environmental hazards as well as damage to the ozone layer. Taken from Annex I of the CLP Regulation

Acute toxicity	Skin corro-sion/ irrita-tion	Serious eye damage/eye irritation	Respiratory or skin sen-sitisation	Germ cell mutagenicity	Carcinogenicity	Reproductive toxicity	Specific target or-gan toxicity — sin-gle exposure	Specific target or-gan toxicity — re-peated exposure	Aspiration hazard	Hazardous to the aquatic environment	Hazardous to the ozone layer
H300 H301 H302 H310 H311 H312 H330 H331 H332	H314 (≥1%) H315 (≥10%)	H318 (≥1%) H319 (≥10%)	H334 (≥0.1%) H317 (≥0.1%)	H340 (≥0.1%) H341 (≥1%)	H350 (≥0.1%) H351 (≥1%)	H360 (≥0.3%) H361 (≥3%) H362 (≥0.3%)	H370 (≥1%) H371 (≥10%) H335 (≥20%) H336 (≥20%)	H372 (≥1%) H373 (≥10%)	H304 (≥10%)	H400 H410 H411 H412 H413 (≥25%)	H420 (≥0.1%)

Appendix 2. List of analytes

List of analytes and reporting limits in the target analyses

SoC	Note on method	Substances analysed	Reporting limit [mg/kg]
Zinc oxide	Speciation analyses was not available and total zinc is analysed in the samples.	Zinc	1
Polycyclic aromatic hydrocarbons (PAH)	Detection of light aromatic hydrocarbons depends on the purity of the used solvent naphtha	5-Methylchrysene	0.1
		Acenaphthene	0.1
		Acenaphthylene	0.1
		Anthracene	0.1
		Benzo[a]anthracene	0.1
		Benzo[a]pyrene	0.1
		Benzo[b]fluoranthene	0.1
		Benzo[c]fluorene	0.1
		Benzo[e]pyrene	0.1
		Benzo[g,h,i]perylene	0.1
		Benzo[j]fluoranthene	0.1
		Benzo[k]fluoranthene	0.1
		Chrysene	0.1
		Cyclopenta[c,d]pyrene	0.1
		Dibenz[a,h]anthracene	0.1
		Dibenzo[a,e]pyrene	0.1
		Dibenzo[a,h]pyrene	0.1
		Dibenzo[a,i]pyrene	0.1
		Dibenzo[a,l]pyrene	0.1
		Fluoranthene	0.1
		Fluorene	0.1
		Indeno[1,2,3-c,d]pyrene	0.1
		Naphthalene	0.1
		Phenanthrene	0.1
		Pyrene	0.1
VOC	'Residual solvents' analysed in the dried samples	1,1,1-Trichloroethane	0.1
		1,1,2,2-Tetrachloroethane	0.1
		1,1-Dichloroethane	0.1
		1,1-Dichloroethene	0.1
		1,2,4-Trimethylbenzene	0.1

SoC	Note on method	Substances analysed	Reporting limit [mg/kg]
		1,2-Dibromoethane	1
		1,2-Dichloroethane	0.1
		1,2-Dichloroethylene	0.1
		1,2-Dichloropropane	1
		1,3,5-Trimethylbenzene	0.1
		1,3-Dichloropropylen	1
		1,4-Dioxane	0.1
		1-Butanol	0.1
		1-Propanol	0.1
		2-Butanol	0.1
		2-Butanone	0.1
		2-Propanol	0.1
		3-Chloropropene	1
		3-Methyl-1-butene	1
		4-Ethyltoluene	0.1
		Acetone	0.1
		Benzene	0.1
		Chloroform	0.1
		Cyclohexane	0.1
		Dichloromethane	0.1
		Diethyl ether	0.1
		Butyl acetate	0.1
		Isopropyl acetate	0.1
		Ethanol	1
		Ethyl acetate	0.1
		Ethylbenzene	0.1
		Heptane	0.1
		Hexane	0.1
		Isobutylacetate	0.1
		Methanol	1
		Methylisobutylketon (MIBK)	1
		Pentane	0.1
		Styrene	0.1
		Tetrachloroethene	0.1
		Tetrahydrofurane	0.1
		Toluene	0.1
		Trichlorethene	0.1
		Vinyl chloride	0.1

