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Hazard and exposure assessment of do-it-yourself products for impregnation

Survey of chemical substances in consumer products No. 189

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Editors:
Sara Højriis (COWI A/S)
Frans Christensen (COWI A/S)
Carsten Lassen (COWI A/S)
Vladimir Nikiforov (NILU)
Jorid Birkelund Sørli (NFA)
Alexander Christian Østerskov Jensen (NFA)

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Preface

This report contains the results of the project "Hazard and exposure assessment of do-it-yourself products for impregnation". The project is part of the Political Agreement on new joint chemicals initiatives 2018-21, which i.e. focuses on making consumers feel safe when buying food and products. The project has aimed to build knowledge about impregnating products on the market, as well as to get an indication of whether some impregnating products (aerosol-spray) pose an acute hazard to consumers. In addition, it has been desired to gather knowledge about impregnating products applied by methods other than aerosol sprays[1]. The project has also supported the work of gathering information on an alternative test method to identify potential hazards of consumer products by inhalation. This method is not performed on experimental animals,

The project has been carried out by COWI with the National Research Centre for the Working Environment (NFA) as a subcontractor for in vitro tests and exposure assessment and the Norwegian Institute for Air Research (NILU) as a subcontractor for the chemical analyses. Total fluorine content was measured at Örebro University by Prof. Leo Yeung. NMR spectra were acquired at the University of Tromsø by Dr. Truls Ingebrigtsen.

The project was carried out during the period May 2020 to October 2021.

[1] Aerosol spray is also referred to as "spray can"

Summary and conclusion

Hazard and exposure assessment of do-it-yourself products for impregnation

A large number of do-it-yourself impregnation products are marketed to Danish consumers. The products are typically used for re-impregnation of consumer products immediately after the products have been purchased or when the water and/or dirt-repellent effect begins to diminish. This concerns, for example, products for re-impregnation of footwear and outdoor clothing.

Purpose

The purpose of this project is partly to build knowledge about do-it-yourself impregnation products on the market available for Danish consumers, and partly to get an indication of whether some spray impregnating agents pose an acute hazard to the consumer. Information about what is on the market in terms of alternatives to impregnation products based on aerosol sprays, such as pump sprays, has been collected in order to get an idea of what is available.

The first phase of the project consisted of a survey of typical do-it-yourself waterproofing products available to Danish consumers. This phase was followed by a selection of products for laboratory tests. The laboratory tests, which constituted phases two to four of the project, included a study of acute *in vitro* [2] respiratory toxicity, chemical content analysis and a study of the potential for exposure of consumers, using chamber tests and modelling. The study did not aim to reach a definitive risk assessment of consumer exposure, but the results of the laboratory tests and chemical content analyses may be used as input for such assessments in future studies.

Survey

A total of 110 do-it-yourself impregnation products in ten different use categories were identified. For the vast majority of these impregnation products, the active substance was not indicated in the collected product information (safety data sheets, packaging and supplier's websites). The substance group for the active substance was identified for approx. 1/5 of the products; the identified active substances were primarily "siloxane" and/or "silicone".

In order to assess the tonnage of impregnation products sold in Denmark, ten dealers and distributors in Denmark were contacted. Unfortunately, most of the contacted dealers did not respond to the inquiries or did not return usable information. Consequently, in this project we only managed to collect information on two areas of application, "Outdoor Equipment" and "Furniture". A broader understanding of how large a share of the market the various use categories account for could not be established.

Data for the European market indicate that products for the impregnation of textiles and footwear constitute a significant share of the market for impregnation products for consumers. Using these data, it could be estimated in this report that every household in Denmark buys an impregnation product in one of these two use categories every 3 to 4 years on average (corresponding to approximately 400,000 units per year).

Of the 110 identified do-it-yourself impregnation products, 15 products were selected for initial chemical content analyses and hazard and exposure analyses. The products were selected in

[2] *In vitro* (Latin: in glass) tests are laboratory tests which do not involve living organisms in their normal biological context.

consultation with the Danish Environmental Protection Agency using selection criteria established as part of the investigation. As one product was not received after ordering, only 14 products were included in the analyses. Of these 14 products, 6 products were selected for sample-specific analysis, based on the results of the initial chemical content analysis and the hazard and exposure analyses.

Impregnation and toxic effects

The toxicity of an impregnation product depends on the chemical composition of the product. Typically, an impregnation product consists of active substances, solvents and propellants. In addition, the particle size distribution and the particle concentration of the formed aerosols could affect the toxicity. Active substances, aerosol release, aerosol sizes and solvents have all been shown in previous studies to have an effect on the toxicity of an impregnation product. There is broad scientific consensus that the use of propellants such as propane and butane isomers does not in itself pose a risk to the consumer. However, it cannot be ruled out that synergistic effects between propellants and the active substance may occur. At present, it is not possible to assess whether an impregnation product is hazardous to health without an examination of the individual product.

Impregnation products with per- and polyfluoroalkylated substances (PFAS) are the most studied products as concerns the cause of toxic effects. Several studies have shown that the toxic effect of impregnation products may be caused by the product's effect on the lung surfactant, which is a thin liquid film that covers the bronchioles and alveoli in the lungs. Although the scientific evidence is heaviest for impregnation products with fluorinated compounds, studies have shown that impregnation products without fluorinated components, but with alkylsilane/siloxane, can also affect the lung surfactant and have a harmful effect in humans and mice.

At present, it is difficult to distinguish between impregnation products that can potentially cause toxic effects for the consumer and those that cannot cause damage. However, the results indicate that there is generally a greater risk that the product may cause damage when using aerosol sprays with organic solvents, as aerosol sprays to a greater extent form droplets/particles which, when inhaled, can reach the deeper regions of the lungs where the chemical mixture may affect the lung surfactant.

Chemical content analysis

NMR spectroscopy and gas and liquid chromatography in combination with mass spectrometry (GC/MS and LC/MS) were used for chemical content analysis of 14 impregnation sprays. The main components in the majority of the products were saturated hydrocarbons, but some of the products contained a smaller or larger proportion of oxygen-containing solvents, such as alcohols, ethers, esters or ketones.

Ten products contained mixtures of methylsiloxane derivatives. Their concentration was estimated to be in the range of 1.3 - 5.1% by weight. Such siloxanes are common components in many household and personal care products.

Two products were found to contain an assumed perfluorocarboxylic acid (PFCA) precursor. Data from the chemical analysis suggest that it is a polymer or oligomer containing fragments of perfluorohexylethyl methacrylate (6:2 FTMA). The samples showed the presence of 6:2 fluorotelomeric alcohol (6:2 FTOH) after hydrolysis and C4-C7 perfluorocarboxylic acids after oxidation. The concentration of the polymer (calculated as 6:2 FTMA) was calculated to be 0.53% in one product and 0.27% in the other, but these concentrations must be considered as minimum concentrations with the method used. The “fluorinated polymer” was stated in the safety data sheet (SDS) for one of the products, but not in the data sheets for the other product.

Furthermore, the plasticizer bis(2-ethylhexyl) phthalate (DEHP) was found in all but two products, in concentrations of 0.2-2.1% by weight.

Hazard and exposure assessment

An investigation of the potential hazard of 12 selected impregnation spray products was performed by measuring acute respiratory toxicity using an *in vitro* method that measures the concentration at which the products inhibit the lung surfactant. The lung surfactant covers the inside of the lung; its function is to regulate the surface tension when the surface area of the lungs varies during breathing. As the surface area of the lungs becomes smaller, the lung surfactant lowers the surface tension to very low levels (<5 mN/m). If the function of the lung surfactant is inhibited, the surface tension will not be lowered sufficiently. The consequence is that parts of the lungs collapse and the person have difficulty in breathing and start coughing. Of the 12 products tested, 10 products inhibited the function of the lung surfactant and may therefore potentially be harmful by inhalation. In the test, the products were compared with a PFAS-based product (NFP1), which in previous studies has been demonstrated to have a significant health effect. It has been subject to use restriction at the EU level from 1 January 2021. The only one of the selected products containing PFAS did not show the same inhibitory effect as NFP1, whereas several other impregnation products had a greater inhibitory effect than the PFAS-containing product studied in this project. All selected products had less inhibitory effect than NFP1 in the performed in vitro tests. Thus, no tendency could be demonstrated that products based on PFAS are more effective at inhibiting the lung surfactant than other products, but the number of products is too small to provide a clear conclusion. A number of products based on siloxanes/silicones showed inhibition of the lung surfactant at a dose of 2-4 times the inhibitory dose of NFP1.

The emission rate has a large influence on the exposure of the user. For the exposure assessment, measurements of aerosol composition were made on the same 12 products. The products were sprayed into a chamber and in the chamber, the amount and size of the droplets released from the products were measured. The results from these measurements were used to model the respirable concentrations in the air for two different use scenarios as part of an exposure assessment. The emission rates ranged from 0.28 to 3.35 mg/s. The emission rate of the pump spray product tested resulted, as expected, in the lowest measured emission rate.

Discussion and conclusion

The study shows that the majority of the solvent-based agents that could be tested had an inhibitory effect on the lung surfactant. The only water-based product did not show inhibition of the lung surfactant, which is consistent with previous studies. The product is applied by pump spray, and this resulted in a significantly lower emission rate for respirable particles from this product compared to the other products applied by aerosol spray. The result therefore shows that some products are available to the consumer that are expected to have considerably fewer significant health effects than the majority of the marketed impregnation products which are based on organic solvents and applied using an aerosol spray.

Apart from the importance of solvent, there was no pattern in which ingredients were able to inhibit the lung surfactant in *in vitro* experiments. It could not be demonstrated that the presence of PFAS resulted in an inhibition of the lung surfactant at lower doses; in fact, the lowest inhibitory doses were seen for impregnating agents based on siloxanes/silicones.

One of the products based on siloxanes/silicones and organic solvents did not have any inhibitory effect on the lung surfactant, demonstrating that it is difficult to draw unambiguous conclusions. The results show that the hazardous properties of an impregnation product cannot be determined solely on the basis of the ingredients, and it is therefore necessary to examine the ability of the individual products to inhibit the lung surfactant in connection with a hazard assessment.

The results of the project are part of a larger effort to gather knowledge about how different chemical substances and mixtures in consumer products inhibit the lung surfactant *in vitro*. By comparing results from the *in vitro* test with knowledge on how human and exposed experimental animals react to the same or similar exposures, the project supports the work of using an alternative test method, not performed on experimental animals, to identify hazard by inhalation.

1. Introduction

1.1 Background

A number of different products impregnated/surface-treated by the manufacturer are marketed to Danish consumers. Some of these products are re-impregnated by the consumer immediately after the purchase, or when the water and/or dirt repellent effect begins to diminish. Examples of products that are impregnated with do-it-yourself impregnation products are various types of textiles (e.g. outdoor clothing and tents), footwear, building materials and touch screens on electronics.

Impregnation products used for surface treatment can be both with and without per- and polyfluoroalkyl substances (PFAS). PFAS are used for surface treatment of a wide range of consumer products, as it makes the products water, grease and dirt repellent. However, PFAS have been considered problematic for many years due to negative environmental and health effects.

Denmark and other EU countries regularly report cases where consumers have been poisoned after indoor use of aerosol-spray-impregnation products on larger items without adequate ventilation. The present project consequently focuses mainly on "do-it-yourself" impregnating products applied with aerosol-spray.

As this report concerns waterproofing products marketed to consumers, the term "impregnation products" will be used as a synonym for "do-it-yourself" impregnation products.

1.2 Objective

The purpose of the project is in part to build knowledge about do-it-yourself impregnation products on the market, and in part to get an indication of whether some spray impregnating agents pose an acute hazard to the consumer. The project will also contribute with knowledge about available alternatives to aerosol-spray impregnation products, e.g., products with pump-spray. Impregnation products that have previously caused poisoning have primarily been aerosol-sprays, and the likelihood of alternative products posing an acute hazard is therefore expected to be lower than with products applied with aerosol-sprays. The accumulated knowledge about the market for alternative impregnation products may be included in future projects.

The project consisted of four activities:

- Phase 1: Survey of impregnation products (both spray products and impregnation products applied by other methods) which are marketed to consumers in Denmark.
- Phase 2: Investigation of the potential hazard of selected products by measuring acute respiratory toxicity (*in vitro*).
- Phase 3: Chemical analyses of selected products.
- Phase 4: Investigation of the exposure potential with chamber testing and modelling.

2. Legislation

This chapter contains a description of the legislation relevant to do-it-yourself impregnating products as well as restrictions on the use of PFAS covering the use of these substances in do-it-yourself impregnation products.

2.1 CLP Regulation

CLP Regulation ((EC) No 1272/2008) includes, with certain exceptions[3] chemical substances and mixtures marketed in the EU. Do-it-yourself impregnation products are typically covered by the regulation. The regulation obliges EU companies that produce, import, distribute or use substances or mixtures to ensure uniform classification, labelling and packaging of these products. The regulation covers both substances sold to private consumers and substances for professional use.

Classification and labelling of impregnation products under CLP can be particularly challenging, as the mixture potentially can be acutely toxic by inhalation, although the individual ingredients in the mixture themselves are not toxic by inhalation. According to Article 12 of the CLP, the companies are obliged to take this synergistic effect into account, but in many cases it can be difficult in advance to determine whether this effect will occur. This issue is further described in Appendix 4.

The purpose of labelling is to inform the user of the product of hazard, and how the product is used and disposed safely.

2.2 REACH Regulation

The REACH Regulation ((EC) No 1907/2006) applies to chemical substances marketed in the EU, both for use in industrial processes and in mixtures or articles. The regulation obliges EU companies that produce, imports, distribute or use chemical substances or mixtures, to register import and/or manufacture of the substances. The manufacturing, marketing and use of substances, mixtures and articles are regulated, e.g., through restrictions of use (REACH, Annex XVII) and an authorization scheme (REACH, Annex XIV).

After several reported cases of poisoning after use of impregnation sprays, containing a combination of certain polyfluorosilanes[4] and organic solvents, as well as studies that showed the same type of impregnation spray can penetrate deep into the lung and cause lung damage to mice, the Danish Environmental Protection Agency prepared a proposal to ban the marketing of spray products with this combination of ingredients at EU level. The proposal specifically concerned products that are marketed for consumer use. Following consideration by the EU Chemicals Agency, the European Commission has prepared a restriction on use with a ban on the sale of sprays containing this combination of ingredients after 1 January 2021 (Annex XVII of the REACH Regulation, entry 73).

[3] As an example, chemical substances in medicines are not included

[4] (3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl) silanetriol tri-O- (alkyl). These belong to the group of polyfluorooctyl trialkoxysilanes and are often abbreviated "TDFAs"

Manufacturing, marketing and use of perfluorooctanoic acid (PFOA), its salts and related compounds have previously been included in REACH, Annex XVII (entry 68)[5]. This restriction included the presence of the substance, e.g., mixtures and articles, in concentrations of ≥ 25 ppb (parts per billion) of PFOA and its salts, and 1,000 ppb of a PFOA-related substance or a combination of PFOA-related substances. The restriction of PFOA, its salts and related compounds was regulated in the POPs Regulation ((EC) No 850/2004) [6], [7] as of the 3rd of December 2020. The limit value established for PFOA, its salts and PFOA-related compounds in the POPs Regulation is set at 0.025 mg/kg (25 ppb) for PFOA and its salts, and at 1 mg/kg (1,000 ppb) for each PFOA-related compound or combination of these compounds.

