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Danish Technological Institute Gregersensvej 4, DK-2630 Taastrup Building and Construction

In collaboration with

The Danish Consumer Council Aalborg University Henning Larsen

Published August 2024 Authors: Stine Pagaard Haahr, Nanna Rose Mannov Christiansen Leonidas Vourdougiannis, Irene Tosi, Nadja Lynge Lyng

Quality assurance:

Project manager: Nadja Lyng, tel. 7220 1219, nal@teknologisk.dk Approved by: Thomas Witterseh, tel. 7220 2311, twi@teknologisk.dk

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Summary

This report, prepared by the Danish Technological Institute in collaboration with the Danish Consumer Council, Aalborg University, and Henning Larsen, explores the presence and emission of unwanted chemicals in select interior paints available on the Danish market. The study aims to inform consumers about potentially hazardous substances in paints, thereby enabling them to make safer choices and advocating for the phase-out of harmful chemicals. The study was funded by the philanthropic association Realdania and the Homeowners Investments foundation (Grundejernes Investeringsfond, GI).

The key findings from the study reveal significant concerns regarding the content of biocides and preservatives. Benzothiazolinone (BIT) was detected in over half of the paint samples, with concentrations reaching up to 360 mg/kg. Methylisothiazolinone (MIT) was found in 50% of the samples but at lower concentrations (< 5 mg/kg). Formaldehyde, known for its potential health risks, was present in 11 out of 30 samples, though in low concentrations. The analysis of Total Organic Fluorine (TOF) indicated that organic fluorine was detected in 22 samples generally below the suggested EU restriction limit, with two samples exceeding 300 mg/kg. However, specific PFAS analysis on these two samples with the highest concentrations did not detect any of the 50 specific PFAS compounds analyzed for.

The presence of heavy metals in the paints showed significant variations. Lead, chromium, and zinc were detected in various samples, with some samples the levels of zinc exceeding limits for clean waste. Volatile Organic Compounds (VOCs) emissions were initially higher in plastic paints, though they decreased over time. Notably, two organic solvent-based paints exhibited exceptionally high initial emissions. Ammonia was found in 2/3 of the samples and in 8 samples concentrations was above 400 µg/m³. The odour evaluation indicated that wall paints generally received better ratings than wood/metal paints.

Emission testing revealed that VOC emissions decreased over time, but the initial emissions from some paints could pose acute health risks, particularly affecting respiratory health and potentially causing skin irritation. In three field measurements, 139 different chemical compounds were detected in the indoor air in newly painted rooms. VOC levels generally peaked on painting days, especially for acrylic paints, and generally declined to near-background levels within three days. In contrast, paint containing linseed oil exhibited a slower reduction, taking 14-30 days to reach background levels.

The health implications of these findings are significant. The initial emissions of VOCs, and ammonia from some paints can pose acute health risks, particularly affecting respiratory health and po-

tentially causing skin irritation or sensitization. Long-term exposure to VOCs can contribute to various health issues. It is crucial to emphasize increased ventilation during and after painting to minimize exposure. Environmental implications include the risk of soil and water contamination from improper disposal of paints containing harmful metals. This underscores the need for sustainable paint manufacturing and proper disposal practices within the paint industry.

The study recommends that consumers select paints with lower or no harmful chemicals, guided by reliable labelling and certification schemes. Manufacturers are encouraged to produce paints free of heavy metals and BIT, and with lower initial VOC emissions to reduce health risks and environmental impact. The overall findings emphasize the importance of understanding the specific chemical emissions associated with different paint types and the environmental conditions that influence these emissions. By choosing safer paints, ensuring proper ventilation, and avoiding newly painted rooms for the first 2-3 days, consumers can significantly reduce health risks and contribute to a healthier indoor environment.

Contents

Abbreviations

- SVOC Semi-volatile organic compound, boiling point> 287°C (n-hexadecane C16)
- TVOC Sum of volatile organic compounds (C6-C16) as toluene equivalents
- VOC Volatile organic compound, boiling point 68–287°C (C6-C16)
- VVOC Very volatile organic compound, boiling point < 68°C (n-hexane C6)
- PCB Poly-chlorinated biphenyls
- GC-MS Gas chromatography–mass spectrometry
- HPLC High-performance liquid chromatography
- CIC Combustion Ion Chromatography

1. Introduction

1.1. Purpose

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The purpose of this project is to investigate the differences between interior paints on the Danish market, bring the unwanted chemicals to light, and give consumers the option to avoid unwanted chemicals.

What we want to obtain with this project:

- We want to give consumers an informed choice it must be easy to choose paint without unwanted chemicals.
- Focus on the unwanted chemicals in paints with the purpose to phase out these chemicals in consumer products.

1.2. Scope

In the project, both indoor wall paint and wood/metal paint were examined.

The project focuses on covering the Danish market widely, including both industrially developed and produced paints and natural paints. Paints covered by various labelling schemes, such as the Nordic Swan Ecolabel and the Danish Indoor Climate Label, will be included.

Other types of paint like outdoor, structure, wet room paints are excluded. This project and this investigation involve test of chemicals in liquid as well as solid paint and emissions from paints. This project does not investigate other technical properties like durability of the paint.

Field measurements was preformed to present indoor air quality scenarios illustrating the potential exposure to chemical substances that may arise in typical households during realistic painting activities and in the time after.

2. Background

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2.1. History of paints

Paints are today widely used for several different purposes such as maintenance, conservation and beautification. Paints and colours have been used for decorative purposes for thousands of years. All the way back to stone age cave paintings early humans in South Africa (100.000 BCE) used natural pigments such as red iron oxide and charcoal as main ingredients mixed with bone marrow as a binder to create paint. Cave paintings from around 30,000 BCE used ochre, hematite, manganese oxide, and charcoal as natural pigments. These early paints were made by grinding minerals and mixing them with water, animal fat, or other binders.

In ancient Egypt (3,000 BCE) a variety of natural pigments, including red ochre, yellow ochre, and malachite (green) and azurite was used. They also developed synthetic pigments like Egyptian blue. Complex paint was produced using binders like egg yolk and gum Arabic.

Greeks and Romans (500 BCE-500 CE) advanced paint-making techniques, using natural pigments for frescoes and murals. They developed lime-based paints and created durable, decorative coatings. These early vanishes started the development towards the modern paints found on the market today.

During the renaissance (1400 - 1600 CE) oil paints were invented, using linseed or other drying oils as binders. The development allowed for greater detail and realism in art. Advances in chemistry led to the creation of synthetic pigments, expanding the artistic palette.

During the industrial revolution (1700s - 1800s) paints started to be manufactured on a larger scale. New synthetic pigments and binders were developed, leading to greater availability and variety. Lead-based paints became popular for their durability and vibrant colours, though their health risks were not yet understood.

In the 20th Century the development of synthetic paints like acrylic, latex, and alkyd paints revolutionized the industry, offering improved durability and a wider range of colours.

Due to environmental and health concern, the industry altered the chemistry of its products to control risks. Paint manufacturers started replacing lead pigments in some paints before World War II when safer alternatives became available.

In the 1970, increased awareness of the risk of brain damage promoted a change in the composition from paint with white spirit, a petroleum-derived solvent to water soluble paints. By late 1980s 90% of paint used for buildings in Denmark were water soluble. The change was assisted by technological advances and imposed by the information campaigns of the trade unions, and the regulation by the Danish Working Environment Authority (Hansen et al., 1987).

Increased awareness during the last decades have led to the development of so-called eco-friendly and low level volatile organic compound (VOC) paints. Regulations have been established to reduce environmental impacts.

2.2. Legislation

In addition to labelling schemes, there is a comprehensive legislative framework in Denmark for interior paints to protect human health and the environment. It is regulated and influenced by EU regulations such as REACH Regulation (EC) No 1907/2006, CLP Regulation (EC) No 1272/2008, and the VOC Directive (2004/42/EC), and it is enforced by national bodies like the Danish EPA. Compliance with these regulations ensures that paint products are safe and environmentally friendly.

REACH (Registration, Evaluation, Authorisation, and Restriction of Chemicals) regulation is a European Union regulation of production and use of chemical substances, including those used in paints. Reach applies to all EU member states, including Denmark. Manufacturers and importers must register the substances they produce or bring into the EU. The European Chemicals Agency (ECHA) evaluates the information provided by companies. Substances of very high concern (SVHC) may require authorisation, and certain hazardous substances are restricted.

The CLP (Classification, Labelling and Packaging) Regulation aligns the EU system of classification, labelling, and packaging of chemical substances and mixtures to the Globally Harmonised System (GHS). This ensures that consumers are informed about the hazards associated with chemicals in paints.

The VOC Directive aims to limit emissions of volatile organic compounds (VOCs) due to the use of organic solvents in certain paints and varnishes. The amount of VOCs (g/L) allowed in paints and varnishes is limited. The VOC content label provides information on the volatile organic compounds in the paint, for which it is recommended to choose the lowest possible VOC content (0 g/l). A VOC limit depends on the type of product. There are different limits for deferent types of paints, the use and gloss. The limit is lowest for low-gloss wall paint, while there are higher limits for e.g. high-gloss wall paint and wood paint (Danish Ministry of Environment, 2015).

In Denmark paint pots are beside being labelled with the VOC content also labelled with a MAL code, which is intended to inform professional users/consumers about the health risks of using the paint. The MAL code consists of two numbers (x-x) describing the risks associated with inhalation and skin contact with paint, respectively (Knudsen & Kirkeby, 2023). The higher the first number, the greater the need for ventilation and use of personal protective equipment. The number ranges from 00- to 5-, where 00- is the safest. The higher the last number, the greater the need for skin contact protection. Here the number range from -1 to -6, where -1 is best. In the working environment, there are requirements for personal protection equipment depending on the MAL code.

2.3. Labelling schemes

Several labelling schemes assess and document the properties of products in relation to indoor air and the environment [\(Table 2-1\)](#page-11-0). The purpose of the labels is to assist the consumer in making informed decisions and create awareness about the environmental and health impact of products and buildings. Several paint manufacturers therefore products certified/labelled with one or more of these labels. It is worth noting that even if a product is labelled with indoor climate labels, this does not mean that the product neither contains nor emit chemical substances. It simply means that they comply with the applicable criteria set for the indoor climate label in question.

Certifications that focus on reducing volatile organic compounds (VOCs) and improving indoor air quality are crucial for health in enclosed spaces. [Table 2-1](#page-11-0) below gives an overview of the different labelling schemes relevant to the Danish and European marked, their respective assessment strategy and focus as well as subject focus e.g. building or product.

The French mandatory emission label **"Emissions dans l'air intérieur"** covers building products, including paints, and rates VOC emissions from A+ for very low emissions to C for high emissions, guiding consumers toward healthier indoor environments. **"GreenGuard"** is an international US label certifying products like paints that emit low levels of chemicals and VOCs, contributing to healthier indoor environments in line with sustainable building practices. **"Indoor Air Comfort"**, managed by Eurofins, ensures that products such as paints meet criteria for low VOC emissions and are free from other harmful substances, thus enhancing indoor air quality. The Finish **"M1 Emission label"** certifies building materials, including paints, for low VOC emissions, promoting healthier air quality and suitability for sensitive environments. Lastly, "**Danish Indoor Climate Labelling**" a Danish label, highlights low emission levels from products like paints to enhance the indoor air quality and health in living and workspace areas.

Table 2-1: List of ecolabels

Across various European countries, environmental and health standards are being upheld by several recognized labels. Germany's **"Der Blaue Engel"** (The Blue Angel) serves as an eco-label for products and services, including paints, which signifies low emissions, a reduced environmental impact, and better indoor air quality. The **"EU Ecolabel"** certifies European products such as paints that avoid or restrict certain hazardous substances and minimize environmental impact. Meanwhile, the **" Nordic Swan Ecolabel"** (Svanemærket) is prominent in the Nordic countries for recognizing products, including paints, that adhere to strict environmental and health criteria. Products with this label contain low levels of certain harmful chemicals and VOCs, which according to the label promotes sustainable living and healthier indoor environments.

There are also certifications with a specialized focus on certain types of products or materials, extending to include paints. The German **"AgBB"** is an evaluation system that looks at the healthrelated impacts of VOC emissions from building products, ensuring their safety for indoor air quality. In Sweden, **"SundaHus"** evaluates building materials such as paints for their environmental and health impacts, providing guidance for selecting environmentally friendly and health-conscious paints.

Asthma Allergy Nordic is an allergy certification from Astma-Allergi Danmark and the two equivalent associations in Norway and Sweden, that ensures products minimize the risk of allergic reactions. It signifies that the paint is free from common allergens like the preservative MI and other unwanted substances. It also restricts emissions of VOC.