SoC	Note on method	Substances analysed	Reporting limit [mg/kg]
		Xylene	0.1
		Tert-butyl methyl ether	0.1
Rosin	Analysis of three indicator substances for complex mixture of rosin	7-Oxodehydroabietic acid	1.0
		Abietic acid	1.0
		Dehydroabietic acid	1.0
Siloxanes	Cyclosiloxanes	Hexamethylcyclotrisiloxane (D3)	100
		Octamethylcyclotetrasiloxane (D4)	100
		Decamethylcyclopentasiloxane (D5)	100
		Dodecamethylcyclohexasiloxane (D6)	100
MCCP	Complex mixture of chlorinated paraffins with varying chain length and chlorination degree.	MCCP	1000

Appendix 3. Example ES 2 model with solvent naphtha

General Exposure Calculator For Washing Out Of Brushes (HEEG, The Human Exposure Expert Group (HEEG) opinions, 2010) **The systemic dermal exposure is calculated as follows:**		
Activity and Parameters	**Tier 1** **No gloves**	**Units**
Volume of brush	**200**	**ml**
Volume of paint remaining on brush after painting ($^1/_8$ of 200 ml = 25 ml)	25	ml
Density of paint (Worst case scenario)	**1,50**	**g/ml**
Weight of paint on brush after painting = volume of paint remaining on brush after painting (ml) x density of paint (g/ml)	37,50	g
Concentration of a.s. in paint	**50,00**	**% w/w**
A. Weight of a.s. on brush after painting	18750,0000	mg
B. Residues of a.s. on brush after 1st washing (10% of A)	1875,0000	mg
Amount of a.s. removed from the brush into the cleaning fluid (A-B)	16875,0000	mg
C. Weight of a.s. squeezed out from brush onto cloth (50% of B)	937,5000	mg
Cloth absorbs 90% of a.s. squeezed out of brush therefore, weight of a.s. available to contaminate the hand (10% of C)	93,7500	mg
Penetration of a.s. through gloves (No gloves = penetration 100%)	**100**	**%**
Weight of a.s. on hand	93,75000	mg
Dermal absorption of a.s. (Worst case = 100% absorption)	**100,00**	**%**
Weight of a.s. entering the body	93,75000	mg
D. Weight of a.s. left on the brush after 1st wash and squeezing (B – C)	937,5000	mg
E. Residues of a.s. on brush after 2nd washing (10% of D)	93,7500	mg
Amount of a.s. removed from the brush into the cleaning fluid (D-E)	843,7500	mg
F. Weight of a.s. squeezed out from brush onto cloth (50% of E)	46,8750	mg
Cloth absorbs 90% of a.s. squeezed out of brush therefore, weight of a.s. available to contaminate the hand (10% of F)	4,6875	mg
Penetration of a.s. through gloves	100	%
Weight of a.s. on hand	4,68750	mg
Dermal absorption of a.s.	100,00	%
Weight of a.s. entering the body	4,68750	mg
G. Weight of a.s. left on the brush after 2nd wash and squeezing (**E** – **F**)	46,8750	mg
H. Residues of a.s. on brush after 3rd washing (10% of G)	4,6875	mg
Amount of a.s. removed from the brush into the cleaning fluid (G – H)	42,1875	mg
I. Weight of a.s. squeezed out from a brush onto a cloth (50% of H)	2,3438	mg
Cloth absorbs 90% of a.s. squeezed out of brush therefore, weight of a.s. available to contaminate the hand (10% of I)	0,2344	mg
Penetration of **a.s.** through gloves	100	%
Weight of a.s. on hand	0,23438	mg
Dermal absorption of a.s.	100,00	%
Weight of a.s. entering the body	0,23438	mg
Total weight of a.s. entering the body *(to 4 decimal places)*	**98,6719**	**mg**
Body weight (standard default value)	**60**	**kg**
TOTAL SYSTEMIC DERMAL DOSE OF ACTIVE SUBSTANCE *(to 4 decimal places)*	**1,6445**	**mg a.s./kg bw**