2.3 Stockholm Convention and the POPs Regulation

The Stockholm Convention is a global treaty with the aim of protecting both the environment and humans from highly persistent organic pollutants (POPs). Several organic fluorinated compounds are included in the treaty. Perfluorooctanoic acid (PFOA), its salts and related compounds, as well as perfluorooctanesulfonic acid (PFOS), its salt and perfluoroctanesulfonylfluorid (PFOSF) are included in the Stockholm Convention, resulting in global restrictions on the substances. In addition, perfluorohexanesulfonic acid (PFHxS) and its related compounds are under review for inclusion under the Stockholm Convention but are not yet included in the Convention. The requirements of the Stockholm Convention are in the EU implemented in the POPs Regulation.

[5] Entered into force July 2020

[6] POPs: Persistent organic pollutants.

[7] https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32020R0784&from=EN

3. The chemistry of impregnating agents and their function

Due to the focus on banning/restricting PFAS as an ingredient in impregnation products (see e.g. Chapter 2), various new techniques and chemical substances are undergoing intensive research and development. A comprehensive overview of techniques and chemical substances is limited by the fact that details of these techniques and substances are often considered trade secrets. Appendix 3 provides a general overview of the basic chemistry and functions of impregnation products and various active substances, including various chemical groups: "Paraffin/wax emulsions", "Silanes, siloxanes and silicones", "Vinyl, (meth-) acrylate and di-isocyanate/polyurethane chemistry", "Dendrimers", "Nanotechnology" and "other types of chemistry".

4. Previous projects addressing impregnation products on the Danish market

In this chapter previous studies related to this project are reviewed.

Studies and surveys of the Danish market before 2008 are not included as it is considered that the listed substances and products have largely been replaced, and the indicated substances consequently are not representative of products available to Danish consumers in 2020.

The Danish Environmental Protection Agency (EPA) has previously published two relevant reports on impregnation products on the Danish market:

- "Survey and environmental/health assessment of fluorinated substances in impregnated consumer products and impregnating agents" (Jensen & Poulsen, 2008).
- "Survey and health assessment of possible health hazardous compounds in proofing sprays" (Feilberg et al., 2008).

Both studies are twelve years old, and the likelihood is that the market for impregnation products has changed to a certain extent, both in terms of the product and the chemical content of the products.

Jensen & Poulsen (2008) investigated impregnation products containing fluorine compounds used in Denmark. During the project, it was not possible to map the Danish market for consumer products, and therefore the study does not contain information relevant to the current mapping of impregnation products on the market in 2020.

Two relevant studies identified are described below: Feilberg et al. (2008) and a study published by the Danish Consumer Council THINK Chemicals in 2017 (a study of 11 impregnation products for textiles).

Feilberg et al. (2008)
This report includes a survey and health assessment of possible harmful components in spray products for textile impregnation. The project consisted of a literature review and an information search regarding cases of poisoning after exposure to textile impregnation, a survey of textile impregnation products on the Danish market as well as chemical analyses and a health assessment of a number of selected impregnation products.

During the survey, it was not possible for Feilberg et al. (2008) to estimate the tonnage of sold impregnation products, and selection criteria for products for the further chemical and health analysis were based on: "*… that spray as well as pump products should be represented, that fluorine as well as silicone based products should be investigated and that products with known as well as unknown substances should be examined.*" (Feilberg et al. 2008. p. 40)

The chemical analyses consisted of an elemental analysis for fluorine and silicon in the surface coating of impregnated textiles by X-ray spectroscopy and a screening for the content of volatile and semi-volatile organic substances in the aerosol mist by gas chromatography with mass spectrometric detection (GC/MS). The result of the chemical analysis showed that 13 out of 16 products for impregnating textiles had fluorocarbon substances as active substances, and a single product contained a small amount of fluorine and substantially more silicon.

The analyses of the volatile and semi-volatile organic compounds showed that 10 products contained high levels of hydrocarbons in the form of hydrocarbon mixtures that functioned as organic solvents. In addition, most products contained a varying amount of polar organic solvents. A few products contained aromatic compounds and a single product contained chlorinated solvents.

In addition to the screening of active substances in the impregnation products, Feilberg et al. (2008) also made a quantitative analysis of 14 substances contained in the selected products, e.g., various fluorine compounds. However, Feilberg et al. (2008) did not succeed in identifying the exact chemical structures of the detected fluorinated substances. The explanation may be that the active substance is designed to polymerize on contact with air and thus form an impregnation coating. It would therefore not be present in the products as a detectable single substance. The investigation led to no conclusive health assessment.

The report concluded that the type of solvents, specific fluorinated substances and the aerosol may have an impact on observed cases of poisoning, but the exact reason could not be inferred from the literature available at that time.

The Danish Consumer Council THINK Chemicals' study of textile impregnation (2017)
In 2017, the Danish Consumer Council THINK Chemicals published the results of a study of fluorinated substances in 11 impregnation products on the Danish market[8]. The impregnation products were found in Danish supermarkets, outdoor shops, DIY stores, shoe-repairs shops and shoe shops. The products were sprayed on a film and the surface was screened for fluorine content. Volatile organic fluorinated substances were collected by heating the sprayed film to 80 degrees and then measured. Products shown in the screening to contain fluorine were analysed for the content of specific fluorinated substances in the impregnating product.

Furthermore, a surface was sprayed with the products and screened for silicon, and the positive samples were subsequently screened for siloxanes.

TABLE 1. Results of the Danish Consumer Council THINK Chemicals' chemical screening for fluorinated substances in 11 impregnation products for textiles on the Danish market 2017

Brand	Name	Application method	Fluoride screening
Bulloch	Impregnation spray	Aerosol spray	Negative
Collonil	Carbon Pro protecting impregnation	Aerosol spray	Positive
Fjällräven	PFC Free Waterproof Impregnation	Pump spray	Negative
*Granger's	Xtreme repel	Pump spray	Positive
Derby	Protector	Aerosol spray	Positive
Royal	Protector	Aerosol spray	Negative

[8] https://kemi.taenk.dk/bliv-groennere/test-kemi-i-impraegnering-paa-spray

Brand	Name	Application method	Fluoride screening
Sterling	Textile impregnation	Aerosol spray	Positive
TOKO	Eco Proof textile	Aerosol spray	Negative
Woly	Sport waterproof	Aerosol spray	Negative
Zebla	Impregnation for laundry	Pump spray	Negative
Milano	All-round impregnation	Aerosol spray	Positive

*Grangers International does no longer use fluorinated substances in their products.

The Danish Consumer Council THINK Chemicals identified five impregnation products in the screening containing fluorine. The subsequent analyses of these products showed content of fluorotelomer alcohols (FTOH), which may have been the residues of starting materials used in the production of PFAS or a degradation product of other PFAS. The manufacturers of these products confirmed that they used PFAS in the specific products.

Screening for silicon showed that eight impregnation products had silicon content. Subsequent chemical analyses showed small traces of cyclotetrasiloxane and cyclopentasiloxane in the sprayed film. It is important to note that these two siloxanes are volatile and reactive, which means that negative screening results in the sprayed film does not necessarily mean that the substances do not appear in the impregnating product.

5. Survey of the market for do-it-yourself impregnation products

5.1 Introduction

The purpose of the survey is to build knowledge about do-it-yourself impregnation products available to Danish consumers. The survey was a screening of the typical do-it-your-self impregnations products available, and information about the availability of impregnation products with different application methods (e.g. aerosol spray, pump spray and cloth) was collected. The method of application was important since methods other than aerosol sprays probably do not represent the same risk when inhaled during application.

5.1.1 Scope

The focus of the survey has been on impregnation products for Danish consumers. In the previously mentioned projects published by the Environmental Protection Agency (Feilberg et al., 2008; Jensen & Poulsen, 2008) the projects focused on impregnation products containing fluorinated substances (Jensen & Poulsen, 2008) or specific aerosol spray impregnation products to textiles used by consumers (Feilberg et al., 2008). This project's survey provides an overview of around one hundred (100) typical impregnation products available to Danish consumers.

The data collection has included the following categories of consumer products:

- Outdoor textiles (outdoor clothing, tents, pillows/cushions for outside furniture, prams, etc.)
- Shoes/boots
- Sofas
- Carpets (you can also get professionals to impregnate your carpets)
- Building materials (tiles, concrete, paint, etc.)
- Glass/(car) windows/solar cells
- Ski (ski wax/spray)
- Touch screen (mobile phone, iPad, etc.) (e.g., protection against greasy fingers)
- Dry fly spray (fishing kit)

5.2 The survey

The survey was carried out as a combination of internet searches, individual store visits and telephone contact with selected retailers.

There is a great range of impregnation products available to the Danish consumer. The survey provides an overview of different types of impregnation products available to Danish consumers and cannot be considered exhaustive. The survey also provides an overview as to whether alternatives to the more typical and potentially problematic aerosol spray are available. However, the list of alternatives cannot be regarded as exhaustive.

5.2.1 Internet search

It has been a priority to search for impregnation products on the websites of major business chains in order to identify the more "typical" impregnation products on the market. This has included various sports, outdoor equipment and DIY-store chains, amongst others. The

searches were typically made with a single search using the term "impregnation*" on the websites of the stores/retailers, after which the retailers' selection of impregnations products appeared. To include all consumer categories (see section 4.1.2), a more general site-specific Google search was performed, e.g., with the term "impregnation * " combined with various search terms such as "glass", "screen" or "protection".

Information about specific products that have caused intoxication were obtained from the Danish Poison Information Centre at Bispebjerg Hospital and from the National Poisoning Information Centre in The Netherlands. The general internet search was supplemented with a specific search for these impregnation products.

Identified impregnation products were divided into ten different application categories. The consumer product categories covered by these use categories are shown in parentheses. It is important to note that the categories may cover several product categories:

1. Outdoor equipment (outdoor textiles and skis)
2. Outdoor hard surfaces (building materials for outdoor use)
3. Indoor hard surfaces (building materials for indoor use, glass and touch screen)
4. All-round: leather, suede and textiles (this category covers impregnation products marked as "all-round" impregnating agents and covers many types of impregnating agents, such as outdoor textiles, shoes/boots, carpets and furniture)
5. Textiles - clothing (outdoor textiles)
6. Furniture - leather and fabric (sofas)
7. Footwear (shoes/boots)
8. Fire impregnation (sofas)
9. Other (dry Fly Spray)
10. Rugs (rugs)

In addition to dividing the identified impregnations products into the above categories, further product information was sought through other websites and, if available, supplemented with data from the safety data sheets. The results from the internet search include the following product information:

- Application category
- Specific application (e.g. on composites or plastic surfaces)
- Application method (aerosol spray, pump spray, by wash or other application, e.g., brush, cloth, polishing or nozzle)
- Effect of the impregnation product (protection against water, or water and dirt, etc.)
- Recommended applied quantity
- Active substance of the impregnation product[9] or chemical group to which the active substance belongs
- Further relevant information
- Safety data sheet for the product

Identified impregnation products are shown in Appendix 1 ("Identified impregnation products") which includes a total of 110 impregnation products. The information in Appendix 1 does not include the manufacturer's name or product name.

[9] "Active substance" is used here for substances having an active function in relation to the impregnating effect.

Table 2 below summarises the identified impregnation products and the obtained product information. The table indicates for each application category the number of impregnation products identified, application method, expected average size of the surface which is impregnated, and whether the impregnation is expected to be carried out indoors and/or outdoors.

TABLE 2. Overview of identified impregnation products divided into application categories

Application category	Specific application	Application method	Estimate of average surface, which is impregnated	Typical use - indoor/outdoor
Outdoor equipment	Tents, rucksacks, parasols	Aerosol spray: 3 pcs.	1-25 m²	Outdoor
		Pump spray: 3 pcs.		
		Brush: 3 pcs.		
	Ski gear	Aerosol spray: 1 pc.	0.5 m²	Outside and inside
		Pump spray: 1 pc.		
		Other: 6 pcs.		
Outdoor hard surfaces	Stone composite, nonwood, brick and wood	Pump spray: 2 pcs.	0.5–25 m²	Outdoor
		Other: 9 pcs.		
Indoor hard surfaces	Touch screens	Grease on: 4 pcs.	0, 005 - 0.1 m²	Indoor
	Tiles, stones and the like.	Pump spray: 7 pcs.	0.5-50 m²	Indoor
		Other: 5 pcs.		
	Glass	Pump spray: 1 pc.	0.5-4 m²	Indoor
All-round: leather, suede and textiles	Shoes, jackets and the like.	Aerosol spray: 10 pcs. Pump spray: 1	0.1-1 m²	Outside and inside
Textiles (clothing)	Jackets, trousers and flight suits	Aerosol spray: 1 pc. Pump spray: 5 pcs. Wash: 1 7 pcs. Other: 1 pc.	0.5-2 m²	Outside and inside
Furniture (leather and fabric)	Sofa and blankets	Aerosol spray: 5 pcs.	6, 2 m²	Indoor
		Pump spray: 2 pcs.		
Footwear	Leather boots and sneakers	Aerosol spray: 6 pcs.	0.5 m²	Outside and inside
		Pump spray: 3 pcs.		
		Other/unknown: 6 pcs.		
Fire impregnation	Curtains, Christmas tree, cardboard and lamps	Aerosol spray: 2 pcs.	0.5-20 m²	Indoor
Other things	Pets, fishing tackle and frying pans	Pump spray: 2 pcs.	0.01–0.25 m²	Outside and inside
		Other: 3 pcs.		
Rugs	Rugs	Unknown: 1 pc.	15 m²	Indoor

The focus of the internet search has been impregnation products targeted at the Danish consumer, and the internet search and identified internet sites have therefore been in Danish. Three impregnation products that are not immediately available in Denmark, but are available in other European countries, have been identified via information on cases of poisoning. Generally, impregnating agents available in other EU countries or outside the EU have not

been sought. In addition, it should be noted that the larger producers/brands providing impregnation products to the Danish consumer are located within the EU. Companies marketing products on the internet in Danish, to Danish consumers, may well be located in other countries, and the products are then sent to consumers from addresses outside the country's borders. It is therefore difficult to talk about a "Danish market" as regards online sales.

In the application categories "Outdoor equipment" and "Footwear", a variety of aerosol sprays and pump-sprays, as well as products intended for applying with brush or other application method, were identified. Impregnating products intended for application with brush and/or cloth or the like cannot be expected to have the same wide use as an aerosol spray or pump-spray. They are likely less suitable for impregnating products with uneven surfaces, such as a backpack.

The identified impregnation products for hard surfaces, both indoors and outdoors, were not sold as aerosol sprays. This trend was also seen in the application category "textiles (clothing)", where the typical application method for impregnation products was impregnation by wash. However, a single impregnation product for textiles using aerosol spray was identified.

The impregnation products in the application categories "All-round: leather, suede and textiles" and "Furniture (leather and fabric)", "Fire impregnation" were all applied using aerosol spray except for a single product. "Furniture (leather and fabric)" and "Fire impregnation" must be expected to be used indoors to a large extent by the consumer. The combination of expected indoor use and application method by aerosol spray makes products in this category particularly interesting in terms of hazard assessment. However, impregnation products with a fire-retardant effect are not considered to be the focus of the present project. This is the reason why these products were not selected for further analysis.

During the internet search, product information on the quantity used was available for approximately 1/5 of the products. This implies that the amount to be used was not listed on the retailer's website for approximately 4/5 of the products. Table 3 summarises product information regarding use amount by application category and method of application.