2.4. Literature screening of possible chemical compounds in paints

As a foundation for the present study, a review of literature about chemistry of interior paint, with focus on possible hazardous components and emissions from paints in indoor environments. For the literature search various databases were used, including Elsevier-Science Direct, Google Scholar, SpringerLink, SciVerse Scopus and Indoor air (Wiley).

The increasing incidence of asthma, respiratory problems and sick building syndrome (SBS) has led to great attention for the air quality in indoor environments and many studies have been carried out on the emissions from building materials and their effect on health (Mai et al., 2024a; Norbäck et al., 2021; Ruiz-Jimenez et al., 2022; Saraga et al., 2023; Tao et al., 2022; Xu et al., 2022).

The literature review found that the focus on health and hazardous chemicals in paints increased throughout the 20th century. For example, the literature highlighted the issue of widespread use of Polychlorinated biphenyls (PCBs) in exterior paints, until the ban in the 1970s (Jartun et al., 2009). Similarly, the literature also shed light on the issue of lead in paints, which was widely used until the ban in 2001 (O'Connor et al., 2018). In Denmark the use of lead in paint was banned in 1950.

Thus, the study was extended in the search of chemicals in paint known for their hazardous properties on human health. The use of isothiazolinones and other preservatives, parabens, heavy metals, phthalates, chlorinated paraffines, PFAS and polycyclic aromatic hydrocarbons (PAHs) in paints was explored.

Section 2.5.1 explains the chemistry of paints and coatings, describing the components of the paint and their functions. *Section 2.5.2* gives an overview of the chemicals found in paints, both as components in the liquid phase and as emission from the dry matter during service-life, that may represent a hazard for human health. The chemicals are grouped based on their function in the paint.

2.4.1. Paint components

Paints are heterogeneous materials composed by a suspension of fine particles, like pigments and fillers, in a liquid matrix which is the binder. They are applied as viscous liquids, and they create a solid film after drying. Their primary functions are decorative and protective of the substrate material (IARC Working Group on the Evaluation of Carcinogenic Risks to Humans. Meeting (2008- 2009 : Lyon et al., 2012).

Binders

The binders are the polymeric matrix responsible for the film formation, like resins or drying oils. The physical, aesthetical, and mechanical properties of the paint, such as hardness, resistance to scratches, deformation, and indentation, gloss, flexibility, and others, are strictly connected to the type of binder used. Binders are the largest components of paints, normally constituting between 20% and 60% in weight (IARC Working Group on the Evaluation of Carcinogenic Risks to Humans. Meeting (2008-2009 : Lyon et al., 2012).

Binders can be derived from natural sources: natural resins like colophony, copal, dammar and shellac, or oils, like linseed oil, tung oil, fish oils, soya bean oil, sunflower oil, castor oil and coconut oil. However, natural binders are not common in modern paints due to the large amount of available synthetic resins. Polyesters, acrylates, alkyd, phenolic, melamine, epoxy, polycarboxylic anhydrides, polyurethanes, silicates, polyvinyl acetals, polyamides are some of the most common resins used as paint binders. The mechanisms of film forming can be different depending on the chemistry of the binder; generally, it involves the polymerization reaction and cross-linking creating hard polymers (Brock et al., 2010)

Pigments and fillers

Pigments and fillers are organic or inorganic solid fine particles, usually constituting between 3% and 60% in weight to provide colour and opacity, but also to control viscosity, rheology, and other physical and chemical characteristics.

Only inorganic compounds are used as white pigments, like oxides (TiO₂, ZnO, SnO₂), carbonates (PbCO₃, ZnCO₃) and sulphates (PbSO₄). In the past, lead white was a common white pigment, now, it is replaced due to its health hazard. Titanium dioxide is the most common white pigment due to its excellent covering and whitening power, chemical inertness, and somewhat lower toxicity. TiO₂ can be produced by two synthetic industrial processes: by sulphate process and by chloride process (Brock et al., 2010). Hannah et al. (2022) have identified PCB contamination of the pigment derived from the latter synthetic method. The most common black pigments used are carbon black and iron oxide.

Colour pigments can be organic and inorganic. Pigments derived from heavy metal, have been largely used in the past, but now, they are now replaced due to their hazardous properties. Examples are cadmium pigments and lead chromates for the shades of yellow, orange and red.

Organic pigments can be classified in three categories: azo pigments for yellow and red, polycyclic pigments covering many compounds like the yellow/red diketo-pyrrolo-pyrrole and the violet dioxazine, and metal complex pigments for green and blue copper phthalocyanine.

Paints also contain inorganic fillers that determine some of the final characteristics of the coating, like resistance, adhesion, gloss, viscosity, abrasion resistance and others. Common fillers are carbonates like chalk and calcite, silicon dioxide, silicates like talc, and sulphates. Nanoparticles have also been added to give special properties, for example, $TiO₂$ nanoparticles have been used for the preparation of photocatalytic paints (Larsen et al., 2010). In the early twentieth century, asbestos was also used as a filler for paints, now its use is banned.

Solvents

Solvents are added to control the viscosity of the liquid paint and, thus, allow for a proper application. Organic solvents have been largely used in solvent borne paints due to their high volatility and solubilization power. The type of solvent is strictly connected to the chemistry of the binder in use that needs to be solubilized. Common organic solvents used in paints are hydrocarbons like spirits and turpentine, aromatic hydrocarbons like toluene and xylene, ketones like methyl ethyl ketone (MEK), alcohols and ethylene and propylene glycol ethers. During the 1990s, the awareness of the negative impact of organic solvents on health increased and water-based paints started to substitute solvent-based ones (Spurgeon, 2006). Water soluble coatings use water as solvent; however, they also contain an organic co-solvent, in amounts between 0.1% to 15% to help the solubilization (Brock et al., 2010).

Additives

Additives are chemicals added in low concentrations (normally between 0.1% and 5% in weight) to give specific properties to the coating. Additives are classified by the properties that are modified. The most common are listed below.

Surfactants and dispersing additives – Surfactants are added to paints for many reasons, as dispersants, defoaming agents, emulsifiers for aqueous formulations, wetting chemicals. They form a large class of compounds, including polyphosphates, polysiloxanes, polycarboxylic acids, PFAS and others. Surface-active additives are also used to avoid the formation of surface defects like cratering and to control flow, wetting and levelling.

Driers – Siccative metal salts, cobalt-based are the most common, but also manganese, zirconium and calcium salts are in use.

Rheological additives – Ensure good flowing properties for the application of the paint (but also during production and storage), such as viscosity, sagging and sedimentation. They can be hydrophilic colloids, such as gum arabic, starch, derivatives of cellulose, clays, but they can also be organic compounds like polyurethane derivatives and polyacrylates (Rheology Modifiers Selection for Paints & Coatings, n.d.).

Plasticizers – Increase the elasticity of the coating. Phthalates, but also others like citrates, adipates, carboxylates, sulfonic esters (Plasticizers in Paint & Coatings: Uses, Types and Selection Process, n.d.).

Preservatives – All paints contain in-can preservatives that ensure an adequate shelf-life of the product. They can also contain film preservatives (especially for outdoor applications), to preserve the coating from microbiological deterioration after application (Biocides for Paint & Coatings: Main Types and Selection Criteria, n.d.).

2.4.2. Hazardous components and emissions from paints

In the literature review initially 145 journal papers were found relevant to this project. From the literature the following compounds and chemical groups were identified to be of relevance. At the end of this section an overview of the compounds and chemical groups is listed in table 2-2.

Preservatives in paints

Isothiazolinones and formaldehyde releasers

Paints contain preservatives to ensure durability before and after application. The EU Biocidal Products Regulation (BPR) defines different types of preservatives used for the different product types (PT): PT6 refers to in-can preservatives that ensure an adequate shelf-life while PT7 refers to film preservatives (after application), both types are common biocides used in indoor and outdoor paint formulations European Commission (2012). PT6 biocides are included in all types of paint, but they are mostly needed in water-based formulations. The most common PT6 for paints are

isothiazolinones (Methylisothiazolinone (MIT), Benzothiazolinone (BIT), 5-chloro-2-methyl-4-isothiazolin-3-one (CMIT), 2-octyl-4-isothiazolin-3-one (OIT))**.** Isothiazolinones are found to be skin sensitizers, and they are suspected to induce allergies. A second group of common preservatives used in paints are the formaldehyde releasers (triazines). Formaldehyde releasers act by slowly releasing formaldehyde, which is a carcinogenic gas; These substances should release a low amount of formaldehyde, suppressing biological growth without harming humans (CEPE, 2014; Dutch Ministry of Infrastructure and Water Management, 2021; Karamahmut Mermer et al., 2023)

Most common preservatives used in paints:

- 1- Isothiazolinones MIT, BIT, CMIT/MIT, OIT; very common in-can preservatives
- 2- Formaldehyde releasers Triazines and urea-based compounds Quaternium-15, EDDM (ethylenedioxy)dimethanol), and TMAD (Tetramethylolacetylenediurea). Urea are also known to be able to emit ammonia.

Other preservatives in paints

In addition to isothiazolinones and formaldehyde releasers, many substances have been used in paints as preservatives. Many of them have harmful effects on human health and the BPR is constantly reviewing their use. While some types of preservatives (PT7) are mainly common in outdoor applications, in-can preservatives are ubiquitous, and they are important components for ensuring durability, mainly of water-based paints. A complete list of the approved substances for in-can preservation is presented in the ECHA website under the product type 6 list (ECHA, 2024a).

The list of possible substances used as preservatives is long. Below, some substances that have been used in the past and/or are currently used as preservatives are listed. The list includes PT6 and PT7 preservatives, used in both indoor and outdoor applications.

- ZnO (zinc oxide) is added to prevent fungal growth used mainly for exterior applications, but also as in-can preservative in combination with others - use is allowed (European Commission, n.d.)
- Metals nanoparticles, like nanosilver, nanotitanium dioxide, nanocopper used outdoor for protection against microorganisms and UV light (Kaiser et al., 2013).
- DTBMA (2,2'-dithiobis[N-methylbenzamide]) use is restricted (ECHA, 2024b)
- Organosulfur and pyrithione derivatives ZNPT (zinc pyrithione) used as in-can preservatives in both indoor and outdoor paints – the maximum content is limited, but it is still allowed (ECHA, 2024b)
- Halogen- based compounds BNPD (bronopol) used as in-can preservatives, both indoor and outdoor paints, still allowed (ECHA, 2024b)
- CTL (Chlorothalonil) used mainly in outdoor applications, still allowed (ECHA, 2024b)
- Carbamates IPBC (iodo-propylbutyl-carbamate) mainly for outdoor paints but also used as in-can preservation, still allowed (ECHA, 2024b)
- Benzimidazoles TBZ (Thiabendazole) restricted

- BCM (Carbendazim) used for outdoor paint, still allowed (ECHA, 2024b)
- Azoles- PPZ (Propiconazole) used for outdoor paint, still allowed (Biocides for Paint & Coatings: Main Types and Selection Criteria, n.d.; ECHA, 2024b)

Parabens

Parabens are used as bactericidal and fungicidal in personal care products, food and pharmaceutical products and their presence raised concerns because they are endocrine disruptive compounds. Methyl and propyl parabens have been found also in household commodities like waterbased paints, as indicated in the study of Eriksson et al. (2008). In this study, only a limited amount of information is available because parabens are usually not used in paints, varnish and lacquers and parabens were found in only 1 sample out of 142. Use of parabens is still allowed (ECHA, 2024b).

High pH paints

The main biocide-free alternative paint technologies at the moment (used in white wall paints) are high pH formulations. However, pH is often not stable during the shelf-life and the paints tend to lose the antimicrobial properties. Not applicable to all types of paints (Dutch Ministry of Infrastructure and Water Management, 2021).

Heavy metals and PAHs in paints

Lead has been added to paints for long time as a preservative, however, its use has been phased out due to health concerns (Teknologisk Institut, 2024). In 2018, O'Connor et al. published a review about the use, production, and regulations of lead-based paints around the world. At that time, developing countries like China and India were still commercializing lead-based paints.

Oriji at al. (2012) measured the content of PAHs and heavy metals in water-based paints commercially available in Nigeria from two different suppliers, finding the presence of anthrancene, fluorene, phenanthrene, fluoranthene, pyrene, acenaphthene, arsenic (0.79 mg/kg), zinc (1.54 mg/kg), mercury (<0.001 mg/kg). Heavy metals were determined to be within tolerable concentrations.