Appendix 4. Example ES 4 wet paint model with solvent naphtha

WET PAINT EXPOSURE – Solvent naphtha

Tier 1 Dermal exposure to wet paint

Parameter	Value	Unit
Amount of a.s per unit treated surface area for wet paint		
Application rate for wet antifouling paint (non-professional) application	0,013	ml paint/cm2
Density of wet paint	1,5	g/ml
Application rate for wet paint	0,0195	mg paint/cm2
Concentration of a.s in wet paint	50%	% w/w
Amount of a.s. per unit treated surface area for wet paint	0,00975	mg a.s./cm2
Amount of a.s. on palms of both hands from contact with removed wet paint		
Transfer coefficient of wet paint from treated surface to hand	50%	
Amount of a.s. per unit treated sufrace area for wet paint - that is transferable from treated surface to the hand	0,004875	mg a.s./cm2
Total area of toddler hands in contact with the removed wet paint - palms of both hands	115,2	cm2
Amount of a.s. on palms of both hands from contact with removed wet paint	0,5616	mg a.s.
Systemic DERMAL exposure to wet paint		
Dermal absorption	100%	
Amount of a.s. absorbed through the skin	0,5616	
Toddler body weight	10	kg
Systemic DERMAL exposure to wet paint	0,05616	mg a.s/kg bw/event

Tier 1 Oral exposure via wet paint from hand-to-mouth transfer

Parameter	Value	Unit
Amount of a.s per unit treated surface area for wet paint		
Application rate for antifouling paint	0,013	ml paint/cm2
Density of wet paint	1,5	g/ml
Application rate for wet paint	0,0195	mg paint/cm2
Concentration of a.s in wet paint	50%	% w/w
Amount of a.s. per unit treated surface area for wet paint	0,00975	mg a.s./cm2
Amount of a.s. on palms of both hands from contact with removed wet paint		
Transfer coefficient of wet paint from treated surface to hand	50%	
Amount of a.s. per unit treated sufrace area for wet paint - that is transferable from treated surface to the hand	0,004875	mg a.s./cm2
Total area of toddler hands in contact with the removed wet paint - palms of both hands	115,2	cm2
Amount of a.s. on palms of both hands from contact with removed wet paint	0,5616	mg a.s.
Systemic ORAL exposure to wet paint		
Transfer fraction of wet paint from hand to mouth (i.e. from two fingers only)	10%	
Amount of a.s. transferrable to the mouth	0,05616	mg a.s.
Oral absorption	100%	
Amount of a.s. ingested	0,05616	mg a.s
Toddler body weight	10	kg
Systemic ORAL exposure to wet paint	0,005616	mg a.s./kg bw/event

Tier 1 Combined systemic exposure from wet paint (DERMAL + ORAL)	0,061776	mg a.s./kg bw/event

Appendix 5. Example ES 2 dry paint model with solvent naphtha

DRY PAINT EXPOSURE – Solvent naphtha

Tier 1 Dermal exposure to dried paint

Parameter	Value	Unit
Amount of a.s per unit treated surface area for dried paint		
Application rate for wet antifouling paint (non-professional) application	0,013	ml paint/cm2
Density of wet paint	1,5	g/ml
Application rate for wet paint	0,0195	mg paint/cm2
Concentration of a.s in dried paint*	0,06%	% w/w
Amount of a.s. per unit treated surface area for dried paint	1,17E-05	mg a.s./cm2
Amount of a.s. on palms of both hands from contact with removed dried paint		
Transfer coefficient of dried paint from treated surface to hand	3%	
Amount of a.s. per unit treated sufrace area for dried paint - that is transferable from treated surface to the hand	3,51E-07	mg a.s./cm2
Total area of toddler hands in contact with the removed dried paint - palms of both hands	46,08	cm2
Amount of a.s. on palms of both hands from contact with removed wet paint	1,62E-05	mg a.s.
Systemic DERMAL exposure to dried paint		
Dermal absorption	100%	
Amount of a.s. absorbed through the skin	1,62E-05	
Toddler body weight	10	kg
Systemic DERMAL exposure to dried paint	1,62E-06	mg a.s/kg bw/event