TABLE 3. Overview of the application method and application quantity for products with unambiguous application quantity

Application category	Number of identified products	Application method	Amount used
Outdoor equipment (tents and the like)	3 pcs.	Brush: 1 pc.	18 m²/L
		Aerosol spray: 2 pcs.	5-25 m²/L
Outdoor hard surfaces	6 pcs.	Brush: 3	10-25 m²/L
		Nozzle [a] 2 pcs.	20-30 m²/L
		Not stated: 1 pc.	10 m²/L
Indoor hard surfaces (tiles, stones, etc.)	6 pcs.	Pump spray: 5 pcs.	10-100 mL/m² (3.7-7.5 m²/L [b]
		Polishing: 1 pc.	7-10 mL/m²
Indoor hard surfaces	1 pc.	Pump spray	10-25 mL/m²
All- round leather: leather, suede and textile	1 pc.	Pump spray	30-40 mL/m²
Textiles (clothing)	2 pcs.	Wash	50-100 mL per piece. clothing

Application category	Number of identified products	Application method	Amount used
Furniture (leather)	1 pc.	Aerosol spray	15-20 m²/L
Rugs	1 pc.	Unknown	25 m²/L

[a]: These products must be poured into a syringe.

[b]: For a single product, the amount uses was indicated in another unit.

Table 3 shows that the amount used during the application is reported for only 3 of the impregnation products using aerosol spray.

As also shown in the survey of impregnation products for textiles prepared by Feilberg et al. (2008), information on the chemical components of waterproofing products is largely unavailable. The reason is likely that the composition of the impregnation products are considered trade secrets. It is also noted that information about chemical content, including information concerning the active substances, is provided only for a few impregnation products. Of the impregnated products identified, it was for approx. 1/3 of the products possible to identify, which chemical group the active substance belongs to from the providers' websites, safety data sheets (SDS) or the packaging. Table 4 provides an overview of application category and method of application for these impregnation products. Data are obtained via images of the packaging, SDS and descriptions on the supplier's website.

In cases where "Nano" has appeared on the product, this is noted in the column "Substance group for the active substance". However, this is not a group of substances or a specific active substance, but is considered relevant as it often covers active substances that make a nanofilm (see also Appendix 3). Overall, the term "Nano" is considered to be used for marketing purposes.

TABLE 4. Identified products with indication of substance group for the active substances

Application category	Substance group for the active substance (as specified by the manufacturer or supplier)	Number of pcs
Outdoor equipment	"Nano" [a]	1
	Silicone	2
Outdoor hard surfaces	Silicone	2
	Silicone/siloxane	1
Indoor hard surfaces	"Nano" [a]	8
	Siloxane	2
All-round: leather, suede and textiles	"Nano" [a]	3
	Silicone	2
	Fluorochemical Urethane	1
Textiles (clothing)	Acryl Polymer Technology (APT)	2
	Paraffin and beeswax	1
	Polyurethane-based active substance	1
	Siloxane	1
Furniture (leather and fabric)	No information	
Footwear	Beeswax	1
	"Nano" [a]	1
	Siloxane	3

Application category	Substance group for the active substance (as specified by the manufacturer or supplier)	Number of pcs
	Leather grease and silicone oil	1
Fire impregnation	No information	
Other	Silicone ("nano" [a])	1
	Lard	1
Carpets	Siloxane	1

[a]: "Nano" cannot be categorized as an active substance group, but is considered relevant to include in the table.

In Table 4, only one product states that the active substance is a fluorinated substance. For a number of the products, the active substances belong to the group siloxane/silicone. For several impregnation products, it is stated that they contain a number of other active substance groups, such as polyurethane-based active substances and "acrylic polymer technology", but these do not describe the chemical content further. Since some PFASs may consist of polyurethane and acrylic polymers with per- or polyfluorinated side chains, the information may well cover PFAS-based active substances.

For the vast majority of impregnation products identified by the internet search, a safety data sheet was not directly available on the provider's website. For some products, this may happen because they are mostly/only intended for consumers, for whom a safety data sheet is not required. However, many of the safety data sheets could be obtained by searching for them specifically, most often on the manufacturer's own website. In many cases, the safety data sheets did not contain information regarding the chemical substances of the impregnation product. In cases where ingredients were indicated, the information most often concerned the propellants or solvents in the impregnation product. This is related to the fact that the only requirement is the inclusion of chemical substances which are classified as dangerous under the principles of the CLP-regulation. Some of the active substances are characterized by the manufacturer as polymers, which means they are exempted from registration under REACH and therefore generally not classified according to the CLP.

5.2.2 Shop visits

In order to examine whether the products identified during the internet search were adequate, impregnation products in two physical stores were reviewed. Here, impregnation products identified during the internet search were cross-checked with the range available to consumers in physical stores. The two stores selected for the visit were chosen for their wide range of locations in Denmark possible for cross-checking. The two stores were expected to offer a wide range of typical impregnation products within the selected consumer categories (see section 4.1.2). To cover these parameters, a DIY store and an outdoor store were chosen, both of which belong to larger business chains in Denmark.

Impregnation products identified in the two physical stores are shown in the tables below. The results of the two store visits are also shown in Appendix 1, where the products found in the individual stores are listed.

TABLE 5. Impregnation products in a physical outdoor store

Product no.	Application category	Application method	Also identified by internet search
14	Footwear	Pump spray	Yes

29	Outdoor equipment (tent, etc..)	Brush or pump spray	Yes
64	Textiles (clothing)	Rubbed on [a]	Yes
66	Textiles (clothing)	Pump spray	Yes
82	Outdoor equipment (tents etc.)	Aerosol spray	Yes
90	Textiles (clothing)	Pump spray	Yes
109	Leather	Cloth	No
110	Leather	Cloth	No

[a]: The product is a block that is rubbed on the fabric. [a]

The two products in the table above that were not identified during the internet search are both wax products. These products are applied using a cloth. Such products have not been in focus in the identification of impregnation products. Therefore, it was also to be expected that the assortment in the outdoor store had a range of wax impregnation products that were not identified during the internet search. The other impregnating products in the table above were all identified by internet search.

TABLE 6. Impregnation products identified in the physical DIY store

Product number.	Application category Field of application	Application method	Specific application	Also identified by internet search
24	Indoor hard surfaces (tiles, stones, etc.))	Pump spray	Surfaces e.g. cement, masonry, bricks, concrete, wood cladding, wood panels, plaster, drywall, limed surfaces, etc.	Yes
81	Outdoor hard surfaces	Brush / mop	Stones and tiles	Yes
88	Outdoor equipment (tents etc.))	Aerosol spray	Outdoor textiles	Yes
93	Outdoor hard surfaces	Spray gun (from picture)	Tiles	Yes
101	Outdoor hard surfaces	Brush or roller	Composite / /WPC	Yes
103	Outdoor hard surfaces	Spray or brush [a]	Tree	Yes
106	Outdoor hard surfaces	Pump spray	Garden furniture and fences of plastic or polyrattan [b]	Yes

[a]: Information from the manufacturer's website. The type of spray that can be used for the application is not described.

[b]: "Polyrattan" is often used for braided plastics.

All impregnation products found in the physical DYI store are also identified by internet search.

In summary, only two products were found in the physical stores that had not been identified during the internet search. These two products are both wax products for leather. The focus in the present survey has been to produce a screening of impregnation products for the Danish

consumer, for both aerosol sprays and alternative products for these. Leather wax is not considered as an alternative to the typical uses of aerosol sprays, and therefore the screening has not included such products.

5.2.3 Supplier contacts/tonnage

There is no register in Denmark of chemical products sold to consumers. To get an impression of the tonnage of different products and product areas, different suppliers and distributors in Denmark were contacted: 2 outdoor equipment chains, 2 DIY stores, 3 distributors, 2 furniture stores and 1 shoe chain.

Most contacted retailers did not respond to the inquiries or reply with useful information. We managed to gather information on two areas of application: "Outdoor equipment" and "Furniture".

Outdoor equipment

An outdoor store belonging to the top 5 in Denmark in terms of sales, estimates that they market a total of approx. 30 different impregnation products incl. leather wax and atypical impregnation products (e.g. tubes of silicone elastomer for tents). Of the more typical impregnation products, the store stated that they market 15-20 different products from two major manufacturers. For the sake of confidentiality, the names of these are designated as "Manufacturer - A" and "Manufacturer - B", respectively. Manufacturer - A produces waterproofing products that are used very widely, and Manufacturer - B produces waterproofing products for shoes, clothes and bags. According to the product information, Manufacturer-A's best-selling product contains silicone and it is stated on the product that it is used on parasols, tents and the like, but several retailers of outdoor equipment state that the product has a wider use, including clothing, even though the product is not specifically marketed for these applications. One dealer stated that they advised their clients to use other products for clothing, but some customers specifically asked for the product to be able to use it on clothing. This indicates that consumers of waterproofing products do not necessarily follow the instructions, but focus on the effect of the impregnation product. The same dealer also marketed products from a third manufacturer, and stated that this was typically directed to customers who asked for waterproofing products for outerwear. After contact with dealers in outdoor equipment, it is estimated that these three brands constitute a significant part of the market.

Furniture impregnation

According to discussions with dealers and distributors, one manufacturer in particular accounts for a large share of impregnation products for furniture impregnation. Products from this manufacturer are marketed by several retailers using their own packaging. One of these dealers reported an annual sale of 17,946 pieces of impregnation products for furniture impregnation. The manufacturer of the product was contacted for further information on tonnage and sales, but the manufacturer was not willing to provide information for the investigation.

Feilberg et al. (2008) concluded that it was not possible to obtain information on tonnage from the importers they were in contact with during their survey of impregnation products for textile impregnation, and they were not able to estimate the number of products sold on the Danish market in 2008. In the present project, it has also not been possible to obtain information regarding tonnage, which could contribute to assessing the total tonnage or which areas of application represent the largest tonnages on the Danish market. Several dealers and distributors were accommodating and interested in the present survey and expressed that they would like to submit tonnages and statistics regarding sales of impregnation products. However, these agreements were not met and no further information on sales and tonnage of impregnation products has been received in the present study.

According to the European Aerosol Federation (FEA), in 2018 approx. 4,600,000 units of aerosol products were produced in Denmark (FEA, 2018). One contacted supplier stated that Danish production of aerosol products mainly consists of other products than impregnation products e.g. cosmetic products.

The distribution of production in the EU of aerosol products for households is shown in the table below. "Textile and fabric care products" and "shoe and leather care products " are likely to contain significant amounts of impregnation products. In addition, some of the products within "Furniture wax and polishing" may be impregnation products, but it is unclear whether impregnation products for fabric and leather furniture fall into this category of use. As "others" are not specified, it is not possible to determine the extent to which waterproofing products may fall into this category. If it is roughly assumed on the basis of population that the consumption in Denmark corresponds to 1% of the production in the EU, it can be estimated that in 2018 just over 400,000 units of "textile and fabric care products" and "shoe and leather care products", respectively, were sold. This corresponds to each of the country's 2.7 million households[10] buying one of these waterproofing products every 3 to 4 years.

TABLE 7. Production of household aerosol products, 2018, in the EU, divided into use categories (FEA, 2018).

Application category	Number (in. 000 units)	Impregnation products
Air fresheners	623,773	No
Insecticides and plant protection products	242,492	No
Others	135,286	Maybe
Furniture wax and polishing	75,806	Yes, some
Textile and fabric care products	41,640	Yes
Shoes and leather care products	41,450	Yes
Bathroom and kitchen cleaning	20,335	No
Oven clean	11,800	No

5.3 Labelling schemes for impregnation products

BlueSign

Several products are marketed with the label "Bluesign®". The labelling scheme concerns the manufacture of textiles for consumers and sustainability. The headquarter is located in Switzerland. On the Bluesign® website[11] it is described that a Bluesign® products are offered by companies that have committed to the "Bluesign® system", which stipulates that the product consists of at least 90% Bluesign® approved textiles and 30% Bluesign® approved accessories. On a supplier's website, Bluesign® is described as "... *the leading independent test standard for environmentally friendly products in the textile industry and takes into account all environmental aspects - Both in terms of material content, production conditions, energy conditions during production, environmental impact in use and by disposal* " [12] (translated from Danish)[13]. According to Bluesign ®'s own report, which specifies the brand's limits for chemical substances in consumer products, certain PFASs are limited (Bluesign, 2019).

Nine products marked with Blue Sign were identified.

[10] https://www.dst.dk/da/Statistik/emner/befolkning-og-valg/husstande-familier-boern/husstande

[11] https://www.bluesign.com/en

[12] https://www.spejdersport.dk/toko-eco-textile-proof-500ml-impraegnering

[13] https://www.spejdersport.dk/toko-eco-textile-proof-500ml-impraegnering

"Bra Miljöval"
During the internet search, an impregnation product with the label "Bra Miljöval" ("Good Environmental Choice") appeared. "Bra Miljöval" is the Swedish Society for Nature Conservation's eco-label [14]. The label has been audited under the Global Ecolabelling Network's International Coordinated Ecolabelling System (GENICES), which is operated by the Global Ecolabelling Network (GEN). GEN is an international network of eco-labelling organizations working to promote, improve and develop eco-labelling of products and services.

A single product with the brand with "Bra Miljöval" was identified.

The Nordic Ecolabel (the Swan)
The Nordic Ecolabel is the official eco-label throughout the Nordic region. The Nordic ecolabelling organisations are also members of the Global Ecolabelling Network (GEN), an international network of eco-labelling organizations. The label is a sustainability label and can be awarded to products meeting specific criteria related to the product's overall environmental and health impact. There are no specific criteria for impregnating agents, but some types of impregnating products may be included in criteria for broader product groups. Impregnation products for building materials are e.g. specifically mentioned in the criteria document for chemical building products [15].

A single product with the Nordic Ecolabel was identified, and the product must therefore, among other things, not contain organic fluorinated substances.

[14] https://www.naturskyddsforeningen.se/bra-miljoval/det-har-ar-bra-miljoval

[15] https://www.ecolabel.dk/da/blomsten-og-svanen/kriterier/vis-produktgruppe?produktgruppeid=097&projektgruppe=Svanen#,tab:kriterier

6. Impregnation and toxicity

Existing knowledge of the cause of the toxic effects by inhalation of some spray impregnation products is described in this chapter.

6.1 Intoxication cases in Denmark

The study received information about poisoning cases registered by the Danish Poison Centre in the period 2006 to 2020. For this period, it has not been possible to obtain such detailed information as was presented in a previous study based on information from 1991 to 2007. The previous study is therefore mentioned first.

Cases of poisoning from the Poison Centre at Bispebjerg Hospital, registered from 1991 to 2007, are described in Feilberg et al. (2008). These cases of poisoning were identified retrospectively and included a total of 126 potential cases of poisoning. Of these, 42 cases were excluded because the products were not impregnation products or because the symptoms were not related to inhalation but only exposure of the eyes. The final figure for the period 1 January 1991 to 31 May 2007 therefore included 84 cases. Of these cases, an effect on respiration was reported in 92% of cases; most often together with other symptoms such as fever, nausea, upset stomach/intestinal system and symptoms related to the central nervous system. The severity was reported as moderate to severe for 58% of cases of poisoning, mild for 37% and no poisoning for 4%. The most serious cases could be linked to the treatment/impregnation of furniture, which also constituted the predominant part of poisoning cases. Below is a table showing the application category of the impregnation product and the number of cases of poisoning.