Plasticizers

Phthalates

Phthalates are used in water-based paints for architectural applications and can be released from the dry matter because they are not chemically linked into the structure. Orecchio et al. (2014) measured the content of phthalates in different paintc from buildings in Palermo. They found high concentration in buildings painted 50 years ago; bis(2-ethylhexyl) phthalate, diisobutyl phthalate, di-n-butyl phthalate and diethyl phthalate were the only compounds detected in high concentrations. Phthalates with higher molecular weights, such as bis(2-ethylhexyl) phthalate, are largely used as additives, softeners and plasticizers. They may be leached into the environment and are ubiquitously found in dust, air, water, soil, and sediments. Excluding the dimethyl phthalate (DMP),

which belong to the group of VOCs, PAEs are classified as semi-volatile organic compounds (SVOCs).

The same authors (Barreca et al., 2014) studied the photodegradation by UV light of common phthalates utilized as softener (Di-n-butyl phthalate (DBP) and Bis(2-ethylhexyl) phthalate (DEHP)) and their health effects when found in dust paint from old buildings.

In 2009, Silva et al. developed a method for stabilizing the phthalates used as plasticizers (diethylphthalate (DEP) and dibutylphthalate (DBP)) over ageing and reducing their migration over time. Phthalates are not common components of all paints. They are added to latex paints (water-based) as plasticizers. Apanpa-Qasim (2020) analyzed the concentration of Dibuthyl phthalate (DBP) in paints and studied the increased contamination of phthalates in paints, and the effect on health.

EU Public health identify two specific phthalates used in paints: Di-Isononyl Phthalate (DINP) used in paints and lacquers and Di-Isodecyl-Phthalate (DIDP) used in anti-corrosion and anti-fouling paints (DG Health, 2024).

Chlorinated paraffins

Chlorinated paraffins (CPs) are used as additives in paint for improving the resistance to chemicals and water. They are found in applications, such as marine, road and industrial. They are added also for their fire-retardancy properties in architectural paints.

Medium-chain (C14-C17) CPs are used as plasticizers in paints, their content is normally 1-5% by weight. Used in highly resistant paint applications and fire-resistant paint for wood. Only used in solvent-borne paint. Short-chain (C10-C13) CPs are used in acrylic protective paints (also decorative paints for interior and exterior applications) and intumescent coatings. They have the function of plasticizers, but they are less expensive than phthalates. The content was in 2014 considered to be between 5-20% of the dry weight (Danish Ministry of Environment, 2014).

CPs are also ingredients for fire-retardant coatings, important for many applications, such as architecture and wood. Ducrocq et al. (2006) studied the mechanism of CPs in order to present possibilities for their replacement with more environmentally friendly components. Ai et al. (2022) studied the contamination of soil and air by CPs in contaminated areas in China. They found their presence in the highest concentrations in samples near shipyards due to the presence of CPs in marine paints. Light short-chain CPs are volatile and exists in air, while heavier medium-chain CPs tend to deposit in the soil.

PCB

Polychlorinated biphenyls (PCB) have been largely used in the past as plasticizers for different materials and ingredients for paints. They have been phased out in the '70ies (PCB-guiden.dk, 2024).

Jartun et al. (2009) studied the contribution from paints, due to degradation of outdoor paints especially used in buildings from 1950-1970. They found that regular exterior paint may constitute a

key contemporary source of PCBs to the urban concentrations of polychlorinated biphenyl (PCB). Anezaki et al. (2015) studied the presence of PCB in commercially available paints. These compounds are found in paints as organic pigments: polycyclic containing dioxazine violet, diketopyrrolopyrrole and red dichloroaniline, these are often contaminated with PCB during their synthesis.

PCB can be found as contaminants derived from the synthesis of organic pigments. For a long time, azo-pigments and phthalocyanine were considered the main sources of PCBs in dyes and PCB 11 and PCB 209 were considered the only ones found in paints (Hu & Hornbuckle, 2010; Rodenburg et al., 2015). More recently, Hannah et al. (2022) identified PCB 149 as contaminants of paints and their mechanism of formation from azo-pigments (most common yellow, red and orange), dioxazine (violet), phthalocyanine blue and green, diketopyrrolo pyrrole (yellow and red). PCBs were found also as contaminants of titanium dioxide, one of the most common white pigments, however, the mechanism of formation was not identified, but probably connected to the synthesis via carbochlorination. PCB 206, 208 and 209 were identified as the most common contaminants of TiO₂.

Other additives

PFAS in coatings

Polyfluoroalkyl polymers have been used in different types of coatings and paints, such as powder coatings, radiation curable coatings, anti-reflective, cable and wiring coatings, and coatings for solar panels. Fluoropolymers used as binders in paints give particular properties such as durability, weatherability, resistance to corrosion, barrier to UV and dirt. For this, they have been used mainly in outdoor architectural paints for bridges and steel works.

Fluoro-substances can also be added to the paints as additives known as fluoro-surfactants for improving wettability, water repellence and dirt pick-up resistance. This group include C4 polyethers, such as methyl nonafluorobutyl ether and methyl nonafluoroisobutyl ether, and C6 substances like hexafor. These substances are also added in varnish for wood (and other materials) to give stain resistance properties (OECD, 2023).

These compounds are present also in paints for household applications, where adhesion and antiblock properties are important. PolyFox ™ and Capstone® are substances used with this purpose.

Coatings containing PTFE (polytetrafluoroethylene) or PVDF (polyvinylidene di fluoride) in aqueous dispersion have been used for protection of different types of materials (T Gaines & Linda T Gaines, 2023).

PFAS were found in many consumers products in Norway (Herzke et al., 2012), in wet room sealing paints in low amounts and mainly as PFOS (perfluorooctanesulphonate) which is strictly regulated.

Healthy Building Network (2023) tested 94 paints, including exterior, interior and specialty paints, and found that approximately half of the paints tested positive for fluorine in the range of 42-688 ppm total fluorine content. 18 out of 21 tested paints were positive for EOF: extractable organic fluorine.

Solvents

Solventborne vs waterborne paints

Historically paints were mixtures diluted in organic solvents that dried after evaporation of the solvent. Typically, solvents like xylene, toluene, turpentine (white spirit), methyl ethyl ketone (MEK) have been used (IARC Working Group on the Evaluation of Carcinogenic Risks to Humans. Meeting (2008-2009 : Lyon et al., 2012).

In the 1970s, increased awareness of the risk of brain damage promoted a change in the composition of paint with white spirit, a petroleum-derived solvent to waterborne paints with water as the main solvent. By late 1980s 90% of paints used for buildings in Denmark were waterborne. The change was assisted by technological advances and imposed by information campaigns of the trade unions, and the regulation by the Danish Working Environment Authority (Hansen et al., 1987).

The negative effects on human health caused by the exposure to these substances forced industries to change paint formulations to waterborne technologies. Waterborne paints use water as solvent and in this way reduce painters' exposure to toxic organic compounds. However, VOCs can also be emitted from waterborne paints in much lower concentrations, due to the presence of small amounts of VOCs acting as co-solvents, binders (Texanol) and additives (Stockwell et al., 2021). VOCs emitted from water-based paints have been studied to have long-term duration.

Paints as source of VOC emission

Many studies (Mai et al., 2024b; Norbäck et al., 2021; Ruiz-Jimenez et al., 2022; Saraga et al., 2023; Tao et al., 2022; Xu et al., 2022) have studied how emissions from building materials and dried paint affect indoor air quality and health of the inhabitants. With the life-style changes over the last centuries, the increased amount of time spent in indoor environments has been connected to an increase in respiratory problems and the disease known as Sick Building Syndrome (SBS).

Some aromatic compounds found in paints may cause serious hazards in relation to human health. Bauer and Buettner (2023) quantified odourous components in commercial interior paints, finding high levels of derivatives of benzene and naphthalene. The presence of naphthalene can be derived from by-products of organic pigments. Alkyl benzenes were common solvents for solventbased paints (xylene). Potential carcinogenic compounds can be present in wet paints, however,

every investigated product differed for which specific compound was found in the highest concentration (Bauer & Buettner, 2023).

Ruiz-Jimenez et all (2022) identified paints as important sources of VOC emission indoors, including compounds such as toluene, xylene, aldehydes (formaldehyde and hexanal), ethylbenzene, styrene, n-butanol, hydrocarbons and ethylene glycol. Different types of paints have different emission profiles. Phthalates emitted exclusively from the investigated latex paints.

Xu et al. (2022), analysed the VOC emission from building materials both dry and wet materials, concluding that there is no large difference between dry and wet VOC emission and the most common VOC found in building materials is hexanal, while phenols are those contributing the most to bad indoor odours. TVOC in wet materials (paint and adhesives) ranged from 219 to 3060 μ g/m³ with a median of 252.9 μ g/m³.

Huang et al. (2021) analysed the concentrations of indoor emissions of 43 VOCs and connected those found in highest concentrations with the sources. Regarding paints, they found high concentrations of formaldehyde derived from the hydrolysis of nitro-paints used in wood furniture; C12- C16 alkanes are connected to varnish of wooden floors; N-butanol derived from the hydrolysis of butyl-acrylates coatings, used for wood but also in other applications.

Zhao et al. (2016) studied the effect of binders and substrates on BTEX emissions. Acrylic binders and porous substrates had lower emissions than polyvinyl acetates and inert substrates on the emissions of BTEX (benzene, toluene, ethylbenzene and xylene). The same was the case for carbonyls (formaldehyde, acetaldehyde, acrolein, acetone, 2-butanone, methacrolein, butyraldehyde, valeraldehyde, hexaldehyde, benzaldehyde, and m-tolualdehyde).

The source apportionment study carried out by Liu et al. (2014) identified paint solvents and building materials as the main sources for concentrations of benzene (82.4%) in indoor houses in Beijing. In minor part, paints contribute to the indoor emission also of formaldehyde (1.8%), acetaldehyde (3.7%), acetone (2.5%), acrolein (2.9%), toluene (3.1%), and xylene (0.4%).

Indoor levels of nitrous acid have been attributed to the presence of wall paints and lacquers by Gomez Alvarez et al. (2014). Nitrous acid is not emitted from the paint, but it can form in-situ by NO₂ and light on the surfaces by heterogeneous reaction.

Kang et al. (2012) studied the emissions of naphthalene from household materials, finding that painted walls, wood furniture with finishes and varnishes are important sources of this pollutant in indoor spaces.

Geiss et al. (2012) studied the formation of carbonyl compounds from paints (formaldehyde, acetaldehyde, propanal and acetone and in lower concentrations hexanal, heptanal and octanal), they

proposed a radical mechanism of formation derived from the degradation of the polymer matrix of the paint. They proposed the addition of $TiO₂$ to act as a photocatalyst (see photocatalytic paints) and thereby prevent the formation of the carbonyls, as a strategy for indoor air cleaning technologies and for reducing the emission from paints.

Yuan et al. (2010) characterized the VOC emission from liquid solvent-based paints during applications. High concentrations of toluene, n-nonane, n-decane, n-undecane, m/p-xylene were found. The transition from solvent-based to water-based paints can reduce drastically the emission of VOCs.

However, water-based paints do not completely remove the emission since they also contain some quantities of organic solvents. Chang et al. (2011) studied the emission rates from two standard water-based paints, finding that the VOC emissions from water-based paints are similar to those from solvent-based paints. The most common VOCs found in this work were n-butanol, ethylene glycol and C7 esters.

A natural environmental chamber study (Tao et al., 2022) investigated the occurrence of 9 different organophosphate esters (OPE) in air, dust, and window film samples being emitted from, among others, latex paint. OPEs are used as fire-retardant additives in paint but have been found to have adverse health effects (Chupeau et al., 2020). The study showed that tris(1,3-dichloro-2-propyl) phosphate (TDCIPP) was particularly present in the emissions from latex paint, and that higher air temperatures accelerated the emission of OPEs into the air.

Natural paints emit monoterpenes that are also VOCs. Lamorena et al. (2007) studied the reactions of monoterpenes with ozone in the air, finding that it leads to the production of carboxylic acid (acetic and formic), carbonyl compounds, such as formaldehyde, acetaldehyde and acetone, and nano-sized particles with high concern for human health.

Certification systems may use different definitions of VOCs, and therefore, a certificate/quality label only means that a specific product meets specific requirements under specific conditions - and not that one can ensure products free of chemicals and emissions. Thus, it is not always true that paints labelled as "zero-VOC" have no emissions (Schieweck & Bock, 2015).

Suzuki et al. (2019) studied the emissions from paints labelled as VOC-free, finding low emissions for paint with VOC contents lower than 0.3%, however, paints containing 1% VOC showed high emissions of Texanol, glycol ether and 2-ethyl-1-hexanol, indicating that VOC-free labels do not always mean zero emissions.