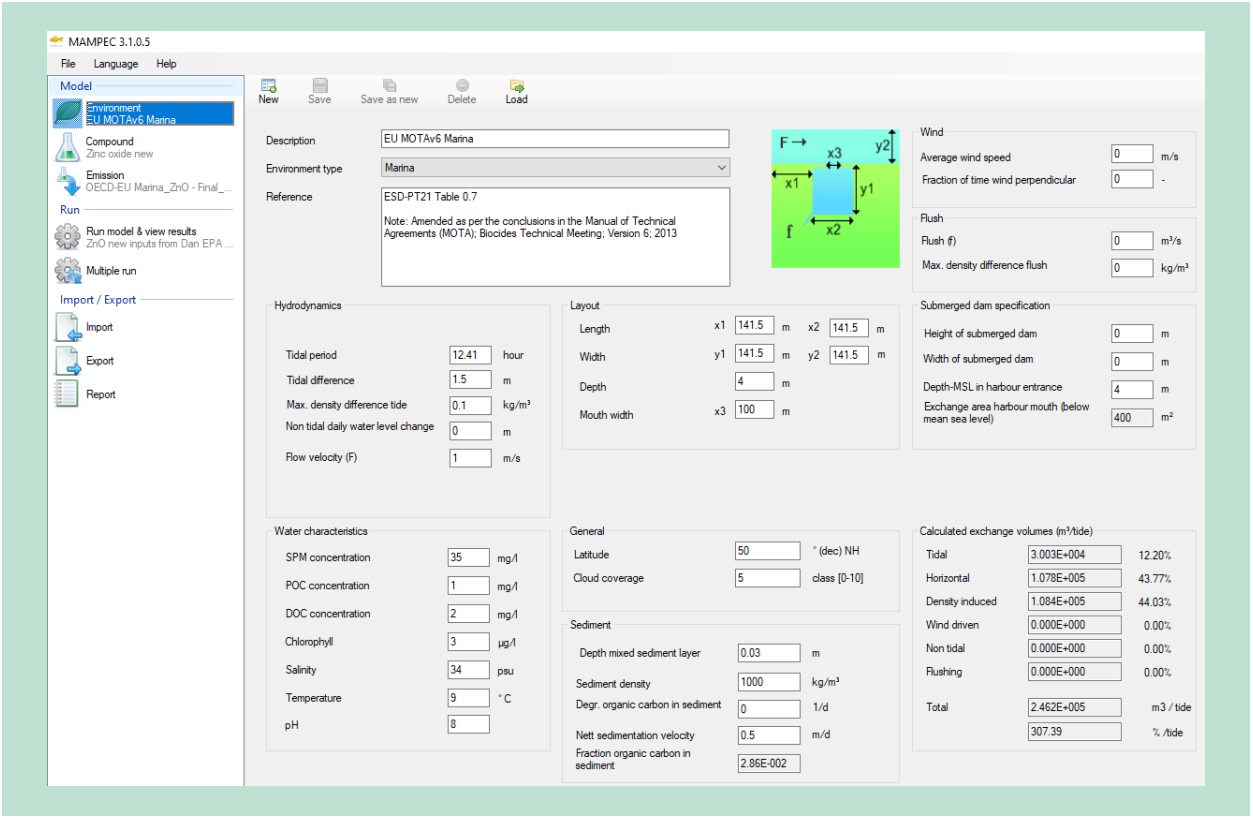
Tier 1 Oral exposure via dried paint from hand-to-mouth transfer