TABLE 8. Poisoning cases registered by the Poison Centre for the period 1991-2007 divided into use categories for impregnation product (Feilberg et al., 2008).

Application category	Number of cases of poisoning
Furniture	54
Textile	9
Footwear	4
Ceramic surfaces	4
Rugs	2
Tents	2
Riding equipment	1
Car seats	1
Sealer for paint	1
Unknown	6

Information on ingredients in the products was available for half of the reported cases of poisoning during the period 1991-2007. The active substances in the impregnation products that caused the most cases of poisoning were fluorinated substances. Silicone was also included in several of the impregnation products, and some products contained both types of active ingredient.

In the present project, the Poison Centre at Bispebjerg Hospital was contacted with a view to updating the number of historical cases of poisoning by spray impregnation products for the

period 2007-2020. However, it has not been possible for the Poison Centre to use the same filter for data extraction from their database as in the period 1991-2007. Therefore, it is not possible to compare the two periods. The figure below contains data received from the Poison Centre for the present project.

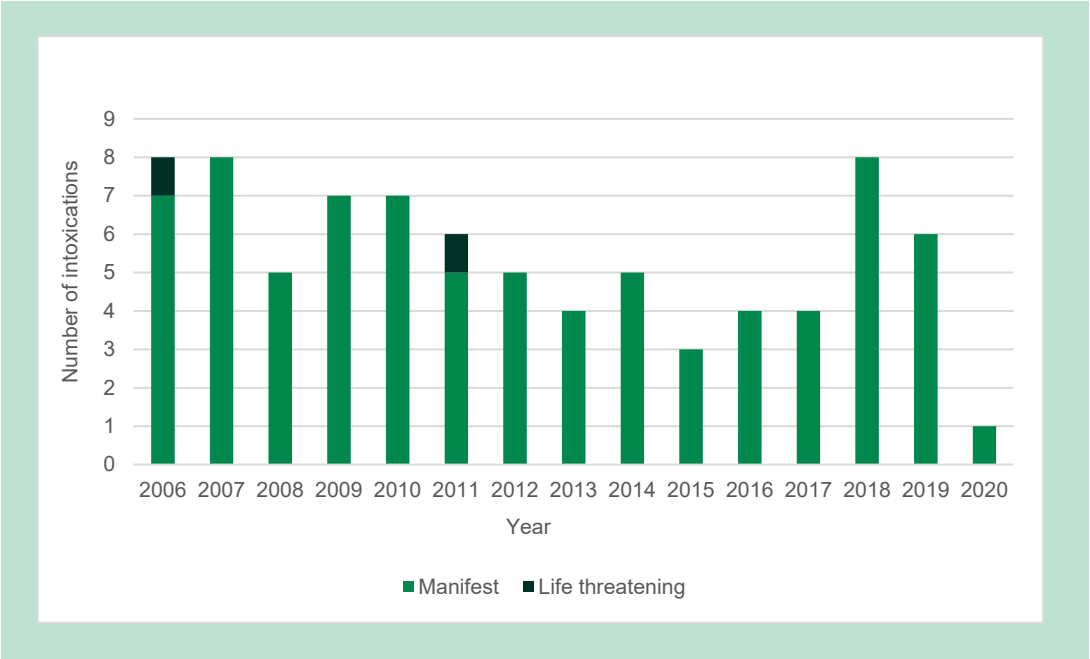


FIGURE 1. Poisoning cases registered by the Danish Poison Centre 2006-2020. (Manifest: very ill but not life threatening)

Below is the product information received from the Poison Centre for the cases of poisoning where medical assistance was sought and information was available. The product information for all relevant cases of poisoning could not be acquired and the product information below is therefore not comprehensive for all cases where medical assistance was sought. For confidentiality reasons, the names of the manufacturer and product do not appear in the cases where it was provided. It also is indicated in the following whether it was possible to identify the product during the present survey:

- 2006 - life-threatening cases of poisoning.
  Symptoms: Chest pressure and fever.
  Product containing dimethyl ether, heptane, ethyl acetate, sec-butyl acetate, fluoropolymer. Impregnation product could not be identified by internet search.

- 2011 - life-threatening poisoning cases.
  Symptoms: Fever, shortness of breath and high infection parameters.
  During the internet search, a product from the same manufacturer was identified, product no. 27. The impregnation product that caused the poisoning was described as a textile impregnation product, whereas product no. 27 is described as an all-round impregnation product. However, it is possible that it may be the same product, as product no. 27 is from the same manufacturer and can be used for textiles. However, product components may have changed since 2011.

- 2019 - very ill, but not life-threatening. Unknown product. Use indoors.
  Symptoms: Fever, shortness of breath, cough. Hospitalized.

Impregnation product could not be identified by internet search.

- 2019 - very ill, but not life-threatening.
  Symptoms: Fever and low oxygen saturation.
  During the internet search, a product from the same manufacturer for the same use was identified, product no. 95. However, it is not entirely certain that it is the same product, as the product name did not appear in the information from the Poison Centre.

- 2019 - very ill, but not life-threatening. Unknown product. Application inside a tent.
  Symptoms: Uncomfortable, shortness of breath, but not hospitalized.
  Impregnation product could not be identified by internet search.

- 2019 - very ill, but not life-threatening. Unknown product. Unknown application. Symptoms: Chest pressure and difficulty in breathing.
  Impregnation product could not be identified by internet search.

- 2020 - very ill, but not life-threatening. Unknown product. Indoor use (sofa impregnation)
  Symptoms: Vomiting, headache, not hospitalized
  Impregnation product could not be identified by internet search.

Poisoning cases registered with the Poison Centre at Bispebjerg Hospital are based on cases where the user of the impregnating product has sought medical assistance after its application. Several studies indicate that there may be cases of minor effects on lung function for which the user of the impregnation product does not seek medical assistance. In the long term these minor effects may have adverse impacts on lung function (e.g. development of asthma or COPD) (Sørli et al., 2019).

6.2 Intoxication cases in other European Countries

For the dossier for restriction of the use of spray products with TDFAs (ECHA, 2017), data for poisoning cases were collected. Data for European countries from the year 2000 onwards are shown in Table 9.

TABLE 9. Reported cases of respiratory exposure following the use of waterproofing products by spray application. The cases are from 2000 onwards and include data from other European countries (DK not included). Based on ECHA (2017), original references appear, as well as information from the National Poisoning Information Centre in the Netherlands.

Country, year	Product name	Application method and application area	Active substances	Likely TDFAs [1]	Solvent	Number affected
Netherlands, 2002-2003	Various products, names not available	Spray products	Fluorocarbon resin	÷	n-heptane mixture of solvents	99
Netherlands, 2011	No information	Aerosol spray Footwear	Fluorocarbon polymer	+	No information	1
Netherlands, 2013-2015	HG protector for untreated wooden furniture HG water, oil, fat & dirt proof for leather	Spray products Area of application wooden furniture,	Fluorocarbon polymer	÷	No information	26

Country, year	Product name	Application method and application area	Active substances	Likely TDFAs [1]	Solvent	Number affected
	HG water, oil, fat & dirt proof for textile Scapino trend spray Unknown for 22 products	leather, textiles and unknown.				
Netherlands, 2016-2020	No information	Unknown application	Unknown	Unknown	Unknown	54
France, 2003	No information	Spray product Leather and textile	No information	÷	Unknown	1 (fatal)
Greenland, 2010	Stain Repellent Super®	High pressure airless spray gun (135 bar) Indoor ceramic tiles	Non-fluorinated alkylsiloxanes	÷	Hydrogenated n aphtha (C_{9}-C_{12})	40
Ireland, 2006-2016 [2]	3-4 different products, names not available	Aerosol spray: 3 pcs. Unknown: 1 pc. Footwear: 2 pcs. Textile: 1 pc. Wood sealer: 1 pc.	No information	+	Unknown Propanol and hydrocarbons Alcohol, iso-propanol and petroleum	4
Switzerland, 2002-2003	RapiAquaStop (46% of incidents) K2R (27% of incidents) RapiIntemp (12% of incidents) Patina- Fala: (3 incidents)	Aerosol spray and pump spray (3 incidents) Leather and textiles Stone-tiled walls and floors (3 incidents)	Fluorinated acrylate polymer	÷	Isoparaffinic hydrocarbons	180
Scotland, 2005	Rucoguard EPF 1610	Spray gun connected to an air compressor Textile	Fluorocarbon polymer	÷	Isopropanol	4
Spain, 2004-2015	No information	Spray Industrial, cleaning and other	Fluorinated silanes and fluorinated compounds	÷	Aromatic or isoparaffinic hydrocarbons	5
Sweden, 2001-2015	6 different products, names not available	Aerosol spray: 3 pcs. Unknown: 3 pcs. Unknown use	Fluorocarbon resins Fluorinated polymer	+	n-heptane, butyl acetate, 2-propanol and isopropyl acetate n-heptane, 2-propanol	98

Country, year	Product name	Application method and application area	Active substances	Likely TDFAs [1]	Solvent	Number affected
					and ethyl acetate	
			Fluorinated polymer		2-propanol and methyl isobutyl ketone	
			Fluorinated polymer		Isoparaffins	
			Fluorocarbons		Tripropylene glycol	
			Fluorinated polymer		Crude oil distillates and acetone.	
Germany, 2006	Magic Nano Glass and Ceramic Magic Nano Bath and WC	Aerosol spray Surface sealants, bathroom	(fluoro) silanes	++	Dimethyl ether and ethanol	154
Germany, 2006	Nano HiTech	Aerosol spray Use: no information	No information	+	No information	16
UK, 2003	No information	Spray products	Fluorocarbon compounds	÷	No information	1 (fatal)

[1] +++ Known to be spray product(s) containing mixtures of TDFAs and organic solvents for the general public. ++ Most likely to be spray product(s) containing mixtures of TDFAs and organic solvents for the general public. + The product might have been spray product(s) containing mixtures of TDFAs and organic solvents for the general public. ÷ Known not to be spray product(s) containing mixtures of TDFAs and organic solvents for the general public.

TDFA's = (3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl) silanetriol tri-O-(alkyl), and any of its mono-, di- or tri-O-(alkyl) derivatives.

[2] Data relating to occupational exposure are not included in the table.

The available data for poisoning cases show that impregnation products containing TDFAs in organic solvents cause many of the cases. Up to 50% of registered cases of poisoning in the EU (DK not included) since 2000 may have been caused by products containing TDFAs and organic solvents. According to ECHA (2017), the cases of poisoning following the use of impregnation products reported in Denmark in the period 1991-2007 were not caused by TDFAs.

6.3 Existing evidence concerning toxicity

Several studies and many reported case studies have shown that impregnation products used by consumers have caused nuisance and poisoning. The symptoms have varied, and are, among other things, dependent on exposure time and quantity as well as ingredients in the impregnation product. Poisoning symptoms reported after the use of impregnation products typically occur with the use of aerosol sprays in a room with limited ventilation.

Symptoms of poisoning after using an impregnation product may occur after a latency time of a few minutes to several hours. The symptoms are most often described as cough, shortness of breath, chest pain, headache, chills, temperature fluctuations and diarrhoea. A closer examination of cases of poisoning has, among other things, demonstrated chemical pneumonia, decreased oxygen saturation in arterial blood and infiltrative changes in the lungs, which are seen on X-rays of the chest (caused by fluid in the lungs; pulmonary oedema). The severity of reported poisonings varies widely, and the vast majority of people who have been poisoned after using an impregnation product recover quickly. However, several case studies also report deaths (ECHA, 2017).

An impregnation product applied by aerosol spray typically consists of solvents, active substance(s) and propellants, as well as other additives and catalysts. The solvents used, along with the active substances, have an influence on the harmful health effects. Scheepert et al. (2017) indicate that products marketed before 2000 typically contained solvents in the form of aliphatic hydrocarbons and sometimes chlorinated or cyclic hydrocarbons. In addition, it is stated that products marketed after the year 2000 typically contain aqueous mixtures of glycols and glycol ethers as solvents. Nørgaard et al. (2010a), however, describe other solvents (2-propanol, ethanol as well as kerosene and water), suggesting that the ingredients in impregnation products vary widely.

The propellants are typically C3-C4 alkanes or CO_2, and the active substances are typically a mixture of siloxanes or acrylate polymers with fluorinated substances (Scheepert et al., 2017). There is a broad scientific consensus that the use of propellants such as propane and butane isomers does not in itself pose a risk to the consumer (Sheepers et al., 2017; Yamashita et al., 1995). However, it cannot be ruled out that synergistic effects between certain propellants and the active substance may occur (ECHA, 2017).

6.3.1 Toxicity and aerosol size distribution

Impregnation products that are applied to a material with a brush or cloth will result in an exposure that is primarily made up of volatile organic substances. By pump spray and aerosol spray, aerosols are formed, which are small droplets of the impregnation product. The toxicity of an impregnation product varies; several studies have shown that the particle size of the aerosols can have an impact on toxicity. When application of an impregnation product generates aerosols, some of these particles may end up in the bronchioles or alveoli (Nørgaard et al., 2010a), which has been demonstrated for both water-based and solvent-based impregnation products (Nørgaard et al., 2014). Aerosol spray provides a smaller average aerosol size than pump spray (Feilberg et al., 2008), which means that a larger proportion of the particles may end up in the bronchioles or alveoli.

Most reported cases of poisoning occur after the use of an impregnation product with aerosol spray containing organic solvents, see Table 9.

Active substances in impregnation products are often solids or liquids with very low vapour pressures. The aerosols contain both active substances and solvents with relatively high vapor pressures, which will partly evaporate. The smaller the aerosols, the faster the evaporation (Hinds, 1999). This means that the aerosols to which the consumer is exposed mainly consist of the active substances.

Feilberg et al. (2008) performed systematic measurements of fine aerosols (<1 µm) and nano-aerosols (<100 nm) formed using selected spray impregnating agents on a piece of fabric (uncoloured cotton) in an analysis chamber. During the analysis, the sizes and amounts of aerosols released into the air in the analysis chamber during use of the products were measured. Measurements of the contents of the chamber were made after 1 and 7 min, respectively. With this experimental setup, the air in the analysis chamber should correspond to the air the user

is exposed to in a use situation. For aerosol spray impregnation products, the authors measured an average mean size of aerosols in the range of 50-200 nm. The mean value of the aerosol diameter was slightly larger for most products after 7 min. than after 1 min., but still within the specified range. Using a pump spray, a very small or negligible release of aerosols in the measured particle sizes (<1µm) was observed. It was concluded in Feilberg et al. (2008) that the use of textile impregnation products applied with aerosol spray (propellant gas) entails a significant exposure to fine and ultrafine aerosols (nano-aerosols).

Therefore, when applying an impregnating agent with aerosol spray, there is potentially a greater exposure to the active substances of the impregnating agent. However, there may also be a significant exposure when using impregnation products applied by pump spray, and cases of poisoning have been reported after the use of such products (Table 9). Nørgaard et al. (2009) examined the particle size distribution of aerosols from three pump sprays on a surface and showed that almost all the measured particle sizes were able to reach the bronchi and bronchioles (<10 µm) and that fractions of these were also able to reach the alveoli in the lungs (<4 µm).

6.3.2 Mechanisms of toxicity

Respiratory exposure to impregnation products can cause acute respiratory disease in the form of chemical pneumonia, pulmonary oedema and pulmonary collapse.