Jørgensen and Solheim (2017) demonstrated that the emission of nanoparticles is not relevant for interior paints (acrylic waterborne paints).

Emissions caused by the binder

Weschler (2009) review the changes in occurring indoor pollutants from the 50s to 2008. He found that in general, water-based paints with lower emissions of VOC had substituted solvent-based paints. A very common binder is Texanol, a mixture of 3-hydroxy-2,2,4-trimethylpentyl-1-isobutyrate and 1-hydroxy-2,2,4-trimethylpentyl-3-isobutyrate, which was found to release monomers after months from the application.

Photocatalytic paints

Photocatalytic paints often contain TiO₂ particles with the aim to degrade organic pollutants in indoor air (like formaldehyde, NO_x and VOCs) by UV-light induced radical reactions. However, they can also react with binders and other ingredients in the paint. J. Morin et al. (2019) studied the effect of the type of binder and the presence of photocatalytic particles on the VOC emissions from paints. When exposed to UV-light, acrylic and acrylic/siloxane binders released VOCs, such as formaldehyde, acetaldehyde, aromatics (alkyl benzene like toluene, xylene and others, benzoic acid), acids (formic, acrylic, propionic, acetic and butanoic acid), and carbonyls (acrolein, acetone, propanal, octanal, Methyl vinyl ketone (MVK,) vinyl acetate, pentanal). Lower emissions were observed from paint with a mineral silicate binder.

Auvinen & Wirtanen in 2008 studied the efficacy of photocatalytic paints finding that they are not efficient either in removing formaldehyde or VOCs. Moreover, radical reactions can lead to the formation of many other compounds that are harmful air pollutants. Binders can be degraded, and thereby form aldehydes and ketones such as formaldehyde, acetaldehyde and acetone.

Polycyclic aromatic hydrocarbons (PAHs)

Oriji at al. (2012) measured the content of PAHs and heavy metals in water-based paints commercially available in Nigeria from two different suppliers, finding the presence of anthracene, fluorene, phenanthrene, fluoranthene, pyrene, acenaphthene, arsenic (0.79 mg/kg), zinc (1.54 mg/kg), and mercury (<0.001 mg/kg). Heavy metals were found to be within the tolerable concentrations.

Overview of possible hazardous compounds

The following table (2-2) presents an overview of possible hazardous compounds found in the identified literature.

Compound family	Relevant in interior paints (yes/no)	Uses	Compound example	Compound found in emis- sion/liquid paint
Preservatives				
Isothiazoli- nones	Yes	Preservatives	MIT, BIT, CMIT/MIT, OIT	Liquid paint
Other in-can pre- servatives	Yes	Preservatives	Water-based paints most likely con- tain in-can preservatives., Isothia- zolinones are the most common, but the list of approved substances is long (most of them with negative ef- fect on health). A complete list of the approved substances for in-can preservation is presented on the ECHA website under the product type 6 list.	Liquid paint
Parabens	No	Preservatives, mainly used in cosmetics	Methyl parabens Propyl parabens	Liquid paint
pH	Yes	Preservative at high pH	$\overline{}$	Liquid paint
Heavy met- als	No	Preservatives, technolo- old gies not used nowadays (at least in EU) (ex- cept Zn)	Arsenic, zinc, mercury, lead, cad- Liquid paint mium, nickel	
Plasticizers Phthalates	Yes		Plasticizers, in Diethylphthalate	Liquid paint
		water-based paints	Dibutylphthalate Di-Isononyl Phthalate Bis(2-ethylhexyl) phthalate	
Chlorinated paraffines	Yes	Plasticizers, four retard- ants	Short-chain (C10-C13) chlorinated paraffins Medium-chain (C14-C17) chlorinated paraffins	Liquid paint (measure of Cl content)

Table 2-2: Principal hazard chemicals found in the literature review, organized by function in the paint system

2.4.3. Substances from SPIN database

The SPIN (Substances in Preparations in Nordic Countries) Database covers the use of substances in products within the Nordic countries. It is publicly accessible and used for tracking chemical substances in various products. The database includes data from the product registries of Norway, Sweden, Denmark, and Finland. It is used for environmental and health safety assessments, regulatory compliance, and research on chemical substances in products. The following is an assessment of the usage of REACH Substances of Very High Concern (SVHC) and Denmark's List of Unwanted Substances (LOUS) (in Danish Listen Over Uønskede Stoffer) chemicals in interior paint industry in Denmark, last updated in 2009. The substances listed in the table below are used for interior paints.

Table 2-3: Identified chemicals of concern used in interior paints in Nordic countries using the SPIN database

CAS	Name	Use	Used in 2 Boiling Notes		
			component point		
			paint	(°C)	
			(yes/no)		

SVHC (Substances of Very High Concern)

(Note that SVHC substances need to be indicated in the SDS, mainly if they are part of resins or main component of paint)

LOUS substances (List of Unwanted Substances)

3. Methods

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3.1. Mapping of common paints on the market

The objective of this market survey is to explore the variety and characteristics of paints available to consumers in Denmark. This investigation ensures that representative samples are selected for further analysis. The study meticulously categorizes paints based on their application and distribution channels, which includes:

- Large DIY Stores: The paints are categorized into two main sections:
	- o Wall paints
	- o Wood/metal paints
- Online Retailers: These platforms also organize their offerings into:
	- o Wall paints
	- o Wood/metal paints

Additionally, the influence of social media trends, especially trends emerging on platforms like Instagram were considered. Instagram users were asked about their paint preferences and input to the selection of paint for test.

The research also extended to understanding the types of paints available, their distribution by various dealers, and various labelling schemes. Information was extracted from Safety Data Sheets (SDS) to enhance the understanding of the chemical composition and safety measures associated with these paints. The goal was to comprehensively cover the market in terms of price, quality, chemical awareness, and consumer popularity.

The methodological approach involved a systematic screening and review of selected online web shops for DIY stores, as well as online retailers. Insights from current trends observed on social media platforms such as Instagram was also incorporated. Additionally, surveys were distributed to consumers to directly gather their insights.

During the survey, detailed information was collected on the name of the paint, the manufacturer or dealers, price, coverage area, any relevant labelling schemes, and warnings indicated in the safety data sheets. This comprehensive data collection aids in understanding the market dynamics and assisting consumers in making informed decisions.

3.2. Selection of paints

In total 232 different white interior paints were identified in the mapping of the paints on the marked. 168 wall and 64 wood paints were identified. Special paints like wet room paints, as well as structure and effect paints, were omitted from this study. Although lime paints are typically considered effect paints, their increased popularity in recent years has led to their inclusion in this

project. This study focuses exclusively on single-component paints and paints intended for indoor domestic use.

To simplify the study, only white pigmented paints are considered, despite some colour pigments containing substances of concern. The scope includes 'wall' paints, 'wood' paints, and some 'wood and metal' paints.

The range of gloss varies between 0-100. Wall paints on the market ranges typically between gloss 5 and 20 whereas the gloss of wood paint typically varies between 20 and 90. The chosen target gloss of the wall paint was 10 and 50 for wood paints. For paints which differs from the chosen values, the gloss closest to the target value was chosen.

Based on the 232 products identified during the mapping, 30 paints (20 wall paints, 10 wood/metal paints) were selected for further testing and analysis based on the following criteria:

- Market availability
- Popularity
- Wide range of brands, types and compositions
- With and without emission labelling
- Information from Safety Data Sheets (SDS)

Included in this study is both water-based and oil-based paints (e.g. acrylic, alkyd, lime, linseed). The table below shows the information on the different paints.

Table 3-1: List of the chosen paints selected for testing and analysis and their properties

¹Water-thinnable oil paint

3.3. Selection of target groups and compounds

Based on the literature study, Safety Data Sheets (SDSs), and the compounds identified as of concern in the SPIN database, the following compounds and compound groups were chosen for investigation in this project. Some compounds of interest, such as nonylphenol ethoxylates, were omitted from the selection due to the availability and cost of the analysis.

The table below lists the chosen analyses, indicating whether the analysis is conducted on liquid (l), dried paint (solid, s), or as an emission (gas, g).

Table 3-2: List of included compounds to be tested

Analytic parameter	Compound specification	Test type ¹			
Biocides, Isothiazoli-	Benzothiazolinone (BIT),	$In-Can (I)$			
nones	2-Butyl-2,3-dihydrobenzisothiazol-3-one,				
	2-Methyl-1,2-benzoisothiazolin-3-one,				
	Methylisothiazolinone (MIT),				
	2-octyl-4-isothiazolin-3-one (OIT),				
	4,5-dichloro-2-octyl-2H-isothiazol-3-one (DCOIT),				
	5-chloro-2-methyl-4-isothiazolin-3-one (CMIT)				
PFAS indication	Total Fluorine (TF),	$In-Can (I)$			
	Total Inorganic Fluorine (TIF),				
	Calculated Total Organic Fluorine (TOF)				
Chlorinated paraffins	Short and Medium-chain chlorinated paraffins (SCCPs	$In-Can (I)$			
	and MCCPs)				
PAHs	Naphthalen,	$In-Can (I)$			
	Acenaphthylen,				
	Acenaphthen,				
	Fluoren,				
	Phenanthren,				
	Anthracen,				
	Fluoranthen,				
	Pyren,				
	Benz(a)anthrecen,				
	Chrysen,				
	Benz(b)fluoranthene,				
	Benz(k)fluoranthene,				
	Benz(a)pyren,				
	Indeno(123)pyren,				
	Dibenz(ah)anthracene,				
	Benz(ghi)perylen				
Phthalates	Diethyl phthalate (DEP),	$In-Can (I)$			
	Di-(2-methoxyethyl)phthalate (D2MEP),				
	Diisobutyl phthalate (DIBP),				
	Dibutyl phthalate (DBP),				
	Dipentyl phthalate (DPP),				
	Diisopentyl phthalate (DIPP),				
	Butylbenzyl phthalate (BBP),				
	Dihexyl phthalate (DHxP),				
	Dicyclohexyl phthalate (DCHP),				
	Di(2-ethylhexyl)phthalate (DEHP),				
	Di-n-octyl phthalate (DnOP)				

Based on the results, a few paints with high levels of TOF or BIT were selected for additional tests. The tests are listed in table 3-3.

Table 3-3.: Additional test and retest on a few selected paints based on the in-can results of TOF and BIT

3.4. In-can analyses

The paint was purchased in cans and plastic buckets in volumes between 1 and 10 L. Each paint was bought in a quantity of three (one for the In-can analysis, one for emission tests and one extra). One unopened container of paint was homogenized using an automatic paint shaker before samples were transferred to smaller containers of different materials, which were sent for analysis. Glass, metal and PE-containers were used, depending on the analysis being performed and agreement with the chemical analysis laboratory.

Table 3-4: Chemical analysis methods and LOQ of phthalates, PAHs, SCCPs - MCCPs, biocides, TOF, formaldehyde and pH of paint (in-can analysis)

3.5. Heavy metal analysis

A sample of each paint was applied on a glass plate and allowed to dry. After curing, the paint was scraped from the glass plate using a cleaned and sharp metal knife. The solid paint samples were then individually wrapped in aluminium foil, placed in Ziplock bags, and sent for analysis.

Table 3-5.: Chemical analysis methods and LOQ of heavy metals (in-can analysis)

3.6. Odour evaluation

In the context of assessing the olfactory characteristics of liquid paints, a structured sensory evaluation was conducted. The study involved an untrained panel of seven participants, encompassing a diverse group in terms of smoking habits and gender: five non-smokers, one smoker, and one individual who uses vapes. The gender distribution included four females and three males, with an age range of 27 to 54 years.

The evaluation was organized into three separate sessions to mitigate olfactory fatigue and ensure accurate assessments. Each session consisted of evaluating ten samples of liquid paint. These samples were presented in small identical and unmarked cans containing 100ml of paint to ensure blinding and prevent any bias based on brand or appearance.

To maintain sensory acuity, a five-minute interval of clean air exposure was provided after the first five samples in each session, allowing the participants' sense of smell to recover before proceeding with the next set of samples.

Participants rated the odour of each paint sample using a 5-point scale (Appendix 7.1.), where 1 represented a "very unpleasant odour" and 5 indicated a "very pleasant odour". This scale enabled a quantifiable measure of odour preference and intensity, facilitating a comparative analysis across different paint formulations.

3.7. Emission testing

The emission test was preformed to determine the chemical emission to air during curing and in the course of 28 days from the sample preparation.

3.7.1. Sample preparation

The paint samples are provided in volumes between 1 and 10 L. Each unopened container of paint was homogenized using an automatic paint shaker prior to application. The paint was applied to a predefined area on a clean glass plate using a smooth paint roller for the wall paints and a narrow paint brush for the wood/metal paints.