Parameter	Value	Unit
Amount of a.s per unit treated surface area for dried paint		
Application rate for wet antifouling paint (non-professional) application	0,013	ml paint/cm2
Density of wet paint	1,5	g/ml
Application rate for wet paint	0,0195	mg paint/cm2
Concentration of a.s in dried paint	0,06	% w/w
Amount of a.s. per unit treated surface area for dried paint	0,00117	mg a.s./cm2
Amount of a.s. on palms of both hands from contact with removed dried paint		
Transfer coefficient of dried paint from treated surface to hand	3%	
Amount of a.s. per unit treated sufrace area for dried paint - that is transferable from treated surface to the hand	3,51E-05	mg a.s./cm2
Total area of toddler hands in contact with the removed dried paint - palms of both hands	46,08	cm2
Amount of a.s. on palms of both hands from contact with removed wet paint	0,001617	mg a.s.
Systemic ORAL exposure to wet paint		
Transfer fraction of dried paint from hand to mouth	50%	
Amount of a.s. transferrable to the mouth	0,000809	mg a.s.
Oral absorption	100%	
Amount of a.s. ingested	0,000809	mg a.s
Toddler body weight	10	kg
Systemic ORAL exposure to dried paint	8,09E-05	mg a.s./kg bw/event
Tier 1 Combined systemic exposure from wet paint (DERMAL + ORAL)	8,25E-05	mg a.s./kg bw/event

Appendix 6. Input and result data from MAMPEC modelling

Environmental scenario data

FIGURE 0-1 OECD-EU Marina Environmental scenario used for the modelling via MAMPEC



Substance specific data

Table 0-3 Substance specific data needed as input for the "Compound" tab in MAMPEC.

Substance Name		Octamethylcyclotetra-siloxane (D4)	Decamethylcyclopen-tasiloxane (D5)	Dodecamethylcyclo-hexasiloxane (D6)	Alkanes, C14-C17, chlorinated (MMCP)	Zinc oxide (ZnO)[i]
CAS Number		556-67-2[ii]	541-02-6[iii]	540-97-6[iv]	85535-85-9[v]	1314-13-2[vi]
EC Number		209-136-7[ii]	208-764-9[iii]	208-762-8[iv]	287-477-0[v]	215-222-5[vi]
Molecular mass [g/mol]		296.62[ii]	370.78[iii]	444.93[iv]	-[vii]	65.4[vi]
Saturized vapour pressure at 20°C [Pa]		132[ii]	33.2[iii]	5[iv]	0.00027[v]	$1x10^{-10}$[vi]
Solubility at 20°C [g/m³]		0.056[ii]	0.017[iii]	0.0051[iv]	0.027[v]	1.5[vi]
Water degradation half-life [d]	Hydrolysis/abiotic (20°C)	3.9[ii]	77.4[iii]	365[iv]	1000000[v]	-
	Photolysis (20°C)	n.a.	n.a.	n.a.	1000000[v]	-
	Biodegradation (aerobic and anaerobic) (20°C)	n.a.	1200[viii]	1200[viii]	186[v]	-
Sediment degradation half-life [d]	Hydrolysis/abiotic (20°C)	131[ix]	n.a.	n.a.	1000000[v]	-
	Photolysis (20°C)	n.a.	n.a.	n.a.	1000000[v]	-
	Biodegradation (aerobic and anaerobic) (20°C)	n.a.	3100[viii]	3100[viii]	186[v]	-
Octanol-water partition coefficient [10 log K_{ow}]		6.98[ii]	8.02[iii]	8.87[iv]	7[v]	-
Partition coefficient K_{oc} [10 log K_{oc} (L/kg$_{OC}$)]		4.22[ii]	5.2[iii]	5.9[iv]	5.77[v]	-
Henry's constant at 20°C [Pa m³/mol]		1214000[ii]	3340000[iii]	2540000[iv]	51.3[v]	-
Melting temperature [°C]		17.7[ii]	-38[iii]	-3[iv]	0[v]	-
Acid dissociation contant pKa		14[ii]	14[iii]	14[iv]	14[v]	-
Kd [m³/kg]		-	-	-	-	110[x]

n.a. = not available or data could not be found in the literature, data on saturized vapour pressure for the three cyclic siloxanes was obtained at 23°C not 20°C, Henry's constant for the cyclic siloxanes was also obtained at 25°C instead of 20°C.