The assessment of whether an impregnation product can be toxic to users is complex as, in addition to the particle size distribution and particle concentration, it also depends on the chemical ingredients, as well as on whether the effect of these ingredients can enhance each other.

The relationship between the ingredients of an impregnating agent and its potential to cause acute respiratory disease has not been definitively uncovered, but several studies suggest that exposure to impregnating products can affect the lungs by the same toxic mechanism (Larsen et al., 2014; Duch et al., 2014). Several studies have shown that the fluid that covers the surface of the lungs is affected and that this has a disease-causing effect (Sørli et al., 2018a; Yamashita et al., 1995; Sørli et al., 2020).

The surface of the bronchioles and alveoli, which are the small branches in the lungs in which an exchange of oxygen and carbon dioxide can take place, are covered by a thin film of fluid called lung surfactant. The lung surfactant is therefore the first barrier between the air that is drawn down into the lungs and the blood. The lung surfactant is produced by cells called "type II pneumocytes"; it consists of a lipid-protein complex consisting of 90% fats, primarily phospholipids, and a small amount of cholesterol. The last 10% of the lung surfactant consists of surfactant proteins (SP). Four SPs have a known function, SP-A, SP-D, SP-B and SP-C. The two proteins, SP-A, SP-D, have an immunoregulatory function and SP-B and SP-C are small hydrophobic proteins which help to maintain the correct surface tension in the bronchioles and alveoli in cooperation with the phospholipids. SP-B and SP-C ensure that the phospholipids cover the surface between air and liquid. This location is essential for the dynamic surface tension when the lungs are alternately played out and compressed during inhalation and exhalation (the entire section is based on Sørli et al., 2018a).

Whether the impregnating agent can potentially cause adverse health effects when used depends not only on the active substance, but also on the other ingredients and the chemical reactions that occur when the product is used. For example, an *in vivo* study in mice showed that the toxic effect was caused by a synergistic effect between a fluorine active substance and the solvent (Nørgaard et al., 2010a). The fact that toxicity of an impregnation product is dependent on both the active substance and the solvents was also demonstrated in Nørgaard et al. (2014). In this study, the toxicity of impregnation products was coupled with the length of

the carbon chain of the solvent. Overall, the study showed that the more fat-soluble the solvent, the more toxic the mixture. Thus, the toxicity of an impregnation product can be highly dependent on the solvents.

Based on the results of the studies (Nørgaard et al., 2010a & 2014; Larsen et al., 2014), which show that there may be a synergistic effect between the active substances and the other ingredients in an impregnation product, it is not enough to know the toxicity of the individual ingredients to assess whether the product can potentially cause acute respiratory effects. In the case of synergistic effects, the effect of the final product can consequently not be calculated with an addition formula (as prescribed in the CLP Regulation, for example) based on the effect of the individual ingredients, but can only be determined experimentally (this problem is discussed further in Appendix 4).

As there has been a special focus on impregnation products containing PFAS, most of the available studies examine these. However, studies demonstrating a toxic effect of impregnation products with active substances other than PFAS are also available. Duch et al. (2014) reported 39 cases of poisoning in Greenland. The study analysed the chemical components of the impregnation product, as well as the toxicological properties both *in vitro* and in *vivo in* mice. The chemical analyses showed that the product contained a non-fluorinated alkylsilane, isooctyl trimethoxysilane, as well as an unknown non-fluorinated alkylsilane and C9-C13 (hydrogenated naphtha) as solvent. The *in vivo* studies showed that the lungs are affected by exposure to the impregnation product, and the *in vitro* study showed that the product affected the function of the lung surfactant.

An assessment of the toxicity of an impregnation product is hampered by lack of information on ingredients. Pauluhn et al. (2008) reported several serious cases of poisoning in Germany in 2006 after using three products, "Magic Nano Glass & Ceramic" and "Magic Nano Bath & WC", the latter both as aerosol and pump spray. Pauluhn et al. (2008) exposed rats to these products for 4 hours but reduced the exposure time of the product "Magic Nano Glass & Ceramic" to 2 hours in some groups, as several animals died before 4 hours had elapsed. The study showed a mortality rate of 2,269 mg/m³ for "Magic Nano Glass and Ceramic", and the following analyses showed that the entire respiratory system was affected. In addition, the rats exposed to "Magic Nano Glass & Ceramic" had inflammation in the lungs as well as bleeding, pulmonary oedema and thickening of the lung tissue. Koch et al. (2009) followed up on this study and analysed the content of the products. According to the manufacturer, the product did not contain fluorine. However, analyses showed fluorine content and the authors found it likely that the active substance was fluorinated silanes.

6.3.3 Other influences

Smoking

Several case studies mention that smoking in conjunction with or shortly after impregnation has been involved in causing poisoning (Sawamoto et al., 2018; Scheepers et al., 2017). The degree of intoxication may also depend on whether the person is a smoker and therefore already has affected lungs (Sawamoto et al., 2018; Bennett et al., 2015). Scheepers et al. (2017) describe a case study in which cigarettes contaminated with fluorinated polymers most likely caused a case of poisoning in the form of severe chemical pneumonia. Teflon compounds are known to cause "polymer fume fever" upon heating; a case of pulmonary oedema due to pyrolytic products of these polymers has been reported (Jinn et al., 1998 as cited in Feilberg et al., 2008).).

6.3.4 Summary

At present, it is not possible to assess whether an impregnation product is toxic or not, without a study of the individual product. The toxicity of an impregnation product depends on the

chemical composition of the product. Typically, an impregnation product will consist of active substances, solvents and propellants (Duch et al., 2014). In addition, the particle size distribution and particle concentration could affect the toxicity. Active substances, aerosol release, aerosol sizes and solvents have all been shown in studies to have an effect on the toxicity of an impregnation product. There is a broad scientific consensus that the use of propellants does not in itself pose a risk to the consumer.

The complexity of the toxicity of an impregnation product has led to a wide variation in effects on the respiratory system. Several studies suggest that differences between individuals (inter-individual differences) make it difficult to find correlations between cases of poisoning and inhalation of impregnation products (Vernez et al., 2006; Duch et al., 2014).

Impregnation products containing fluorine are the most studied products in terms of the cause of toxic effects. As early as 1995, Yamashita et al. (1995) suggested that the toxicity of impregnation products with fluorinated compounds may cause an effect on the lung surfactant. Several studies have shown that the toxic effect of impregnation products may be caused by surfactants in the product affecting the lung surfactant (Yamashita et al., 1995; Fischer et al., 2012; Sørli et al., 2015). Although the scientific evidence is heaviest for impregnated products with fluorinated compounds, studies by Duch et al. (2014), Sørli et al. (2015) and Sørli et al. (2018a) demonstrated that impregnation products without fluorinated components containing alkylsilane/siloxane can also affect the lung surfactant (Sørli et al., 2015; Sørli et al. 2018a), as well as have a harmful effect in humans and mice (Duch et al., 2014; Sørli et al., 2018a).

Therefore, at present, it is difficult to distinguish between impregnation products that can potentially cause toxic effects for the consumer and impregnation products that cannot cause harm. However, the results suggest that there is a greater risk that the product may cause damage when using aerosol sprays with organic solvents.

7. Selection criteria and products selected for analysis

7.1 Selection criteria

On the basis of the survey and information regarding cases of poisoning, 15 impregnation products were selected in consultation with the Danish Environmental Protection Agency for further analysis in phase 2-4 of the project. These impregnation products were selected using selection criteria established in consultation with the Danish Environmental Protection Agency.

Selection criteria
Application method
Tonnage
Quantity used and use categories
Poisoning cases

The following sections describe each selection criterion.

7.1.1 Application method

In this report, a distinction is made between the following three types of application methods for impregnation products:

- Aerosol spray
- Pump spray
- Spray free

For the further analyses, priority was given to impregnation products which are applied with aerosol spray, in part because this application method has previously been shown to produce smaller aerosols (on average) than pump spray, and in part because impregnation products with aerosol spray are noted in most of the poisoning cases where product information is available.

7.1.2 Tonnage

In the present project, it has not been possible to get an overview of which application categories have the largest market share for impregnation products. However, the results of the survey show that relatively few manufacturers in each use category cover large market shares. When selecting the products, priority was given to selecting products from larger business chains, which are expected to be sold on a larger scale both via internet sales and in physical stores. Areas of application with the highest number of identified products during the survey were also prioritized.

7.1.3 Application amount and category

Impregnating products, which are typically used indoors, were given priority in the selection. Of these, impregnation products applied to larger surfaces were of particular interest. Relevant information obtained for this selection criterion is shown in Table 2.

7.1.4 Intoxication cases

Product-specific information for some of the impregnation products that have caused poisoning cases in Denmark (2006-2020) was received from the Danish Poison Centre at Bispebjerg Hospital. This product information was used to investigate whether these impregnation products were available on the market, among other things. This specific product search was supplemented by a search for impregnation products that have caused poisoning cases registered in The Netherlands in the period January 2015 to June 2020 (received from the National Poisoning Information Centre in The Netherlands). In general, the product information received from both institutions was sparse, and it was difficult to assess whether impregnation products identified by the Internet search were identical to the impregnation products that have caused cases of poisoning. Some of the product information relates to products that caused cases of poisoning several years ago and it is unknown whether the chemical ingredients have been altered in the meantime. However, it appeared likely that they may have been the same product; these products are therefore considered relevant for further analysis.

7.2 Products selected for further analysis

Using the above selection criteria and in consultation with the Danish Environmental Protection Agency, 15 products were selected for further analysis in the present project. Fourteen out of 15 products are applied with aerosol spray, and one is applied with pump spray. A single product, no. 108, was not received after ordering and the order was cancelled. The total number of products analysed was 14.

TABLE 10. Products selected for further analysis.

Product no.	Geography	Category	Application method	Other information
9	DK	All-round: leather, suede and textile	Aerosol spray	Contains silicone
26	DK	All-round: leather, suede and textile	Aerosol spray	Contains silicone
27	DK	All-round: leather, suede and textile	Aerosol spray	"Nano" Use of the product may have resulted in poisoning
35	DK	All-round: leather, suede and textile	Aerosol spray	Contains silicone
40	DK	All-round: leather, suede and textile	Aerosol spray	Contains silicone "Nano"
45	DK	Indoor hard surfaces (tiles, stones, etc.)	Pump spray	Contains methanol
54	DK	Footwear	Aerosol spray	Contains silicone Use of the product may have resulted in poisoning
70	DK	Outdoor equipment (skis.	Aerosol spray	"Biodegradable"
82	DK		Aerosol spray	Contains silicone
88	DK	Outdoor equipment (tents and the like)	Aerosol spray	
89	DK	Furniture (leather)	Aerosol spray	
91	DK	Furniture (leather)	Aerosol spray	
100	DK	Textiles (clothing)	Aerosol spray	PFOA-PFOS free

Product no.	Geography	Category	Application method	Other information
102	NL	Outdoor equipment (tents and the like)	Aerosol spray	
108 [a]	UK	All-round: leather, suede and textile	Aerosol spray	Contains fluorinated substance

[a] This product was not received after ordering and the order was cancelled, so this product is not included in the further analyses.

8. *In vitro* test of lung surfactant inhibition

8.1 Introduction

As described in chapter 6, the main toxic effects of the impregnation agents are linked to changes in the function of the lung surfactant. Inhibition of the lung surfactant may consequently be used as an indicator of the hazard potential of the products. Previous studies have shown that inhibition in the lung surfactant bioassay predicts the effects *in vivo* (inhalation in mice) with 86% accuracy (Sørli et al., 2018b).

Initially the 14 selected products were tested for their compatibility with the test system. Two of the products (product no. 89 and 100) could not be tested as they damaged the equipment. The 12 products for impregnation of different surfaces were tested for their ability to inhibit the function of the lung surfactant in an *in vitro* assay described in detail by Sørli et al. (2018b). In this assay a drop of lung surfactant is placed on a pedestal with a hollow base. The base is connected to a liquid filled syringe mounted in a computer-controlled stepping motor. This allows liquid to be pushed into and removed from the drop in a frequency and extent that mimics the surface area change during breathing. The drop is placed in an exposure chamber where aerosols of the test product can be introduced in the top of the chamber and removed in the bottom of the chamber. The deposited dose of the test product can be estimated from the mass deposited onto a quartz crystal microbalance placed adjacent to the drop.

8.2 Materials and methods

8.2.1 Product aerosolization and exposure

All the products were aerosolized[16] in the same way. One product was a pump-spray; for this product the liquid was removed directly from the bottle. The rest of the products (11 of 12 products) came in a pressurized aerosol spray can; for these, the product was sprayed into a glass vial (approximately 5 mL was collected prior to aerosolization). The liquid was immediately drawn into a gas tight syringe and placed in a syringe pump (Legato 100 Syringe Pump, KD Scientific, USA). The infusion rate (how much is expelled from the syringe during a given time) can be adjusted on the pump. All products were tested with an infusion rate of 0.1 mL/min for up to 5 min exposure. If this infusion rate did not inhibit the lung surfactant function during the 5 min, the infusion rate was increased. The product was led from the syringe into a pressurized air nebulizer (Pit no. 1 (Wong et al., 1982)). The nebulizer was connected to the exposure chamber by glass tubes. The exposure chamber has a hollow base with aeration holes, and air was sucked out through the baseplate to assure flow through the chamber. A QCM was placed close to the lung surfactant droplet (see below) to measure the deposited mass of aerosols during the experiment. The measured mass was used to estimate the dose needed to inhibit the lung surfactant function.

8.2.2 Lung surfactant measurements

A droplet of lung surfactant (10 µL of 2.5 mg/mL Curosurf in a buffer containing 0.9% NaCl, 1.5 mM $CaCl_2$, and 2.5 mM HEPES, adjusted to pH 7.0) was placed on a hollow pedestal. The pedestal was connected to a motorized syringe pump that can be set to add and remove liquid from the droplet at a defined volume and frequency. The droplet was cycled with a change of the area of approximately 30% and a frequency of 3 seconds cycles, to simulate breathing

[16] Aerosolization is the process where small aerosols of the impregnation agent are prepared.

lungs. During the test, a camera took 5 pictures per second of the backlit drop. An ADSA[17] software (Saad & Neumann 2016) was used to analyse the pictures and calculate the surface tension of the droplet. After a baseline period of 40 seconds, the lung surfactant droplet was exposed for up to 5 min, and the data analysed immediately after completion of the test.

8.2.3 Data analysis and internal control

A well-functioning lung surfactant should reach a low minimum surface tension at the set conditions (30% compression, 3 seconds cycles). Therefore, the aerosol exposure was not started until a baseline with a minimum surface tension below 5 mN/m was reached, and any experiments not fulfilling this criterion was excluded from analysis. The inhibitory dose was defined as the dose on the quartz crystal microbalance at the time that the first minimum surface tension was above 10 mN/m.

To assess function across experimental days, an internal control was included (NFP1 in Table 11 and Figure 2). Due to time constraints, NFP1 (nanofilm product 1) was included on half of the testing days. The positive control was a TDFA in an organic solvent which has been studied extensively earlier. NFP1 is described in several papers and its toxicity both to lung surfactant function and to aerosol-exposed mice has previously been published (NFP1 has also been referred to as “POTS” (1H,1H,2H,2H-Perfluorooktyltriethoxysilane) and “non-absorbing floor materials”) (Sørli et al., 2018b; Nørgaard et al., 2010a; Nørgaard et al., 2014). This product is now restricted for sale to private consumer according to Annex XVII, entry 73 of REACH as described Chapter 2.