The layer thickness of the paint is defined by the weight of paint applied to the predefined area. The weight of paint applied is defined by the lower limit of the recommended coverage rate (m²/L) and the reported density for each paint. The determined weight of paint is applied with an allowed tolerance of +/-5%. The glass plate is placed in the test chamber no more than 5 minutes after finishing the application of paint.

3.7.2. Test conditions for climate chambers

The horizontal reference method EN 16516:2017+A1:2020, "Construction products: Assessment of release of dangerous substances - Determination of emissions into indoor air", specifies a reference room, emission test in climate chambers, collection of air samples and chemical analysis of volatile substances by reference to ISO 16000-3/6/9. These standards were used as reference in the emissions tests.

Emissions of chemical substances from paint was measured in climate chambers by standardised methods derived from ISO 16000-9:2006. Test condition in the climate chambers was a temperature of 23 ± 1 °C and 50 ± 5% relative humidity (RH), with an air change rate of 0.5 h⁻¹ for wall paints and 1.0 h^{-1} for wood paints.

According to EN 16516 the loading factor for wall surfaces is 1.0 m²/m³ at an air change of 0.5 h⁻¹. This was the test condition for the wall paint. According to EN 16516 the loading factor for small surfaces like windowsills and skirting boards is 0.05 m²/m 3 at an air change of 0.5 h 1 , which corresponds to a loading factor of 0.1 m²/m³ at 1.0 h⁻¹ which was the test condition for the wood and metal paints.

The emission testing and reporting deviates from EN16516 in a few points: VOCs and aldehydes are by the standard only required to be reported in concentrations above 5 µg/m³, except for carcinogenic substances Cat. 1A and 1B, which are reported as low as 1 μ g/m³. In this project VOCs and aldehydes are reported in concentrations from 1 μ g/m³. Also, air samples are by the standard supposed to be sampled on day 28. Sampling for VOCs was carried out after 4 and 24 hours, and 3, 14 as well as 28 days after placement in the chamber.

3.7.3. Sampling times

An overview of the analysis plan for testing of emissions from paint samples is given in Figure 3-1.

Figure 3-1: Emission testing timeline

3.8. Field measurement

For the field survey, a total of 3 cases were selected, where rooms in private homes were to be painted. The cases were recruited through work contacts or social media. All cases were bedrooms in dwellings located on Zealand in Denmark. Acrylic paint was used in Case 1 and 2 and linseed oil was used in Case 3. In Appendix 7.2. a description of each case is presented. The field surveys were carried out during March and April 2024. Air measurements were performed and included measurements of volatile organic compounds (VOC), aldehydes, ammonia, 1,2-Benzisothiazol-3(2H)-one (BIT) and 2-octyl-1,2-thiazol-3-one (OIT). The selection of measured substances was based on results from the literature screening and In-can analyses. The registrations included room sizes, ventilation conditions and user habits.

3.8.1. Sampling times

The measurement program consisted of 5 measurement days distributed over a period of approximately one month. A background measurement was conducted before the rooms were painted to determine the existing chemical compounds in the rooms. Measurements were also conducted on the day of the last painting activity (Day 0). In addition, measurements were conducted 3, 14 and 30 days after the last painting activity. An overview of the conducted measurements on each measurement day can be found in Figure 3-2.

Windows and doors were kept closed prior to and during the measurements to ensure minimum interference with the surrounding air.

*Figure 3-2: Measured chemical compounds * Some of the measurements were performed at Day 15 and Day 31 due to coordination with participants.*

Air change rate

The air change rate was measured once in all cases. Tracer gas (R 134a) decay method was used for this purpose. Windows and doors were kept closed during the measurement to ensure that the measured air change rate was as close as possible to an outdoor air exchange and not an internal air exchange with the rest of the dwelling.

Temperature, relative humidity, and CO²

Momentary measurement of temperature and humidity during air quality measurements was carried out with an electronic thermometer/hygrometer, mk Testo 440.

In addition to the momentary measurements, the temperature, relative humidity and $CO₂$ -concentration was recorded continuously during the measurement period by a data logger, mk Lufft Opus20. Continuous recordings were not carried out in case 3.

Chemical compounds

Air samples have been collected for analysis of Volatile Organic Compounds (VOC), aldehydes, ammonia and BIT/OIT. The air samples were collected by sampling a controlled amount of room air through collection media specific to the chemical compounds, as listed in Table 3-6. The pumps used are of the brand GilAir Plus.

* The sampling and analysis were performed with duplicate determination

3.9. Chemical analysis of air samples

Analytical principles for measuring volatile substances in air consist of active sampling of a volume of air via controlled flow with a pump. During collection, the substances are adsorbed onto a test tube (with an adsorptive medium) which is subject to laboratory analysis. Sample tubes are extracted either with solvent or by thermal desorption (TDS), analysed by liquid chromatography (HPLC) or gas chromatography (GC), and the substances are detected by spectroscopy (UV, MS, or MS/MS).

Aldehydes and ketones (VVOC/VOC carbonyls) are determined by collecting approx. 60 L of air on DNPH tubes and analysis by HPLC-UV. ISO 16000-3:2022 Indoor air - Part 3: Determination of formaldehyde and other carbonyl compounds in indoor and test chamber air - Active sampling method.

Volatile organic compounds (VOCs) are collected on Tenax TA (approx. 1-6 L of air) and analysed by TDS-GC/MS (ISO 16000-6). The detection limit is approx. 1 μ g/m³. ISO 16000-6 can be used for screening for SVOCs, up to the boiling point of docosane (C22), approx. 369°C.

For the analysis of BIT/OIT content, calibration was performed using authentic references of BIT/OIT.

Ammonia was sampled on sulphuric acid coated silica gel tubes and analysed using spectrophotometry. The concentration of ammonia (NH₄₊) is determined using the indophenol-blue method, which is modified from NIOSH 6015, 4th Ed. 8/15/94). and Hach-Lange's LCK colour reagent kits for ammonia determination. LOQ is 9 µg/m³.

4. Results and discussion

4.1. In-can analysis

Biocides

In the analysis, the selected preservatives were found in a little more than half of the samples (16 out of 30), in both wall and wood paints (Figure 4-1). The most predominant compound detected was benzothiazolinone (BIT), with concentrations reaching up to 360 mg/kg. This compound is known to be used in paints and other consumer products.

Figure 4-1: Distribution of biocide concentrations in the paint samples

In most paints where BIT was detected, the compound was accompanied by other preservatives, though in lower concentrations. Figure 4-2 illustrates the concentration of preservatives apart from BIT. Note the changed concentration axis.

Figure 4-2: Distribution of biocide concentrations in the paint samples, excluding BIT

OIT and 4,5-Dichloro-2h-octyl-2(2H)-isothiazolone was not detected in any of the paints. MIT was found in 50 % of the samples in concentrations up to 4.6 mg/kg. 2-Butyl-1,2-benzothiazol-3(2H) one, 2-Methyl-1,2-benzothiazol-3(2H)-one and CIT/MIT, was found in 4, 6 and 8 paints respectively. The highest measured concentration was that of 2-Methyl-1,2-benzothiazol-3(2H)-one in ID-13 in a concentration of 31 µg/kg. It is unknown whether some compounds and concentrations are due to degradation or impurities.

In Lundow et.al. (2014), 19 water-based paints were analysed for the MIT and BIT content, showing a content of MIT in all samples and for 17 out of 19 paints the content of MIT was greater by a factor of two than the content of BIT. This indicates how the use shifted from MIT to BIT in the last 10 years.

The EU Classification, Labelling, and Packaging (CLP) regulation has classified MIT as a skin sensitizer. Additionally, EU has restricted the concentration of MIT in products that come into direct contact with the skin. While MIT primarily causes allergic skin reactions through direct contact, there is some evidence that airborne exposure can also lead to sensitization. In recent years increase in cases of MIT allergy among consumers have led to the legal requirement to label products containing MIT in 2017. BIT is known to be less potent compared to MIT, although sensitive individuals have shown reactions, especially when in direct skin contact with BIT.

The analysis of the biocide content in the paint samples reveals noticeable variability across different types of paints, with distinct differences tied to the type of binder used and the paint composition. Plant-based paints, using linseed oil as a binder (ID-12, 16, 28 and 30), generally exhibit low to undetectable levels of biocides, suggesting inherent antimicrobial properties (Díez-Pascual, 2018). Mineral paints (ID-1,14,15,17), such as those based on lime or potassium silicate, also tend to have low biocide content compared to plastic paints.

In contrast, plastic paints, particularly those with acrylic or styrene-acrylic copolymer binders, exhibit higher biocide concentrations, indicating a higher susceptibility to microbial growth. Paints with REPLEBIN® and polyvinyl acetate binders, and non-water-soluble alkyd resin paints show lower biocide levels.

Total Organic Fluorine content (TOF)

The analysis was carried out by first determining the Total Fluorine (TF) content and the Total Inorganic Fluorine (TIF) content. The Total Organic Fluorine (TOF) content was then obtained by subtracting the TIF from the TF.

As illustrated in Figure 4-3 below, TF was detected in 22 of the paint samples. TIF was found in three of these samples, but organic fluorine was present in all 22 samples. Levels below 50 mg/kg are considered background contamination from production processes and other sources.

Two samples, identified as ID-9 and ID-20, exhibited the highest levels of TOF, ranging between 350 and 600 mg/m³. For the remaining samples, the TOF concentration was below 100 mg/m³.

Figure 4-3: TOF and TIF concentration in all paint samples

For the two paints with the highest TOF levels (ID-9 and ID-20), an additional in-can analysis of 50 specific PFAS compounds was performed. The list of the 50 PFAS compounds can be found in Appendix 7.3. None of these specific PFAS compounds were detected.

This underscores the importance of not only analysing specific compounds but also performing a broad screening of TOF to thoroughly investigate the presence of PFAS.

Chlorinated paraffins, PAHs, phthalates

For all 30 paints, the in-can analysis for chlorinated paraffins, polycyclic aromatic hydrocarbons (PAHs), and phthalates showed that none of these compounds were detected.

Formaldehyde

Formaldehyde is used in paints primarily for its preservative properties and its role in the production of resins and binders that enhance paint performance. However, due to health and environmental concerns, the paint industry is moving toward reducing or eliminating formaldehyde in formulations, offering safer and more sustainable products to consumers.

The in-can concentration of formaldehyde is shown in the figure 4-4 below. Formaldehyde was detected in 11 out of the 30 paint samples, with concentrations reaching up to 9 mg/kg. Formaldehyde was found in both wall and wood paints.

Figure 4-4: In-can formaldehyde concentration in the paint samples

Low formaldehyde paints typically contain less than 0.01% formaldehyde by weight. Standard paints typically have formaldehyde concentrations ranging from 0.01% to 0.1% by weight.

High formaldehyde paints have concentrations above 0.1% by weight which is considered high and are less common today due to regulatory restrictions and health concerns. All 30 paints have concentrations below 0.001%. Since the emission of formaldehyde was also measured, the correlation of the in-can concentrations and the emission of formaldehyde can be found in figure 4-17.

pH

The measured pH values of the paints are shown in the figure 4-5 below. None of the paints are acidic (pH < 6). The skin's natural pH typically ranges between 4.5 and 5.5. None of the paints are in the range. A few of the paints have a mildly alkaline pH between 6 and 7 (n=4), whereas most of the paints are moderately alkaline with a pH between 7 and 9 (n=21). The remaining paints (n=5) are highly alkaline with a pH above 9, likely to cause significant skin irritation, dryness, and damage to the protective barrier. A high pH can have a preservative effect on paints. Of the seven paints with a pH of 9 or above, only one contains detected biocides, specifically BIT.

Figure 4-5: In-can pH levels in the paint samples

The analysis of paint samples reveals that the pH levels are significantly correlated with by their binders and overall compositions. Plant-based paints, which use linseed oil combined with carbonate, exhibit consistent pH values ranging from mildly acidic to neutral, indicating a balanced formulation. In contrast, plastic paints show more variability, with REPLEBIN® and styrene-acrylic copolymer binders resulting in higher pH values (above 10), suggesting more alkaline conditions. Polyvinyl acetate and Decovery® binders have neutral pH levels, while acrylic-based paints tend to be slightly alkaline. Non-water-soluble alkyd resin paints display slightly acidic to neutral pH values. Mineral paints exhibit the widest pH range, from slightly acidic to highly alkaline, with lime-based paints showing the highest alkalinity.

4.2. Heavy metal analysis

The metals analysed include arsenic (As), lead (Pb), cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), nickel (Ni), and zinc (Zn). The data reveals significant variations in metal concentrations depending on the paint formulations (figure 4-6, 4-7 and Appendix 7.4).