[i] The amount of needed input data for MAMPEC concerning metals is lower, as such many fields are left empty using "-".

[ii] This data was retrieved from the ECHA REACH D4 Dossier (accessed 26.10.2023).

[iii] This data was retrieved from the ECHA REACH D5 Dossier (accessed 26.10.2023).

[iv] This data was retrieved from the ECHA REACH D6 Dossier (accessed 26.10.2023).

[v] This data was retrieved from the ECHA REACH MCCP Dossier (accessed 26.10.2023).

[vi] This data was set to the sole weight of zinc assuming complete dissociation and other values were set to the values used for modelling/calculations of biocides according to instructions from the Danish EPA.

[vii] A specific molecular weight is not available, as the substance is made up of molecules bearing different masses.

[viii] This data was also retrieved from the corresponding ECHA REACH Dossier of the substances, however the data is not experimental but simulation data from a reliable study.

[ix] This data was taken from the environmental risk assessment report by the environment agency of the UK. "Environmental Risk Assessment Report: Octamethyltetracyclosiloxane", 2009, ISBN: 978-1-84911-031-0

[x] This data was obtained from Zarime et al. 2014, *American Journal of Environmental Sciences 2014,10 (6): 523,529*, "Adsorption of Nickel and Zinc by Residual solids", 10.3844/ajessp.2014.523.529

Emission scenario data and leaching rate

Table 0-4 Input parameters and their sources used for the calculation of the leaching rate

Substance Name	Octamethylcy-clotetrasiloxane (D4)	Decamethylcy-clopentasilox-ane (D5)	Dodecamethyl-cyclohexasilox-ane (D6)	Alkanes, C14-C17, chlorin-ated (MCCP)	Zinc oxide (ZnO)
Percentage of biocide that is released dur-ing lifetime [%]	90[i]				
Mass fraction of bio-cide in biocidal ingre-dient	1[i]				
Lifetime of antifoun-ling paint [months]	6[i]				
Dryfilm thickness [µm]	94[ii]	66[iii]	150[iv]	40[v]	40[v]
Concentration in weight-%	0.3[vi]	0.3[vii]	1[viii]	5[ix]	1.16[x]
Density wet [kg/L]	1[vi]	0.945[vii]	1[viii]	1.57[ix]	1.57[ix]
Amount of VOC [kg/L]	0.05[ii]	0.286[iii]	0.213[iv]	0.517[v]	0.517[v]
Density dry [g/L]	0.95[xi]	0.659[xi]	0.787[xi]	1.053[xi]	1.053[xi]
Volume of solids con-tent (based on weight) [%]	95	69.7	78.7	67.1	67.1
Estimated total mass of biocide release per unit are of paint film over the lifetime of the paint [µg/cm²]	26.72	24.06	171.54	421.16	97.86
Average biocide re-lease rate over the lifetime of the paint = Leaching rate, input MAMPEC [µg/cm²d]	0.15	0.13	0.94	2.31	0.54

[i] These assumptions have been made to be the same for all coatings and are further explained, why they were made in chapter 5.2.
[ii] This information was taken from the product data sheet for the paint obtained from the supplier.
[iii] This information was taken from the product data sheet for the paint obtained from the supplier.
[iv] This information was taken from the product data sheet for the paint obtained from the supplier.
[v] This information was taken from the product data sheet for the paint obtained from the supplier.
[vi] This information was taken from the safety data sheet for the paint obtained from the supplier.
[vii] This information was taken from the safety data sheet for the paint obtained from the supplier.
[viii] This information was taken from the safety data sheet for the paint obtained from the supplier.
[ix] This information was taken from the safety data sheet for the paint obtained from the supplier.

[xi] Dry density was calculated by subtracting the VOC content from the liquid density, neglecting a decrease in volume.