8.2.4 Aerosol measurements in the surfactometer chamber

The number concentration and size distribution in the surfactometer chamber was measured using an electrical low-pressure impactor (ELPI, ELPI+, Dekati, Finland). All measurements in this series were performed on the same day and followed the same protocol. The product was aerosolized as described above at an infusion rate of 0.1 mL/min. The aerosol was allowed to reach a steady state in the chamber as determined by the concentrations measured with the ELPI. After measuring at steady state, the nebulizer was flushed with 1 mL 96% ethanol. Prior to aerosolization of the next product, the chamber was allowed to empty by flushing with air. The next aerosolization was started when the ELPI measured background levels of particles (<800 particles/cm^3).

8.2.5 Comparison of toxicity

The inhibitory dose was compared to the inhibitory dose of NFP1 (the positive control) and expressed as inhibition factor.

8.3 Results

The inhibitory dose was for each spray product determined for each repetition of the test. The mean inhibitory dose and the standard deviation (SD) was calculated for each product (summarized in Table 11). The lowest inhibitory dose was found for the positive control (21.48 ± 13.5 ng/cm^2). Of the tested products product no. 88 had the lowest inhibitory dose (53.4 ± 17.7 ng/cm^2), and product no. 70 had the highest inhibitory dose (293.8 ± 29.3 ng/cm^2). The inhibitory dose could not be determined for 2 products (no. 54 and no. 45); these were tested at infusion rates of 0.75 and 1 mL/min respectively for 5 min, without inhibition.

The inhibition factor was calculated to rank the products. The inhibition factor expresses the ratio between the inhibitory dose of the product as compared to the inhibitory dose of the control NFP1; i.e., the higher the value, the lower the ability of the product to inhibit the lung surfactant.

[17] ADSA: Axisymmetric Drop Shape Analysis

TABLE 11. Results of *in vitro* test of lung surfactant inhibition (each experiment was performed at least 3 times)

Product no.	Type	Inhibitory dose ± sd (ng/cm^2)	Inhibition factor [a]	Number of repeats	Highest infusion rate tested (mL/min)	Positive control included
9	Aerosol-spray	78.0 ±97.0	4	5		Y
26	Aerosol-spray	139.3 ±49.6	6	4		Y
27	Aerosol-spray	171.5 ±72.4	8	4		N
35	Aerosol-spray	78.7 ±50.3	4	3		N
40	Aerosol-spray	142.9 ±109.1	7	3		N
54	Aerosol spray	Not inhibitory			0.75 (not inhibited)	N
70	Aerosol spray	293,8 ±29,3	14	4		N
82	Aerosol spray	135,1 ±62,8	6	4		N
102	Aerosol spray	134,2 ±81,7	6	4		N/Y
88	Aerosol spray	53,4 ±17,7	2	3		Y
45	Pump spray	Not inhibitory			1 (not inhibited)	Y
91	Aerosol spray	79,0 ±22,6	4	5		N/Y
NFP1	Pump spray	21.5 ±13.5		7		-

N: no, Y: yes

[a] The inhibition factor express the ratio between the inhibitory dose of the product as compared to the inhibitory dose of the control NFP1.

The inhibitory dose of each product is further illustrated in the figure below. The line in the box plot corresponds to the median inhibitory dose; crosses denote mean inhibitory dose.

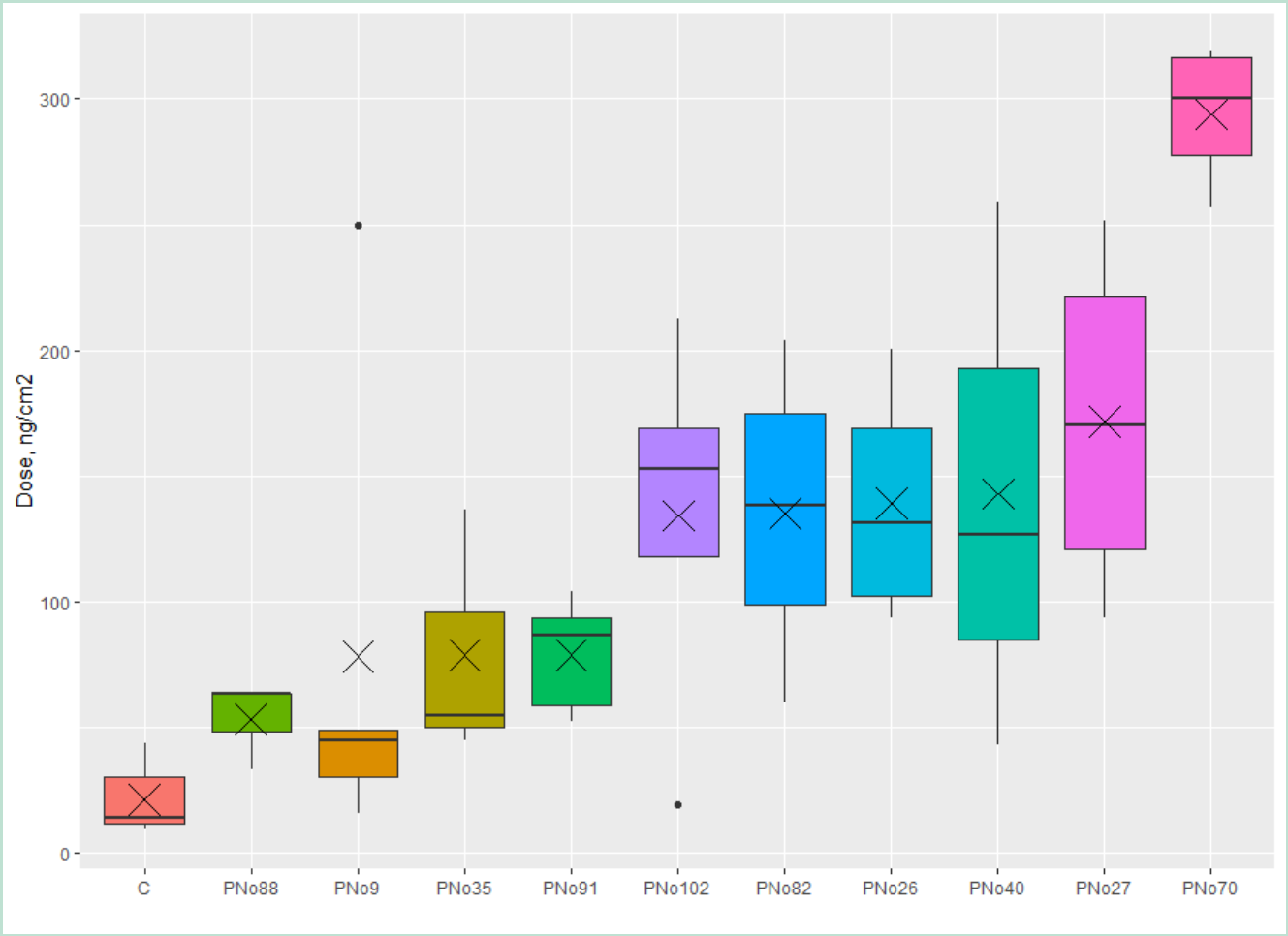


FIGURE 2. The inhibitory dose of each product. The line in the box plot corresponds to the median inhibitory dose, and the cross denotes the mean inhibitory dose. Outliers are marked with dots. C is the control product NFP1.

The particle size distribution of the aerosols in the surfactometer chamber showed that the particle size distributions of the different products were similar when generated using the nebulizer (Figure 3, top panel). The particle size distribution from the exposure chamber was generated using the original aerosolization mechanisms of the product cans as described in section 8.2: i.e., the nozzle of the aerosol spray or pump spray. The results show that this particle size distribution differs from that measured in the surfactometer chamber (Figure 3, lower panel). The nebulizer forms a particle size distribution in the tested range (0.01 - 10 µm), which is comparable to the distribution within this range observed during normal use of the products.

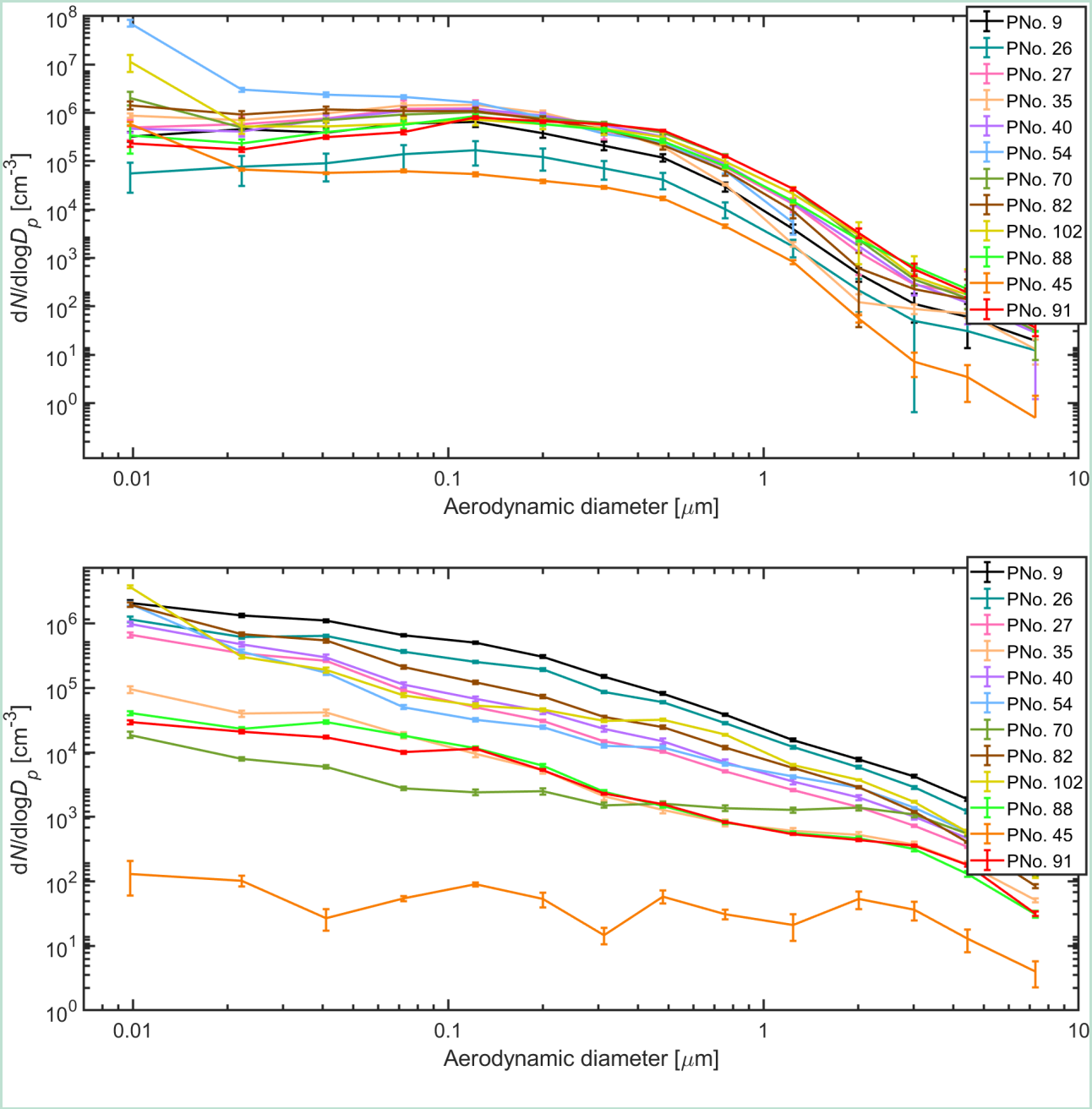


FIGURE 3. Aerodynamic diameter of aerosol generated by different products. In the top panel: the measurements done in the surfactometer chamber. In the lower panel: measurements done in the exposure chamber used for making simulations for use as described in section 8.2.

8.4 Discussion

By calculating the inhibition factor, the products could be ranked. Two products did not inhibit the lung surfactant function (products no. 54 and no. 45). Of the remaining 10 products, the inhibitory concentration was 2 to 8 times higher than that of NFP1. For 1 product (no. 70) the inhibitory concentration was 14 times higher than the inhibitory concentration of NFP1. The physiological relevance of the concentration for inhibition cannot be determined at this point; however, as mentioned above, it has been shown earlier that inhibition in the lung surfactant bioassay (*in vitro* measurements as done here) predicts the effects *in vivo* with 86% accuracy.

There were several challenges in the setup and testing of the products as the products could not be tested with their original aerosol generation device, i.e. the nozzle of the can. Testing the lung surfactant function requires an even and controlled stream of the product. Using the same aerosol device may substantially change the aerosol particle size distribution for some of the products compared to the original generation device, e.g., product no. 45 (Figure 3). Some of the products, particularly no. 26 and no. 102, generated a great deal of gas in the syringe during testing. This made it difficult to control the amount of product aerosolized, i.e., the bubbles/gas pushed most of the product from the syringe into the nebulizer in a short time. The difficulty in aerosol generation resulted in variation of the inhibitory dose calculated.

9. Chemical analyses

9.1 Introduction

In order to obtain more information on the chemical composition of the impregnating agents, all 14 selected and acquired products were analysed for the presence of total fluorine, PFASs and siloxanes, as well as major organic components.

The chemical analysis consisted of an initial screening followed by a sample-specific analysis of selected products. The product-specific analyses were undertaken for products selected on the basis of the initial screening and the results of the *in vitro* test for the inhibition of function of the lung surfactant (Chapter 8).

The chemical analysis within this project was carried out using Nuclear Magnetic Resonance (NMR) spectroscopy in combination with Gas or Liquid Chromatography/Mass-Spectrometry (GC-MS or LC-MS). Traditionally, mass-spectrometry has been used as a primary method for detection, identification and quantification of unknown components. NMR spectroscopy allows for acquisition of neat liquid (pure substance in the liquid phase), and solid samples preserving their integrity in full, or with minimal alteration. Certain NMR methods allow quantification without use of internal standards. It is not common to use NMR spectroscopy as a primary method for product analysis, as done in this project, but the outcome of previous studies has shown it to provide good results.

9.2 Initial screening

9.2.1 Sampling

Samples from the products were taken with a flexible plastic tube attached to the nozzle on the product. No vigorous evolution of gas was observed. The content was collected into a plastic test tube. From each container, 2-5 mL was collected. The weight and volume were measured for density calculation.

Subsamples were taken soon after the samples were received. However, it was difficult to measure the subsample volume accurately and preserve the integrity of the products, as the samples still contained liquified gases (propellants: propane/butane mixture, or dimethyl ether, or carbon dioxide) and evaporated quickly during handling. Therefore, all measurements were semi-quantitative.

Product no. 45 is water-based. Therefore, it was extracted with dichloromethane for NMR analyses and mixed with MTBE (methyl tert-butyl ether) prior to dilution with methanol for the LC-MS analysis and hexane for the GC-MS analyses.

9.2.2 NMR spectroscopy

Two types of both ^{1}H and ^{13}C- spectra in deuterochloroform (with the heavier hydrogen isotope deuterium, ^{2}H) were acquired of the intact sample and of the sample after evaporation of volatile products. The deuterochloroform was used as solvent in order to avoid recording an interfering signal from the protons of the solvent. The relative content of the components was determined.