Lead was detected in multiple samples, with the highest concentration found in ID-18 (26 mg/kg). Notable concentrations were also observed in ID-2 (7.5 mg/kg), ID-6 (4.8 mg/kg), and ID-20 (4.9 mg/kg). Chromium was found in significant amounts in several samples, with the highest in ID-19 (190 mg/kg) and other high concentrations in ID-10 (95 mg/kg) and ID-11 (84 mg/kg). Zinc concentration was extremely high in ID-28, ID-29 and ID-30 (94,000, 7,600 and 23,000 mg/kg respectively), marking them as outliers, with other high concentrations in ID-26 (1,100 mg/kg) and ID-27 (690 mg/kg). Cadmium and mercury were found in lower concentrations compared to other metals but were present in samples such as ID-13 (0.051 mg/kg for Cd) and ID-17 (0.27 mg/kg for Hg). Nickel was highest in ID-19 (45 mg/kg) and present in several samples with varying levels.

Figure 4-6: Concentration of lead, chromium and nickel in all samples

Paint samples based on different types of binders and compositions exhibit distinct patterns in heavy metal concentrations. Water-based emulsions with acrylic and styrene-acrylic copolymer binders tend to have higher chromium and zinc levels. For example, acrylic paints such as ID-7, ID-8, ID-10, and ID-11 show significant concentrations of chromium and zinc, with ID-8 containing 44 mg/kg of chromium and 370 mg/kg of zinc. Similarly, samples like ID-4, ID-5, and ID-6 using styreneacrylic copolymer also show varied concentrations, with ID-6 notably having a concentration of 250 mg/kg of zinc.

Oil-based paints, particularly those using linseed oil as a binder (ID-12, ID-28, and ID-30), exhibit high zinc concentrations. For instance, ID-28 has an extraordinarily high zinc concentration (94,000 mg/kg). Alkyd-based paints (ID-23 and ID-29) also show moderate zinc levels, with ID-29 containing 7,600 mg/kg.

Lime and potassium silicate-based paints generally have lower heavy metal concentrations. Lime paint samples ID-14 and ID-17 have lower heavy metal concentrations compared to other types, with ID-17 showing 4.6 mg/kg lead and 0.16 mg/kg cadmium. Potassium silicate-based paint (ID-15) shows modest levels of chromium (2.5 mg/kg) and zinc (1.5 mg/kg).

According to local and national legislation for contaminated and toxic waste, only nickel and zinc exceed the levels for clean waste. For Paint ID-19, the concentration of nickel at 45 mg/kg categorizes it as contaminated waste. Similarly, paints ID-13, 20, 26, and 27 have zinc levels ranging from 540 to 1,100 mg/kg, classifying them as contaminated waste. Paints ID-28, 29, and 30, with zinc concentrations ranging from 7,600 to 94,000 mg/kg, are categorized as dangerous waste. These classifications apply to the paint fraction; for painted materials such as wood, the concentrations are often likely to be diluted below levels of concern, but not always.

4.3. Odour evaluation

For the odour evaluation a 5-point scale was used (Appendix 7.1). On the scale, the endpoint 1 represented a very unpleasant odour and the endpoint 5 indicated a very pleasant odour. The results for all paints are shown in figure 4-8 below. Wall paints ID-1 to ID-20 are overall rated better (average evaluation of 3.4) than the wood paints ID-21 to ID-30 (average evaluation of 2.5). The lowest scores were found for paints ID-23 and ID-29 which are both organic solvent-based alkyd paints.

Figure 4-8: Panel evaluation results of odour of in-can paint samples on a 1-5 scale

In figure 4-9 below, the odour evaluations are shown grouped after binders. Apart from one plantbased paint (ID-16) with the highest score (worst evaluation of 4.75) the plastic paints have the widest span in evaluations and both the mineral, and the remaining plant-based paints are within the odour evaluation range of the plastic paints.

Figure 4-9: Panel evaluation results of odour of in-can paint samples grouped according to binder type

4.4. Emission testing

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Emission testing of painted glass plates involved collecting air samples after 4 hours, 24 hours, 3 days, 14 days, and 28 days without preconditioning. The initial air samples showed high concentrations and a large number of identified compounds (VOCs). Appendix 7.4., lists all identified compounds and their concentrations for all 30 paints and measurements (VOC and aldehydes). The graph below provides an overview of the number of detected compounds ranging from 18-91 individual compounds grouped by the type of paint binder (Figure 4-10).

Figure 4-10: No. of identified VOCs in all paint samples

The analysis of total volatile organic compound (TVOC) concentrations over time revealed significant differences between the three types of paints: plant-based, plastic, and mineral. Figure 4-11 clearly illustrates that some of the plastic paints exceed plant-based and mineral paints. However, the number of plastic paints in this study was more than 73% making the overall variation in emission more likely.

The TVOC concentration after 4 hours was as high as 60-70 mg/m³ for two organic solvent-based plastic paints. These sampling tubes (Tenax) were overloaded. These two paints are highlighted in red in Figure 4-11 below. Indoor air concentrations of 60-70 mg/m³ TVOC are very high and can pose acute health risks. Appendix 7.5 provides the TVOC values for all measuring points for all paints.

Figure 4-11: TVOC concentration after 4 hours in chamber without preconditioning for in all paint samples

As seen in figure 4-12 the overall concentration decreases, however for some paints and compounds the peak in concentration has some delay in the figure illustrated by paint ID-3.

Figure 4-12: Concentration at different sampling days for selected paints

Initially, on Day 0 (4 h), the plastic paints exhibited the highest TVOC concentrations, with an average of 8,725 μg/m³ (Figure 4-13). This is apart from the two organic solvent paints likely also due to the various synthetic binders used in these paints, such as acrylic, polyvinyl acetate, and styreneacrylic copolymers, which tend to release higher levels of volatile compounds. In contrast, the mineral paints had a lower initial TVOC concentration of 2,406 μg/m³, while the plant-based paints exhibited the lowest levels, with an average of $1,132 \mu g/m^3$.

Figure 4-13: TVOC (µg/m3) for all groups, Day 0, 1, 3, and 14. Note the difference in y-axis values

Over time, the measurements show a significant decrease in TVOC concentrations for all paint types. However, the rate of decline varied among them. The plastic paints experienced a sharp drop from Day 0 to Day 1, followed by a steady decrease in subsequent days. This rapid decline suggests that the volatile compounds in these paints emit relatively quickly after application.

The mineral paints, on the other hand, exhibited a more gradual decrease in TVOC concentrations over time. While their initial levels were lower than plastic paints, the decrease was not as steep. This could be attributed to the binders used in mineral paints, such as potassium silicate, which may release volatile compounds at a slower rate.

The plant-based paints consistently maintained the lowest TVOC concentrations throughout the observation period. The graphs show a steady, but relatively minor, decrease in their TVOC levels over time, indicating a lower overall emission of volatile compounds.

In order to evaluate the TVOC level, the German Committee on Indoor Air Guide Values (AIR), Umwelts bundesamt, Germany gives the following evaluation of TVOC values. TVOC ≤300 µg/m³ hygienically safe. 300 – 1,000 μ g/m³ hygienically still safe, if indoor air guide values are not exceeded for single substances or substance groups. 1,000 – 3,000 µg/m³ hygienically noticeable. 3,000 – 10,000 μ g/m³ hygienically alarming, >10,000 μ g/m³ hygienically unacceptable. After 14 days the TVOC for all paints were below 1,000 μ g/m 3 , and for 24-hour measurements 2/3 of all paints were below 1,000 μ g/m³.

The risk factor is a metric used to evaluate the potential health risks associated with VOC emissions from the paint samples. In this report an R-value (Risk value) has been calculated as:

$$
R = \sum \frac{C_i}{LCI_i}
$$

The R-value is the sum of risk factors calculated as ratios of the measured concentration (Ci) of each VOC to its corresponding AgBB LCI (Lowest Concentration of Interest) value. LCI (Lowest Concentration of Interest) values are specific concentrations of individual VOCs that are considered to present minimal risk to human health when emitted from building products. They are used to evaluate the impact of VOC emissions on indoor air quality. Building materials are tested for VOC emissions after a 28-day period to simulate long-term exposure. The AgBB values are set by the Committee for Health-related Evaluation of Building Products (AgBB) in Germany. The List of LCI values currently counts more than 200 single compounds and compound groups. A higher risk value indicates a greater potential health risk due to elevated VOC levels. According to the AgBB and Danish Indoor Climate Labelling schemes the Risk value should not exceed 1 after 28 days. In Appendix 7.4. the AgBB LCI as well as the EU-LCI values are given for each detected compound. The EU LCI values are part of a standardized European framework aimed at assessing the emissions of volatile organic compounds (VOCs) from building materials.

The analysis of risk values for the paint samples revealed that several samples had risk values greater than 1 at the initial time point (Day 0), suggesting potential indoor air quality concerns due to elevated VOC concentrations in the initial time during and after painting. However, for most samples, the risk value decreased significantly over time, indicating a reduction in VOC emissions and, consequently, a lower potential health risk (Appendix 7.4).

At Day 28, the majority of the samples exhibited lower TVOC concentrations and relatively low risk values, typically below 0.1 (Figure 4-14). There were two exceptions, ID-6 (risk value = 0.30) and ID-26 (risk value = 0.11). All paints well below 1 after 28 days. This suggests that the potential health risk associated with VOC emissions from all tested paint samples was generally low after an extended period (Figure 4-15).

Figure 4-14: (a) TVOC (µg/m3) for all groups and (b) risk value, Day 28

For a few paints, compounds classified as CMR (Carcinogenic, Mutagenic and Reprotoxic) were found after 4 and 24 hours (ID-1, -2, -12, -15, -16, -20, -22 and -27). After 3 days these compounds were all below the detections limit. Formaldehyde and acetaldehyde are omitted from this though both are CMR categorized compounds. It is worth noting that in a standard testing with measurements after 3 and 28 days, these compounds would not have been revealed. These results substantiate the need for ventilation during and in the first days after painting activities.

In the analysis of ammonia levels after 24 hours in relation to paint types, plant-based paint consistently showed ammonia concentrations below the limit of quantification (LOQ), indicating negligible ammonia emissions. In contrast, some plastic paint samples exhibited the highest ammonia concentrations, notably ID-6 (7,200 μg/m³), ID-7 (1,400 μg/m³) and ID-8 (600 μg/m³).

According to EPA's toxicological review of ammonia: Noncancer Inhalation: Executive summary, Sep. 2019, ammonia has a No-Observed-Adverse-Effect Level (NOAEL) of 5,000 μg/m³ and a Chronic reference Concentration (Chronic RfC) of 500 μg/m³, described as the continuous inhalation exposure without risk of health effect during a lifetime. Paint ID-6 exceeds the NOAEL and paints ID-7 and ID-8 exceeds the RfC. However concentrations may decrease rapidly, but this was not studied in this project.

Mineral paints had a low to moderate ammonia average concentration of 120 μg/m³. Within the plastic paints category, those containing either acrylic or styrene-acrylic copolymer binders had an average ammonia concentration of approximately 730 μg/m³ (figure 4-15).

The measured ammonia levels from some paints emphasizes the need for ventilation during and in the days after painting activities.

Figure 4-15: Measured ammonia (NH3) concentration in µg/m³ measured after 24 hours and average odour evaluation

Since ammonia is known to have an unpleasant smell and relatively low odour threshold, the measured ammonia concentrations are shown together with the odour evaluations of the paints in figure 4-15. As seen in the figure, there is no clear correlation between the measured ammonia emission and the odour evaluation.

The analysis of formaldehyde concentration data reveals notable differences among the paint categories. Formaldehyde emissions from the paints can be linked to the type of binder and composition used in the formulations (Figure 4-16).

Plant-based paints, while demonstrating no in-can formaldehyde concentrations, varied significantly in emissions on Day 3 and Day 28. The emissions on Day 3 ranged from 0.7 to 12 μ g/m³, and on Day 28, the range was below detection limit to 1.3 μg/m³. This pattern suggests that while plantbased paints do not contain formaldehyde initially, they can release it in the early days after application, with emissions decreasing significantly by Day 28. The high initial emissions could be due to the decomposition of organic components, the presence of formaldehyde releasers or other chemical reactions occurring shortly after application.

Plastic paints exhibited the lowest range of formaldehyde emission levels on Day 3, ranging from 0 to 3.9 μg/m³. On day 28 the emissions ranged from below detection limit to 2.7 μg/m³, suggesting a more persistent emission profile, where paints continue to release formaldehyde over a longer period, albeit at reduced levels.