Formulars for calculating leaching rate

$$M_{rel} = \frac{L_a \times a \times W_a \times \rho \times DFT}{VS} \quad (1)$$

$$\overline{R} = \frac{M_{rel}}{\left(\frac{365 \times t}{12}\right)} = 0.0329 \times \frac{M_{rel}}{t} \quad (2)$$

Parameter	*Symbol*	*Unit*
Percentage of biocide that is released from the paint film during the lifetime of the paint	L_a	%
Mass fraction of biocide in the biocidal ingredient	a	-
Content of biocidal ingredient in the paint formulation as manufactured	W_a	% by mass
Density of the paint as manufactured	ρ	Kg dm^{-3} (g cm^{-3})
Dry film thickness specified for the lifetime of the paint	DFT	µm
Volume Solids content (Volume of dry paint film versus volume of pain as manufactured)	VS	% by volume
Lifetime of the antifouling paint	t	Months
Estimated total mass of biocide released per unit area of paint film over the lifetime of the paint	M_{rel}	µg cm^{-2}
Average biocide release rate over the lifetime of the paint = Leaching rate, input MAMPEC	R	µg cm^{-2} d^{-1}

Emissions scenarios:

Table 0-5: Parameters used to simulate the Service life scenario of pleasure crafts.

Category	Value	Comment/Justification
Boat length	0-10 m	As most boats in the harbour are Pleasure crafts that don't exceed this length
Surface area	30.7	This value is based on a report by the European Commission[1], in which it was determined based on surveys and experience
Number of boats	276	This was the number of boats agreed upon with the Danish EPA
Application factor*	100%	In a worst-case scenario, it was assumed, that for all boats the same paint with the same concentration was used

* Most relevant factor that can be changed for a tier 2 exposure assessment.

Table 0-6: Parameters used to simulate the consumer paint removal of pleasure crafts.

Category	Value	Comment/Justification
Removal period	90 days	This value is based on a report by the European Commission[1], in which this was determined form experience and surveys.
No. of ships treated per period	193	According to the report EC 2004[1], for roughly 70% of the ships in the harbour, consumers are annually removing the paint themselves,10% of paint removals are performed professionally and the paint of 20% of boats is not maintained each year.
Fraction of paint removed by high pressure washing (HPW)	1	In EC 2004[1], it is discussed, that HPW usually removes the top coat completely, and as this assessment is focusing on the removal of the top coat only, the fraction removed is set to 1.
Fraction of paint removed by abrasion	-	As described above, only removal of the top layer is considered in this scenario. Further if sanding (abrasion) is done, the model assumes, that it is performed in appropriate places, as such the removed paint cannot enter the sea water directly. As this is a worst case calculation, the parameter was set to 0.
Concentration of active ingredient in the paint	-	No uniform factor was used, as the concentration was depended on the substance used

[1] Harmonisation of Environmental Emission Scenarios: An Emission Scenario Document for Antifouling Products in OECD countries." EC 2004

Fraction of active ingredient remained in exhausted paint by HPW	0.1	As the leeching rate is calculated with a loss of 90% of the active ingredient over the service lifetime, only 10% remain.
Fraction of active ingredient remained in exhausted paint by abrasion	-	As no abrasion is evaluated in this scenario, this factor is irrelevant.
Amount of paint applied per boat	2.5 L	This value was obtained as a rough estimate of paint needed for the average boat surface area considering the average paint thickness. The value is also taken from EC 2004[1].
Fraction to surface water*	1	This value is set to 1 as a worst-case scenario as if all boats are high pressure washed in the close proximity of the harbour leading to all the washing water being released back into the ocean.

* Most relevant factor that can be changed for a tier 2 exposure assessment.

Further, the background concentration used in this assessment was assumed to be 0.