Several products deposited insoluble white precipitates upon slow evaporation of volatile part, which were not analysed further.

9.2.3 GC-MS analysis

GC-MS analyses were performed on the GC-Orbitrap instrument in full-scan and at the highest possible mass-resolution of 120,000. Two types of techniques were applied: injection of a diluted liquid sample and injection of a gas phase over non-diluted spray content. Different temperature programs were used. The outcomes of these two different tests were rather similar.

9.2.4 LC-MS analysis

Diluted samples (methanol solutions) were analysed in three ways: in a scan mode for positive ions (m/z – 30-1,500), in a scan mode for negative ions (m/z – 30-1,500) and in SRM (selective reaction monitoring) mode for a standard set of perfluorocarboxylic acids and perfluorosulfonic acids. In scan mode special attention was paid to ions reported for. None of these ions were detected.

9.2.5 TOF - Total Organic Fluorine

Unfortunately, background contamination was high in all products, and the analysis only confirmed that fluorine content was below 0.3% by weight in all products except product no. 45, where it was below 0.7%. This product was found to be a water-based mixture, shown not to have an inhibitory effect on the lung surfactant in the *in vitro* tests (Chapter 8) and was excluded from further chemical analysis.

9.2.6 Results of the initial screening

The results of the initial screening are shown in Table 12 along with data on chemical composition from safety data sheets (SDS).

Suspected organosilicon compounds related to polydimethylsiloxane (CAS No 63148-62-9, “Dimethicone”), a common component of personal care products, were found in all but three samples. Their identification was based on ^{1}H NMR spectra and the signals were in the characteristic region of 0-0.2 ppm. In Phase 2 these findings were further investigated by NMR spectroscopy of authentic standards and by specialized GC-MS methods (see section 9.3).

Products no. 35, 82, 88 and 91 were similar and all were comprised of a solution of hydrogenized naphtha in light hydrocarbons such as pentane, hexane, isohexane and heptane, with indications of the presence of polydimethylsiloxane and propane/butane mixture as propellant[18].

Product no. 9 and 26 were also similar; unlike the previous group, they had rather low content of heavy naphtha hydrocarbons. Polydimethylsiloxane was present.

Another group consisted of 27, 40 and 54, where the heavy part was naphtha-based, but the solvent was isopropanol with the addition of butylacetate. Polydimethylsiloxane was also present.

Product no. 45 was a water-based product and contained traces of ethanol, hydrocarbons, and polydimethylsiloxane.

Product no. 70 was unique compared to the other products: it was a simple mixture of dihexyl ether (ca. 20%) and ethanol (ca. 80%). No polydimethylsiloxane was present.

Product no. 89 was also unique. It had a low content of hydrocarbons, but also included diisobutylketon as a heavier component and butanone as the main solvent with addition of iso-propanol and tert-butanol, as well as butylacetate. Dimethyl ether as propellant was confirmed. No polydimethylsiloxane was present.

[18] The SDS for product no. 91 indicates the propellant is CO_2.

Product no. 100 was unique as well. It was made of hydrocarbons with ca. 1% of isopropyl acetate. No polydimethylsiloxane was present. However, in this product, traces of an organofluorine substance, perfluorohexylethylmetacrylate, were detected (< 1 ppm). This could be an indication of a presence of polymers with fluorinated sidechain or fluorosilicon compounds.

Product no. 102 was also unique and consisted mainly of a hydrocarbon mixture, but also contained isopropylacetate (ca. 4%). However, in this product, traces of organofluorine substances (perfluorohexanoic acid and perfluorohexylethylmetacrylate) were detected (< 1 ppm). This could indicate the presence of polymers with fluorinated sidechains or fluorosilicon compounds.

Thus, from the set of 14 products, 8 different formulations were identified. No clear indication of the presence of hazardous substances was found in the initial screening.

TABLE 12. Results of the initial screening in percentage of the weight of the impregnation agent. Concentrations in weight-% from SDSs are indicated in parentheses.

Product no.	9	26	27	35	40	45	54	70	82	88	89	91	100	102
Density g/cm^3	**0.65**	**0.66**	**0.74**	**0.77**	**0.73**	**1.01**	**0.73**	**0.79**	**0.72**	**0.76**	**0.77**	**0.77**	**0.68**	**0.68**
Hydrocarbons	96 (72-100)	93 (72-100)	41 (71-100)	95 (-)	36 (62-100)	Trace (-)	43 (65-100)	n.d. (-)	95 (30-60)	95 (95-100)	4 (-)	96 (90-100)	98 (-)	88 (90)
Methyl siloxanes	2.5 (+)	5.0 (-)	2.1 (+)	3.8 (-)	1.3 (-)	trace (-)	1.4 (+)	n.d. (-)	4.6 (-)	4.1 (-)	n.d. (-)	4.0 (-)	n.d. (-)	5.1 (-)
Isopropanol	n.d. (-)	n.d. (-)	47 (20-30)	n.d. (-)	52 (+)	n.d. (-)	46 (+)	n.d. (-)	n.d. (-)	n.d. (-)	n.d. (-)	n.d. (-)	n.d. (-)	n.d. (-)
Butyl acetate	n.d. (-)	n.d. (-)	10 (1-5)	n.d. (-)	11 (2.5-10)	n.d. (-)	9 (1-5)	n.d. (-)	n.d. (-)	n.d. (-)	n.d. ()	n.d. (-)	n.d. (-)	n.d. (-)
Ethanol	n.d. (-)	n.d. (-)	n.d. (-)	n.d. (-)	n.d. (-)	trace (-)	n.d. (-)	84 (75-80)	n.d. (-)	n.d. (-)	n.d. (-)	n.d. (-)	n.d. (-)	n.d. (-)
Dihexyl ether	n.d. (-)	n.d. (-)	n.d. (-)	n.d. (-)	n.d. (-)	n.d. (-)	n.d. (-)	16 (15-20)	n.d. (-)	n.d. (-)	n.d. (-)	n.d. (-)	n.d. (-)	n.d. (-)
Isopropyl acetate	n.d. (-)	n.d. (-)	n.d. (-)	n.d. (-)	n.d. (-)	n.d. (-)	n.d. (-)	n.d. (-)	n.d. (-)	n.d. (-)	n.d. (-)	n.d. (-)	2 (-)	6 (-)
Dimethyl ether	n.d. (-)	n.d. (-)	n.d. (-)	n.d. (-)	n.d. (-)	n.d. (-)	n.d. (-)	n.d. (-)	n.d. (-)	n.d. (-)	3 (-)	n.d. (-)	n.d. (-)	n.d. (-)
Methyl ethyl ketone	n.d. (-)	n.d. (-)	n.d. (-)	n.d. (-)	n.d. (-)	n.d. (-)	n.d. (-)	n.d. (-)	n.d. (-)	n.d. (-)	76 (-)	n.d. (-)	n.d. (-)	n.d. (-)
Diisobutyl ketone	n.d. (-)	n.d. (-)	n.d. (-)	n.d. (-)	n.d. (-)	n.d. (-)	n.d. (-)	n.d. (-)	n.d. (-)	n.d. (-)	14 (-)	n.d. (-)	n.d. (-)	n.d. (-)
DEHP [a]	1.0 (-)	2.1 (-)	0.3 (-)	0.9 (-)	0.3 (-)	n.d. (-)	0.3 (-)	n.d. (-)	0.3 (-)	0.8 (-)	1.9 (-)	0.3 (-)	0.2 (-)	1.0 (-)

[a] Bis(2-ethylhexyl) phthalate (DEHP), detected in the initial screening as "unknown component" was identified and quantified during the sample-specific analysis. n.d.: not determined. (+) – presence mentioned but the concentration is not indicated. (-) – presence not mentioned

9.2.7 Discussion and conclusions

In general, the content corresponds to the declarations on the safety data sheet. All macrocomponents declared in the set of SDSs were found in one or several products except ethyl

acetate, which was reported at 10-20% in the SDS for product no. 89, but not found in the chemical analysis. In all products, except product no. 70 and product no. 45, an unknown component with distinct spectral features was detected and its content was estimated at 0.1-3%. This was investigated further in the sample-specific analysis.

The solvent composition deviated from the SDSs in several cases: in some cases, non-declared solvents were present and in others declared solvents were not found. The solvent ratios also deviated from the declared ratios. However, all identified solvents are commonly used solvents. In most products, a saturated hydrocarbon mixture is a main component. For such mixtures it was difficult to distinguish between isomers and/or homologs.

It was possible to confirm the presence and identity of the propellants in some cases.

9.3 Sample-specific analysis

Six products were selected for further sample-specific analysis, in consultation with the Danish EPA. The products were chosen based on the effect on the lung surfactant (Chapter 8), the initial chemical screening (section 9.2) and) product information from the survey (Chapter 5) on use and estimated market share. Two products, nos. 82 and no. 91, were selected from the largest group of similar products, and one product from each of the two smaller groups (products no. 26 and no. 27) were selected as representative for each of their groups. Product no. 100 and 102 were selected based on detection of traces of PFASs. Product no. 45, 70 and 89 were not included, as their composition was already established; no traces of organofluorine or organosilicon compounds were detected. Thus, product nos. 26, 27, 82, 91, 100 and 102 were the final set for the second round of chemical study.

The following analyses were included:

- **Total oxidizable precursors (TOP)** – oxidation of all PFAS precursors into known perfluorocarboxylic or perfluorosulfonic acids, followed by LC/MS analysis.
- **Neutral PFAS with hydrolysis** – experimental method, developed at NILU. Was shown to detect fluorotelomer alcohols (FTOHs), which may originate from the manufacture or decomposition of other PFASs.
- **NMR/MS investigation of model fluorosilanes –** the aim was to use commercially available samples of model fluorosilanes of the same type as the substance found in the product NFP1 to investigate their possible presence in selected products.
- **NMR/MS investigation of siloxanes –** the aim was to use commercially available samples of model siloxanes to determine the possible presence of these components in the samples.
- **Attempt to identify the unknown component**, present in small but significant quantity in all but two samples (products nos. 45 and 70), which was not declared in any of the SDSs.

9.3.1 TOP (Total Oxidizable Precursors)

The samples were oxidized with potassium persulfate and the reaction mixture was analysed for the standard set of ionic PFAS: perfluorocarboxylic acids (C_4-C_{18} PFCAs) and perfluoroalkanesulfonic acids (C_4-C_{10} PFSAs). The concentration of acids in all samples except C_4-C_7 PFCAs in product no. 100 and product no. 102 were below 0.0002% (Table 13). No other PFAS were detected in the full-scan LC-MS analysis.

TABLE 13. Concentration of perfluorocarboxylic acids C_4-C_7 in product nos. 102 and 100 as calculated theoretical amount of suspected precursor 6:2 FTMA (perfluorohexylethylmethacrylate) presumably incorporated in a polymer or in an oligomer. Unit: weight%.

Product	PFBA	PFPeA	PFHxA	PFHpA	Sum of PFCAs	6:2 FTMA
Product no. 102	0.044	0.100	0.186	0.014	0.344	0.53
Product no. 100	0.027	0.049	0.092	0.010	0.178	0.27

PFBA – Perfluorobutanoic acid, CAS No. 375-22-4; PFPeA – Perfluoropentanoic acid, CAS No. 2706-90-3; PFHxA – Perfluorohexanoic acid, CAS No. 307-24-4; PFHpA – Perfluoroheptanoic acid, CAS No. 375-85-9; PFCAs – Perfluorocarboxylic acids; 6:2 FTMA – Perfluorohexylethylmethacrylate, CAS No. 2144-53-8.

Concentrations in Table 13 shall be considered as minimum concentrations, as certain amounts of precursor could have been converted to shorter chain derivatives or other products during the analysis.

The analyses indicate that only product nos. 100 and 102 contained PFAS; the PFAS was most likely a derivative of 6:2 fluorotelomer monomer. The detection of 6:2 FTMA traces in the initial analysis of these two products indicates the original monomer is 6:2 FTMA.

9.3.2 Neutral PFAS after hydrolysis

Further confirmation came from detection of 6:2 FTOH after basic hydrolysis of the samples. It was shown recently that hydrolysis reveals bonded FTOHs in textile samples (Nikiforov, 2021). The samples after hydrolysis were analysed for a standard set of volatile PFASs: 4:2-, 6:2-, 8:2- and 10:2-FTOHs[19,20,21,22], for FOSA[23], MeFOSA[24], EtFOSA[25], MeFOSE[26], EtFOSE[27].

Only in product nos. 100 and 102, the volatile PFAS, 6:2 FTOH, was detected at 2.28 and 0.81 mg/g, respectively, corresponding to 0.27% and 0.096% content of the 6:2 FTMA precursor. These values shall be considered as minimum concentrations as possible incomplete hydrolysis or partial loss of volatile 6:2 FTOH may result in an underestimation of the concentration. In accordance with the TOP results (Chapter 9.3.1), the content of fluorinated products in product no. 102 was found to be higher than in product no. 100. These levels are sufficiently high to presume intentional use of these PFAS, as they are polymers or oligomers based on perfluorohexylethylmethacrylate (6:2 FTMA).

The chemical transformations involved in the analyses described above are shown in Figure 4.

[19] 4:2 FTOH - 1-Hexanol, 3,3,4,4,5,5,6,6,6-nonafluoro-, CAS No 2043-47-2

[20] 6:2 FTOH - 1-Octanol, 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-, CAS No 647-42-7

[21] 8:2 FTOH - 1-Decanol, 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-, CAS No 678-39-7

[22] 10:2 FTOH - 1-Dodecanol, 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-heneicosafluoro-, CAS No 865-86-1

[23] FOSA - perfluorooctane sulfonamide, CAS No 754-91-6

[24] MeFOSA - N-methyl perfluorooctane sulfonamide, CAS No 31506-32-8

[25] EtFOSA - N-ethyl perfluorooctane sulfonamide, CAS No4151-50-2

[26] MeFOSE - N-methyl perfluorooctane sulfonamidoethanol, CAS No 24448-09-7

[27] EtFOSE - N-methyl perfluorooctane sulfonamidoethanol, CAS No 1691-99-2

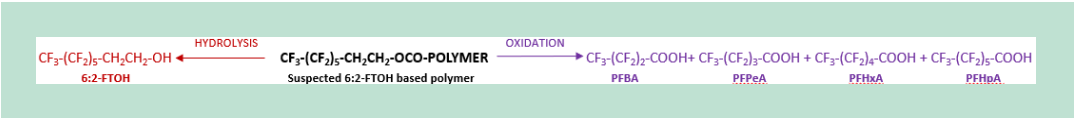


FIGURE 4. Chemical transformations of possible related substances by oxidation and hydrolysis.

9.3.3 NMR/MS investigation of model fluorosilanes

Three commercially available model substances were acquired: Perfluorohexylethyl triethoxysilane (Silane, triethoxy(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)-, CAS No 51851-37-7), perfluorooctylethyl triethoxysilane (Silane, triethoxy(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)-, CAS No 101947-16-4) and perfluorooctylethyl trimethoxysilane (Silane, (3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)trimethoxy-, CAS No 83048-65-1). Their NMR and MS spectra were acquired and retention times recorded. No match or characteristic features was found in the investigated samples of impregnation sprays; therefore, the presence of fluorosilanes of the same type as in NFP1 was ruled out.