Mineral paints, with moderate in-can formaldehyde levels, showed emissions on Day 3 ranging from 0 to 5.1 μg/m³ and on Day 28 from 0 to 1.8 μg/m³. The sample with the highest emissions on Day 3 also had the highest emissions on Day 28, indicating a consistent emission pattern similar to plastic paints.

Figure 4-16: Formaldehyde emissions from paint samples on Day 3 and Day 28

Figure 4-17: Correlation of formaldehyde in-can and air concentrations on Day 3 (a) and on Day 28 (b)

In figure 4-17, the emission of formaldehyde as a function of the in-can concentration is shown for Day 3 (left) and Day 28 (right). No correlation (R^2 <0.2) was found. As seen on both graphs several paints with in-can concentrations of formaldehyde below detection limit emits formaldehyde illustrating the decomposition of organic components, the presence of formaldehyde releasers or other chemical reactions occurring.

1,2-Benzisothiazolin-3-one

The two samples with the highest content of In-can BIT, ID-8 and ID-13 were analyzed for emission of BIT. Air samples were taken 3 days after the samples entered the chamber without preconditioning. For paint ID-8 the air concentration reached 50 μ g/m 3 , whereas Id-13 reached 60 μ g/m 3 .

4.5. Field measurements (cases)

The results of the continuous recordings of temperature and relative humidity during the measurement period can be seen in Appendix 7.6.

During the air quality measurements, both temperature and relative humidity were recorded. These results are presented in Figure 4-18. The temperatures ranged from 16.4°C to 22.0°C across the case rooms. The lowest temperature was observed in Case 3 on Day 3, while the highest temperature was recorded in Case 1 on Day 14. The variations in temperature can be attributed to weather and outdoor temperature conditions, differences in heating and ventilation or varying usage patterns of the room.

The room air temperatures on measurement days were generally slightly higher in Case 1 and 2 compared to Case 3 (with 1-4°C lower air temperatures). High temperatures accelerate the emission process, which can be a smaller contributing factor to a quicker off-gassing process.

The relative humidity was measured in the range of 45% to 78% across all cases. Case 1 showed the most significant variation, with a relative humidity reaching 78% on the day of painting. This measurement was taken towards the end of the painting activity, when the high level of painting activity, combined with the absence of open windows or doors, likely contributed to the elevated humidity. The same applies to Case 2 on Day 0, where a relative humidity of 62% was measured.

*Figure 4-18: Temperature and relative humidity on measurement days. * Some of the measurements were performed at Day 15 and Day 31 due to coordination with participants.*

The air change rate was measured in the three cases in a range of 0.6 to 1.7 air changes per hour (ACH). According to the building regulation BR18, the air change rate should be at least 0.30 l/s pr. m² heated floor area. With a regular ceiling height this corresponds to 0.5 ACH. The measurements in these cases are all relatively high, particularly in Case 2 and Case 3.

In Case 2, a visual assessment of the windows indicated that they were not completely sealed/tight. This could be a contributing factor to the high air change rate observed.

In Case 3, the room conditions changed multiple times during the measurement period. During most of the measurement period, the door was not installed, letting the room air to be mixed with not only the rest of the first floor, but also partially with the floor beneath. To be able to measure the air change rate, the measurement was conducted at the end of the measurement period when the openings towards the staircase were sealed and with the door installed and closed. There was a large gap beneath the door, which made it possible for the room air to partially mix with the air in the rest of the house. Due to the conditions of the room, it is difficult to determine the outdoor air exchange rate, as the room air is also mixed with other air volumes in the house.

The air change rates measured in the three cases were generally high compared to what is typical for dwellings. However, the high measured air change rates may mimic a more typical behavior with higher air change rate when the user is likely to e.g. open windows during and after painting activities.

Table 4-1: Measured air change rate

Total emission of VOC and VVOC

A total of 139 different chemical compounds were detected in the air samples from the case dwellings. The concentration of all detected compounds from each measurement day can be found in Appendix 7.7.

The measured total concentration of VOC (TVOC) and VVOC can be seen in figure 4-19 the SVOC are not shown due to low concentrations.

Figure 4-19: Total concentration of VOC and VVOC

In Case 1 where acrylic wall paint was used, the initial VOC concentration before painting was 419 µg/m³. During painting (Day 0), the VOC level increased significantly to 1060 µg/m³. This increase was followed by a decrease to around background levels around Day 3 where it stabilized for the rest of the measurement period. The VVOC concentration showed similar behavior increasing from 265 µg/m³ (background) to 2030 µg/m³ (Day 0). The VVOC concentration is elevated on Day 31 compared to the background concentration. The major component is, however, ethanol, which may be emitted from many other sources and is likely not related to the painting activity on this day. The maximum SVOC concentration was on Day 15 with a concentration of 14 μ g/m 3 .

In Case 2 where acrylic wall paint was used, the VOC levels before painting were relatively low at 101 μ g/m³. However, there was a significant increase to 20666 μ g/m³ during painting on Day 0. Concentrations of this magnitude overloaded the sampling tube, which means that there is a high uncertainty in the results, and that the concentrations may have been underestimated. This sharp increase was followed by a significant reduction to $344 \mu g/m³$ by Day 3, further decreasing to 270 μ g/m³ by Day 14, and eventually to 213 μ g/m³ by Day 31. The VVOC concentration increased significantly to a concentration of 5403 µg/m³ on Day 0 compared to a background concentration of 50

µg/m³. Background concentrations were reached by Day 3, but were higher at later measurements, likely due to other sources. No SVOCs were detected.

Case 3, where linseed oil paint was used, showed an initial VOC-concentration of 357 μ g/m³ before painting. During painting (Day 0), the VOC levels rose to 1159 µg/m³ and continued to increase to 1317 µg/m³ by Day 3. Subsequently, the VOC levels decreased to 699 µg/m³ by Day 14 and further reduced to 419 μ g/m³ by Day 30. The VVOC also increased after painting, reaching a maximum of 1340 μ g/m³ on Day 14, compared to the background of 715 μ g/m³. It is suspected that there may be another source during the measurement on day 14, as particularly the ethanol concentration was high (819 µg/m³) along with limonene (often used for fragrance) being more than twice the concentration of the background measurement. The highest SVOC concentration was found on the day of painting, at 7 μ g/m³.

The data indicates that painting significantly contributed to the emission of VOCs in indoor environments. There is a notable decline in VOC levels over time, reaching concentrations close to background levels relatively quickly (within 3 days for the acrylic paints, and between 14-30 days for the linseed oil paint). Other studies have shown that linseed oil products, including paints, can contribute to higher emissions of certain aldehydes and carboxylic acids, especially when wood and clay surfaces are painted or treated (Danish Ministry of Environment, 2019; Realdania, 2018).

The results of Case 1 and 2 with acrylic paint generally show a peak of concentrations on Day 0, whereas the results of Case 3 with linseed oil continue to increase on Day 3. The reason for this could either be found in the hardening of the used paints or the circumstances of which the measurements were taken. Although the measurements were taken on the day of painting in all cases, the circumstances and painting activities were different, which can influence the results. In Case 1, the painting activity was almost done when the measurements started. This could result in higher concentrations in the room. In Case 2 the measurements were conducted while wall areas were being painted, hence larger areas with exposed, wet paint were present. In Case 3, the measurements were conducted when the painting activity had just started, hence smaller areas with wet paint were exposed.

As for the painting process, the choice of paint type also has an impact on potential exposure. Applying linseed oil, as in Case 3, requires a thin layer, resulting in a slower application process compared to acrylic paint, which can be applied more quickly. Consequently, this can lead to a longer exposure time doing the painting activity.

The high ventilation rates measured in the three cases likely accelerated the emission of chemical compounds, resulting in faster off-gassing. Consequently, this not only sped up the process of offgassing but also facilitated the quicker exchange of air in the room, allowing concentrations to reach background levels more rapidly. This highlights the importance of ventilating rooms during and after painting activities to minimize the exposure to unwanted chemicals.

Emission of specific chemical groups

The analysis of painting activity contributions across three different cases reveals distinct patterns in the presence of various chemical compounds and groups.

When discussing the trends the compounds have been grouped into the following categories: aldehydes; ketones; alcohols; glycols, ethers, esters; aliphatic hydrocarbons (including cyclic compounds); aromatic hydrocarbons; terpenes; organic acids; and others.

The distribution of compounds by functional group can be found in figure 4-20.

Case 1

The largest contributors, making up over 10% of the total concentration, are aldehydes; alcohols; glycols, ethers, and esters. Aldehydes, particularly acetaldehyde and formaldehyde, show a clear correlation with painting activities, with levels quickly returning to background concentrations within days. Ketones, including acetone and 2-butanone, also seem to be correlated with the paint. Alcohols such as ethanol, isopropanol, n-butanol, and tert-butanol increase noticeably on the day of painting. Ethanol is the largest contributor but has many different sources and indoor air concentrations can vary a lot. The group '*Glycols, ethers, and esters'* is strongly correlated with paint use, with ethyl acetate and dibutyl ether being the largest contributors, but 1,2-propanediol exceeding the UBA guideline value. Aliphatic hydrocarbons show a correlation but at lower concentrations, primarily involving unidentified iso/cyclo-alkanes. The concentration of aromatic hydrocarbons is low but shows a slight increase, due to xylenes only being detected on the day of painting. Terpenes and organic acids do not correlate with paint activities. '*Other compounds*' generally show minimal changes individually.

Case 2

The largest contributors to room air concentrations are aliphatic hydrocarbons and aromatic hydrocarbons, though aldehydes, alcohols, ketones, glycols, ethers, and esters are also higher in concentration than any concentration measured in the other two cases.

Aldehydes, mainly acetaldehyde, and ketones, primarily acetone and 2-butanone, exhibit clear correlations with the painting activity. Alcohols, especially ethanol and 2-propanol, show significant increases, with 2-butanol and tert-butanol also correlated but at lower concentrations. Glycols, ethers, and esters, mainly ethyl acetate, display clear correlations with the painting activities. Aliphatic hydrocarbons, including 3-methyl hexane and C6-C11 iso/cyclo-alkanes, are significantly correlated with the painting activities. Aromatic hydrocarbons, such as various benzenes, xylenes, and p-cymene, also show clear correlations. Terpenes, mainly limonene, correlate with the painting activities, as it peaks on the day of painting. As limonene is a frequently used perfume compound,

it may have other sources. Organic acids are difficult to correlate due to fluctuation, with only acetic acid detected. Other compounds do not show a strong correlation.

The spot sealer contains several aliphatic hydrocarbons and cycloalkanes (declared in the safety data sheet). Due to the spot sealer being an aerosolizing spray, it can be assumed that the spot sealer most likely impacted the results of VOC concentrations. This emphasizes the importance of not only focusing on the paint itself but on all used products during a renovation process.

The measured concentrations of VOC decreased to a background level 3 days after the painting activity, which is notably quick. A ventilation rate of 1.6 was measured in this room, which is high considering that the room is naturally ventilated and does not have direct/open connections to other rooms, an attic, or other spaces. However, the room contains several hatches (one in the ceiling and one in the wall) and is generally not airtight, allowing air to seep in and out. It is likely that the high ventilation rate contributed to the rapid decrease in VOC concentrations.

Case 3

The largest contributors are aldehydes, organic acids, and alcohols. Aldehydes, including propanal, n-hexanal, and acetaldehyde, correlate with paint. Ketones, mainly acetone, also correlate. Alcohols fluctuate significantly, mainly due to the ethanol concentration, 1-penten-3-ol however seems paint-related. Glycols, ethers, and esters, mainly hexylene glycol, correlate with paint. Aliphatic hydrocarbons generally do not correlate. Aromatic hydrocarbons, mainly xylenes, correlate with paint. Terpenes do not correlate, while organic acids show the highest levels on Day 3, possibly due to curing of the paint. Other compounds generally show no overall correlation, except for 2 ethylfuran and other furanes, though they are at a low concentration.

Figure 4-20: Distribution of detected compounds by functional group

Overall, the data indicates that compounds within the chemical groups; aldehydes; ketones; alcohols; glycols, ethers and esters, were correlated with painting activities across all cases using different paints. Hydrocarbons were emitted from both acrylic paints in Case 1 and 2, but not notably in Case 3 with the linseed oil paint. Terpenes were detected at all locations but are likely from other sources. Organic acids were mainly found in Case 3, with some acids seemingly well-correlated with the painting activities.

Emission of ammonia and BIT/OIT

The results of ammonia, 1,2-Benzisothiazol-3(2H)-one (BIT) and 2-octyl-1,2-thiazol-3-one (OIT) can be seen in Figure 4-21.