Table 0-7: PEC-values obtained if during the scenario only service life is taken into account disregarding maintenance

PEC values	Octamethylcyclotetrasiloxane (D4)	Decamethylcyclopentasiloxane (D5)	Dodecamethylcyclohexasiloxane (D6)	Alkanes, C14-C17, chloro (MCCP)	Zinc oxide (ZnO)
Harbour water "freely dissolved" (average concentration) [µg/L]	$1.48x10^{-2}$	$1.11x10^{-2}$	$4.82x10^{-2}$	$1.39x10^{-1}$	$1.18x10^{-2}$
Harbour "suspended matter" (average concentration) [mg/kg dw]	$7.0x10^{-3}$	$5.01x10^{-2}$	1.09	2.34	1.29

Table 0-8: PEC/PNEC values obtained if during the scenario only service life is taken into account disregarding maintenance

PEC/PNEC values	Octamethylcyclotetrasiloxane (D4)	Decamethylcyclopentasiloxane (D5)	Dodecamethylcyclohexasiloxane (D6)	Alkanes, C14-C17, chloro (MCCP)	Zinc oxide (ZnO)
Harbour water "freely dissolved" (average concentration)	$9.84x10^{-2}$	$9.22x10^{-2}$	-[i]	$6.98x10^{-1}$	$3.5x10^{-3}$
Harbour "suspended matter" (average concentration)	$2.33x10^{-2}$	$4.55x10^{-2}$	$8.1x10^{-1}$	$9.03x10^{-1}$	$2.65x10^{-2}$

[i] A value could not be determined, as no PNEC value was available

Table 0-9: PEC-values obtained if during the scenario only maintenance is taken into account disregarding service life

PEC values	Octamethylcyclotetrasiloxane (D4)	Decamethylcyclopentasiloxane (D5)	Dodecamethylcyclohexasiloxane (D6)	Alkanes, C14-C17, chloro (MCCP)	Zinc oxide (ZnO)
Harbour water "freely dissolved" (average concentration) [µg/L]	$7x10^{-5}$	$6x10^{-5}$	$1.2x10^{-4}$	$1.09x10^{-3}$	$9x10^{-5}$
Harbour "suspended matter" (average concentration) [mg/kg dw]	$3x10^{-5}$	$2.5x10^{-4}$	$2.67x10^{-3}$	$1.83x10^{-1}$	$1x10^{-1}$

Table 0-10: PEC/PNEC values obtained if during the scenario only maintenance is taken into account disregarding service life

PEC/PNEC values	Octamethylcy-clotetra-siloxane (D4)	Decamethylcy-clopenta-siloxane (D5)	Dodecamethyl-cyclohexa-siloxane (D6)	Alkanes, C14-C17, chloro (MCCP)	Zinc oxide (ZnO)
Harbour water "freely dissolved" (average concentration)	$4.5x10^{-4}$	$4.6x10^{-4}$	-[i]	$5.45x10^{-3}$	$3x10^{-5}$
Harbour "suspended matter" (average concentration)	$1.1x10^{-4}$	$2.3x10^{-4}$	$1.98x10^{-3}$	$7.06x10^{-3}$	$2.1x10^{-4}$

[i] A value could not be determined, as no PNEC value was available

Survey and risk assessment of chemical substances in non-biocidal antifouling paints for private pleasure boats

An increasing number of antifouling products without biocides are placed on the market as environmentally better alternatives to biocidal antifouling products for protecting pleasure boats against fouling. The objective of this study is to clarify whether there are functional, non-biocidal alternatives to biocidal antifouling coatings and to gain knowledge about their environmental and health risks.

65 coatings marketed as biocide-free were identified, and 13 of these were evaluated as relevant for the Danish market. Chemical analyses on selected coatings were performed to obtain additional data about the presence of substances of concern, supplementing the data available for the products' safety data sheets.

The human health risk assessment on consumer uses of the antifouling coatings concluded that five of the 13 assessed non-biocidal antifouling coatings contain hazardous substances for which the health risks cannot be regarded as controlled, while no health risk was identified for the other eight coatings.

The environmental risk assessed for the water and sediment compartment can be anticipated to be controlled based on the simple quantitative risk assessment method and supplemented by a qualitative evaluation of the environmental exposure.

Overall, the study documents that non-biocidal antifouling products are available, and most of them can be regarded as safe for both human health and environment. Health risks related to the use of some non-biocidal anti-fouling products cannot be excluded. Partly, the risks are related to a substance that may also be present in biocidal coatings, making the risk not specific for non-biocidal antifouling coatings.

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