Ammonia was detected in two out of three cases. In Case 1, the measured concentration of 40 μg/m³ on Day 3 corresponds to the concentration measured before the painting activity. Therefore, it is assumed that the measured concentrations do not originate from the paint but from other sources in the room.

In Case 2, ammonia was measured at a concentration of 140 μg/m³, which is over four times higher than the concentration measured before the painting activity. This indicates that the painting activity results in elevated ammonia emission persisting several days after the activity.

On Day 3, BIT was detected in two out of three cases. The measured concentrations were 60 μg/m³ in Case 2 and 20 μ g/m³ in Case 3. According to the safety data sheets, the paints used in Case 1 and Case 2 contained BIT in specified amounts. However, BIT was not detected in Case 1.

OIT was not detected in any of the cases.

Figure 4-21: Total concentration of ammonia and BIT

Exceedances of guideline values

The results are evaluated in relation to the German Committee on Indoor Air Guide Values I (precautionary guide value). These guideline values "*describes the concentration of a substance in indoor air for which or below which, according to current knowledge, adverse effects on health are not to be expected even after a lifetime of exposure*" (Umwelt Bundesamt, 2023). Some of the guideline values are for specific compounds while others are for a sum of several compounds or a calculated risk factor. Exceedances of UBA guideline values are listed in Table 4-2.

In most cases the exceedances are only on the day of painting, whereafter the concentrations decrease to an acceptable level. However, the sum concentration of C4 - C11 aldehydes in case 3 is above the guideline values during a period of more than 14 days before decreasing to an acceptable level on the Day 30 measurement.

Table 4-2: Exceedances of UBA guideline values, unit [µg/m3]

***Calculated as a risk factor [without unit].**

Dash (-) indicates a concentration below the guideline value.

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5. Conclusions

The primary objective of this study was to investigate the presence of unwanted chemicals in interior paints available on the Danish market. The goal was to provide consumers with the necessary information to make informed choices and to push for the phase-out of harmful substances from consumer products. The importance of identifying and mitigating these chemicals cannot be overstated, given their potential health and environmental impacts. The final evaluation of each paint, based on these results, will be conducted by the Danish Consumer Council and published online for public access.

The in-can analysis revealed that biocides, especially benzothiazolinone (BIT), were prevalent in over half of the samples. This raise concerns due to BIT's potential as a skin sensitizer. Formaldehyde was detected in 11 out of 30 samples, though in low concentration, indicating the effect of the compound being regulated. The pH levels varied widely, with some paints being highly alkaline, which can cause skin irritation.

Heavy metal analysis showed significant variations, with lead, chromium, and zinc detected in various samples. Some samples contained heavy metals at levels exceeding safe limits for clean waste, posing potential health and environmental risks. The odour evaluation indicated that wall paints generally received better ratings than wood/metal paints, with plant-based and mineral paints showing less difference in ratings.

Additionally, the analysis of total organic fluorine (TOF) content revealed that 22 samples contained organic fluorine. Most samples (n=17) showed concentrations below 50 mg/kg and are considered as background contamination levels and not intended. Two samples showed particularly high levels >300 mg/kg. A specific analysis of 50 PFAS compounds performed on these two paint samples did not result in any detected specific PFAS compound. This underscores the importance of not only analyzing specific compounds but also performing a broad screening to thoroughly investigate the presence of PFAS.

Emission testing highlighted higher initial TVOC emissions from plastic paints, which decreased over time. Especially two organic solvent paints had a very high emission rate in the first days. For all paints, emission of TVOC and the calculated risk value decreased to an acceptable level in the course of weeks. The emission of formaldehyde was relatively low for all paint samples. Some paints with In-can concentrations of formaldehyde below detection limit were found to emit formaldehyde indicating presence of formaldehyde releasers. Ammonia emissions were noted in certain plastic paints, indicating potential respiratory risks. And for some paints, CMR compounds were detected in the first day's emissions. Also, the risk value was high in the first week.

There are some health implications in these findings. Initial emission of VOCs, biocides, and ammonia from some paints can pose acute health risks, particularly affecting respiratory health and potentially causing skin irritation or sensitization. Long-term exposure to VOCs can contribute to

various health issues. However, emission of both VOCs and formaldehyde decreased over time. It is worth mentioning that during the emission test, the paint samples were well ventilated. Ventilation and temperature are crucial for the curing of the paint and the decrease in emissions.

Environmental implications include the impact of improper disposal of paints containing harmful metal, which can lead to soil and water contamination. This underscores the need for manufacturing sustainable paints and proper disposal practices within the paint industry.

In the field measurements, 139 different chemical compounds were detected across three cases. Volatile organic compounds (VOCs) and very volatile organic compounds (VVOCs) levels peaked on painting days for the two acrylic paints, then rapidly declined to near background concentrations within three days. In contrast, linseed oil paint exhibited a slower reduction, with background levels reached between 14-30 days, resulting in prolonged exposure. The use of an aerosolizing spot sealer in Case 2 likely inflated VOC concentrations on the painting day, highlighting the importance of considering all products used, and not just paint.

The data indicates that painting activities are significant sources of indoor VOCs, influenced by paint type and timing within the painting process. Aldehydes; ketones; alcohols; and glycols, ethers, and esters were closely correlated with painting activities, while hydrocarbons were predominantly linked to the two cases using acrylic paints. Ammonia increased due to the painting activity in one of the three cases, and BIT was detected in two, including one where it was not declared in the safety data sheet.

Exceedances of the German Committee on Indoor Air Guide Values I were primarily observed on the painting day, with most concentrations returning to acceptable levels within days. However, Case 3 had prolonged exceedances of aldehyde concentrations, indicating a need for extended ventilation for linseed oil paints.

This study underscores the necessity of adequate ventilation during and after painting to expedite off-gassing and exchange polluted air, reducing exposure to harmful compounds.

The overall findings emphasize the importance of understanding the specific chemical emissions associated with different paint types and the environmental conditions that influence these emissions. Consumers are encouraged to select paints with lower or no harmful chemicals, guided by reliable labelling, certification schemes, and the Danish Consumer Council's recommendations. Choosing paints with absence of heavy metals, BIT and lower initial VOCs emission is encouraged, resulting in a lower health risk and reducing the environmental impact.

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7. Appendix

7.1. Odour evaluation scale

7.2. Description of Field Cases

Case 1

Case 1 is a bedroom on the first floor in a villa built in1938. The villa spans approximately 150 sqm across two floors and a basement and has been renovated within the last 5 years. The house is equipped with a mechanical ventilation system, which, however, remains inactive. Hence, the house is naturally ventilated. The bedroom, that was painted, has a volume of approximately 38 $m³$ and has windows orientated towards south and east. The wall facing south was a sloping wall. The paint used for the painting activity was an acrylic wall paint, gloss 5. According to the safety data sheet the paint contained the chemical compounds BIT, CIT, and C(M)IT/MIT (3:1). The painted surfaces were primarily gypsum.

The bedroom was furnished with a bed, closet, a clothes rack and decoration during the entire measurement period. This can be seen in the pictures.

Case 2

Case 2 is a bedroom on the first floor in a villa built in 1919 and renovated in 1943. The houseowner recently bought the house and plans to paint most of the interior walls. The house is naturally ventilated. The bedroom has a volume of 16 m³ and has two sloping walls facing north and south and a window towards east. The paint used for the activity was an acrylic wall paint, gloss 5. The painted surfaces were gypsum and profiled boards. In addition, the house owner informed that a great amount of spot sealer was used before the painting activity. According to the safety data sheet the wall paint contained the chemical compounds BIT and C(M)IT/MIT (3:1). The safety data sheet of the spot sealer informed about several compounds such as acetone, titanium dioxide, nbutyl acetate, ethyl acetate, cyclohexane, n-hexane, as well as the following three groups: Hydrocarbons, C6-C7, n-alkanes, isoalkanes, cyclics, <5% n-hexane; hydrocarbons, C9-C10, n-alkanes, isoalkanes, cyclics, <2% aromatics; fatty acids, tall-oil, compounds with oleylamine. The last three groups having the respective REACH identification numbers: 01-2119475514-35, 01-2119471843- 32, and 01-2119474148-28.

The room was unfurnished at the measurements taken before, during and 3 days after the painting activity. After that, some furniture was placed in the bedroom, but it was kept unused during the entire measurement period.

Case 3

Case 3 is a bedroom on the first floor of a house from 1917. The house was under renovation during the measurement period and had been so for the past 4 years. The house is naturally ventilated. The room is approximately 13 $m³$ and has a sloping wall facing southeast, where the window is also located. The paint used for the activity is a paint based on boiled linseed oil, grinded color paste and siccative. The paint was mixed by the house owner. The painted surfaces were primarily oriented strand boards (OSB) and solid pine wood.

During most of the measurement period, the internal door to the room was not installed, which means there was an open connection to the hallway, the open staircase, and thus the entrance on the lower floor. The room was left unfurnished during the entire measurement period.

7.3. List of 50 specific PFAS

PFBA (Perfluorobutanoic acid) PFPeA (Perfluoropentanoic acid) PFHxA (Perfluorohexanoic acid) PFHpA (Perfluoroheptanoic acid) PFOA (Perfluorooctanoic acid) PFNA (Perfluorononanoic acid) PFDA (Perfluorodecanoic acid) PFUdA (Perfluoroundecanoic acid) PFDoA (Perfluorododecanoic acid) PFTrDA (Perfluorotridecanoic acid) PFTeDA (Perfluorotetradecanoic acid) PFHxDA (Perfluorohexadecanoic acid) PFODA (Perfluorooctadecanoic acid) PFBS (Perfluorobutanesulfonic acid) PFPeS (Perfluoropentanesulfonic acid) PFHxS (Perfluorohexanesulfonic acid) PFHpS (Perfluoroheptanesulfonic acid) PFOS (Perfluorooctanesulfonic acid) PFNS (Perfluorononanesulfonic acid) PFDS (Perfluorodecanesulfonic acid) PFUnDS (Perfluoroundecanesulfonic acid) PFDoS (Perfluorododecanesulfonic acid) PFTrDS (Perfluorotridecanesulfonic acid) 6:2 FTS (Fluorotelomer sulfonate) 8:2 FTS (Fluorotelomer sulfonate) 0:2 FTS (Fluorotelomer sulfonic acid) 6:2 diPAP (Fluorotelomer phosphate diester) 8:2 diPAP (Fluorotelomer phosphate diester) 6:2 FTOH (Fluorotelomer alcohol) 8:2 FTOH (Fluorotelomer alcohol) 0:2 FTOH (Fluorotelomer alcohol) 2:2 FTOH (Fluorotelomer alcohol) EtFOSA (N-ethylperfluorooctane sulfonamide) EtFOSAA (N-ethylperfluorooctane sulfonamide) EtFOSE (N-ethylperfluorooctane sulfonamido ethanol) MeFOSAA (N-methylperfluorooctane sulfonamide)

MeFOSE (N-methylperfluorooctane sulfonamide) MeFOSA (N-methylperfluorooctane sulfonamide) FOSAA (Perfluorooctane sulfonamidoacetic acid) PFBSA (Perfluorobutane sulfonamide) PFHxSA (Perfluorohexane sulfonamide) PFOSA (Perfluorooctane sulfonamide) 3:3 FTCA (Fluorotelomer carboxylic acid) 5:3 FTCA (Fluorotelomer carboxylic acid) 7:3 FTCA (Fluorotelomer carboxylic acid) Capstone B (6:2 FTAB) Capstone A (DPOSA) 6:2/8:2 diPAP (Fluorotelomer phosphate diester) diSAmPAP (Perfluorooctane sulfonamide phosphate diester) HFPO-DA (GenX)

7.4. Heavy metal concentrations

7.5. VOC results from emission tests

Separate excel file

7.6. TVOC results of all paints and measuring times

7.7. Temperature and relative humidity

Day 0 = 03.03.2024, day 3 = 06.03.2024, day 15 = 18.03.2024, day 30 = 02.04.2024

There are no continuous measurements from Case 3.

Day 0 = 11.03.2024, day 3 = 14.03.2024, day 14 = 25.03.2024, day 31 = 11.04.2024

7.8. VOC results of field measurements

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Compounds detected in field measurements and their concentrations in μ g/m³. <C6 indicates that the compound elutes from the gas chromatograph before hexane, classifying it as a VVOC, similarly >C16 indicates that the compound elutes from the gas chromatograph after hexadecane, classifying it as an SVOC. Unlabeled compounds fall in between in the VOC (TVOC) category. Parentheses as subscripts indicate that the detected compound has been quantified against a standard of the compound in the subscripted parenthesis.