9.3.4 NMR/MS investigation of siloxanes

NMR and MS spectra of two model substances (1,1,1,3,3,5,5,7,7,9,9,9-dodecamethylpentasiloxane, CAS No. 141-63-9 and cyclotetrasiloxane, 2,4,6,8-tetramethyl-2,4,6,8-tetrakis(3,3,3-trifluoropropyl)-, CAS No. 429-67-4) were acquired. In addition, the previously recorded MS spectra as well as NMR and MS spectra from the literature were used to confirm presence of siloxane compounds.

10. Assessment of potential exposure

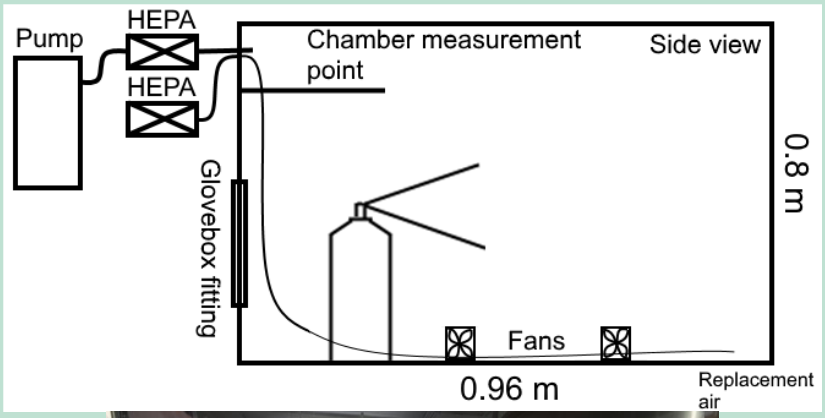
10.1 Introduction

Twelve impregnation spray products (as in Chapter 8, i.e., no. 9, 26, 27, 35, 40, 45, 54, 70, 82, 88, 91, and 102) for indoor and outdoor use were selected for testing of aerosol emissions with the purpose of determining concentrations during use in a chamber, and calculating emission rates. Emission rates, i.e., how much mass of the product is released per unit time, were determined from experiments using new products which had not been opened before. Emission rates were used to model two realistic exposure scenarios based on two case studies and to calculate average respirable mass concentrations during the activity.

10.2 Materials and methods

A small-scale chamber of 0.8 m x 0.96 m x 0.71 m (h x w x d) with a total volume of 0.55 m^3 was used for the experimental work (Figure 5). Two 9V computer fans were placed in the chamber to provide air mixing for the duration of the experiments. Emissions from the fans were characterised prior to the experiments and subtracted from spray activity concentrations. Respirable concentrations from fans were 0.0051 mg/m^3. An external pump provided additional flow out of the chamber with the replacement air entering through an inlet attached to a HEPA filter.

Prior to spraying, the new aerosol spray cans or pump spray bottles were shaken vigorously for 30 seconds. Spray activity was conducted by spraying continuously for 30 seconds inside the chamber. The spray activity was conducted either as continuous spray for the aerosol spray or by a continuous series of pumps on the lever for the pump spray. For the pump spray bottle, 60 pumps in 30 seconds were performed. The spray was directed towards a thin piece of MDF (medium density fibreboard) set up at the end of the wall for easy cleaning of the chamber. The distance from the spray point to the MDF was approximately 50 cm.



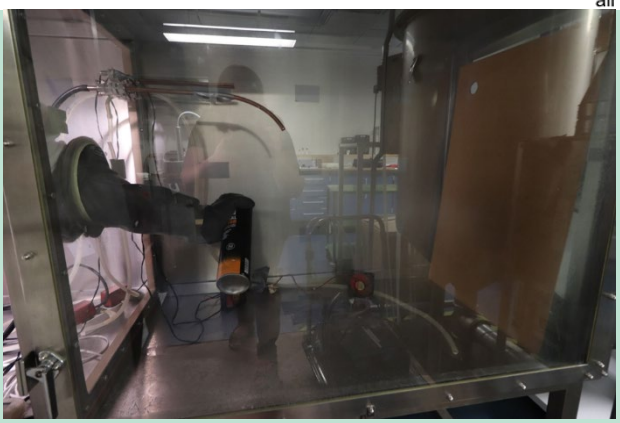


FIGURE 5. Chamber experimental setup. Conceptual drawing and photography during spraying.

Particle number concentrations and particle size distributions of particles between 5 nm and 10 µm were measured using an Electrical Low-Pressure Impactor (ELPI, HR-ELPI+, Dekati, Finland) in 14 channels with a 1 s time resolution. The measurements from the channels of the ELPI up to the channel having D_{50}[28] of 4.4 µm were used to calculate the respirable fraction of the mass concentration.

For the conversion to respirable mass, spherical particles with a density of 1 g/cm^3 were assumed. The midpoint of each product was used to convert the aerodynamic number concentration into mass concentration.

The total respirable concentrations were used to calculate the respirable mass emission rates. Respirable mass emission rates, ER_{resp}, were calculated according to Ott et al. (2006) under the assumption of a fully mixed system:

$$ER_{resp} = \frac{V_{tot} \cdot (C_m - C_0) \cdot \exp\left(-\gamma \cdot (t_m - t_0)\right)}{t_m - t_0}$$

where, V_{tot} is the total volume of the chamber, C_m is the maximum respirable mass concentration, t_m is the time at C_m, C_0 is the respirable concentration at the start of the experiment, and t_0 is the time at the start of the experiment. The loss rates, γ, were calculated for each experiment by fitting a first order exponential decay function to the calculated respirable mass concentrations (Figure 6).

[28] Geometric mean for the diameter

10.3 Modelling

The model used here was based on Jensen et al. (2018) where a mass balance model was developed. A two-box model was used with a near field (NF), which is the area near the atomizer and a far field (FF), which is the area outside the near field, where exposure may still occur. Calculated respirable mass emission rates from each product were used as source input into the model.

Two scenarios were used to assess exposure by calculating respirable mass room concentrations in each scenario.

Scenario 1 consist of a 36 m^3 room with a defined NF volume of 1.2 m x 1.2 m x 1.2 m (h x w x l) and an air exchange rate of 1.5 h^{-1} corresponding to multiple opened windows (Howard-Reed et al., 2002). Spray time is assumed to be 30 min and total model time representing the time a person would stay inside the room during and after spraying is 120 min. This means that after the 30 min of spraying, the person would stay inside the room for another 90 min.

Scenario 2 consist of a 90 m^3 room with a defined NF volume of 1.2 m x 1.2 m x 1.2 m (h x w x l) and an air exchange rate of 1.0 h^{-1} corresponding to a fully opened door (Howard-Reed et al., 2002). Spray time is assumed to be 90 min and total model time representing the time a person would stay inside the room during and after spraying is 90 min. This means that the person would leave the room after the 90 min of spraying.

The average respirable mass concentrations [mg/m^3] were calculated in each computational domain in both scenarios and for each product.

10.4 Results

Maximum respirable concentrations in the chamber after 30 seconds of spraying reached between 5 (product no. 45) and 150 mg/m^3 (product no. 9). Fitted loss rates, γ, were between 0.0021 and 0.0029 s^{-1} with $R^2 > 0.95$ for the logarithmic residual fit in all cases except one case, where $R^2 = 0.91$ (Figure 6).

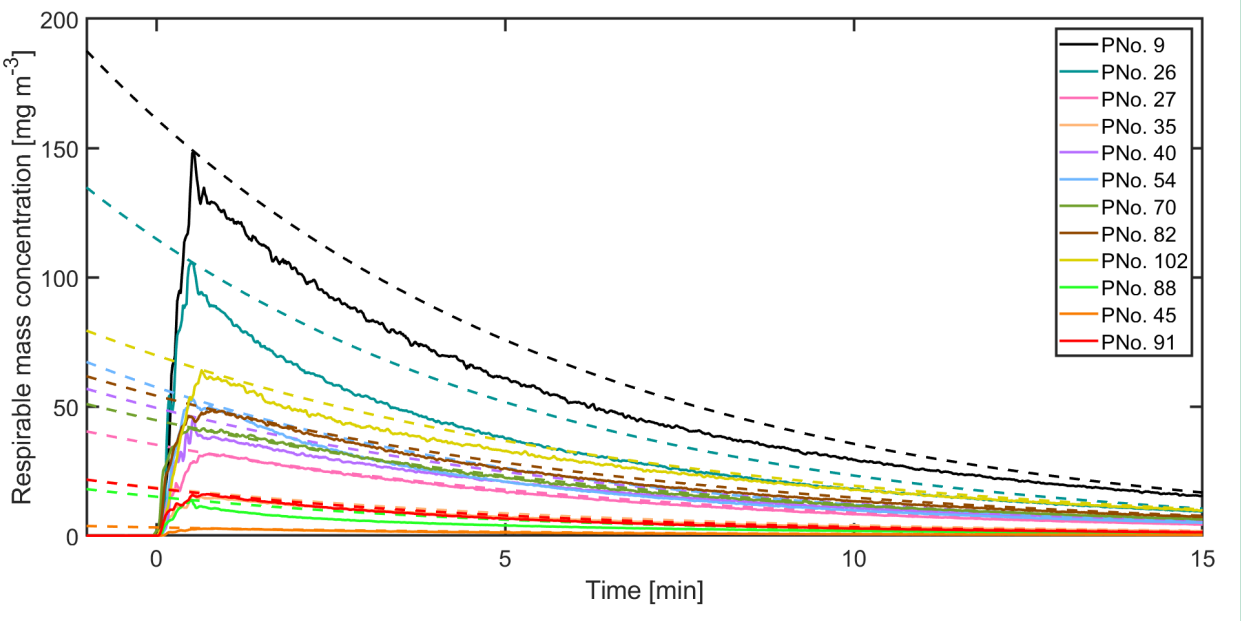


FIGURE 6. Respirable mass concentrations measured in the chamber with fitted decay functions (shown with dashed lines) for each of the 12 tested products.

Respirable mass emission rates were calculated to be in the range of 0.05 (product no. 45) to 3.35 mg/s (product no. 9) (see Table 14).

TABLE 14. Samples and results from the modelling and scenarios

Product no.	Type	Respirable emission rate (mg/s)	Average respirable mass concentration (mg/m^3)			
			Scenario 1 NF	**Scenario 1 FF**	**Scenario 2 NF**	**Scenario 2 FF**
9	Aerosol spray	3.35	107	51	194	63
26	Aerosol spray	2.40	77	37	139	45
27	Aerosol spray	0.71	23	11	41	13
35	Aerosol spray	0.39	12	6	22	7
40	Aerosol spray	0.90	29	14	52	17
45	Pump spray	0.05	2	1	3	1
54	Aerosol spray	1.04	33	16	61	20
70	Aerosol spray	0.82	26	13	47	15
82	Aerosol spray	0.95	30	15	55	18
88	Aerosol spray	0.28	9	4	16	5
91	Aerosol spray	0.32	10	5	19	6
102	Aerosol spray	1.25	40	19	73	24

NF: near-field; FF: far-field

For the modelling, average respirable mass concentrations in the NF scenarios were calculated to be 2 - 107 mg/m^3 and 3-194 mg/m^3 for scenario 1 and scenario 2, respectively, and in the FF scenarios, 1 - 51 mg/m^3 and 1-63 mg/m^3 for scenario 1 and scenario 2, respectively (Table 14). As an example, the concentration over time for product no. 9 is shown in Figure 7. In general, Scenario 2 gave rise to higher average respirable mass concentrations, whereas highest peak concentrations were found for Scenario 1 (Figure 7). The density of the particles was assumed to be 1 g/cm^3. Any differences between the assumed density and the density of the impregnation spray particles would cause differences in the calculated mass concentrations and emission rates.

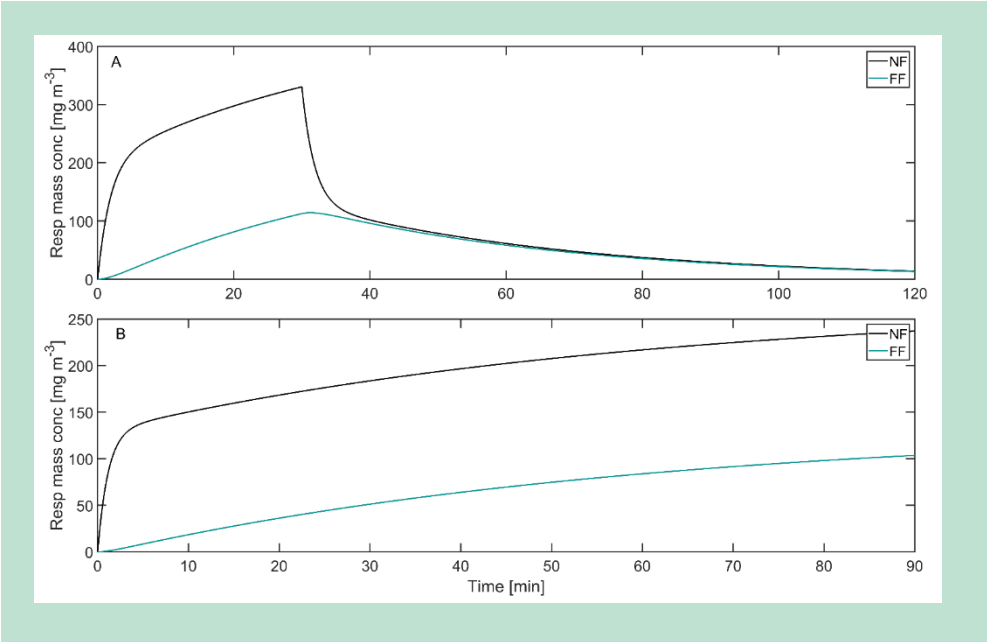


FIGURE 7. NF and FF respirable mass concentrations calculated for use of product no. 9 in (A) Scenario 1 and (B) Scenario 2. Shown as an example of the modelled concentrations.

10.5 Discussion

All analysed spray product released particles in the respirable fraction, whether from spray can or pump spray use. These particles have the potential to reach and deposit in the deep lung regions. To assess the possible exposure during use, two scenarios were chosen to compare the 12 spray products; however, the scenarios are not necessarily representative of the intended use of the spray products. For example, product no. 54 is intended for use with footwear and the expected spray time during use is likely to be shorter than the 30 and 90 minutes, respectively, defined in Scenarios 1 and 2.

For the calculation of the respirable emission rates used in the modelling of the two scenarios, the measurements of the channels of the ELPI up to the channel with a D_{50} of 4.4 µm were used. The 4.4 µm channel has an upper cut-off diameter, D_{50}, of 5.38 µm. According to the Danish definition, the respirable fraction is <5 µm[29], whereas international standards define the D_{50} of the respirable fraction to 4 µm (ISO 7708). Therefore, the chosen ELPI channel is the most representative for calculating the respirable fraction but may overestimate PM_4 (Particle sizes <4 µm used internationally) and underestimate PM_5 (Particle sizes <5 µm used in Denmark).

[29] AT-vejledning: Grænseværdier for stoffer og materialer C.0.1

11. Discussion

For the 14 selected and purchased products, selected information from the survey as well as results from the tests and chemical analyses performed are summarized in Table 15. In addition to a brief description of the products from the survey, the table indicates the inhibitory dose of lung surfactant function (compared to the inhibitory dose of a positive control (NFP1)), identified ingredients from the chemical analyses, and the emission rate of respirable particles as an expression of the relative potential for exposure of the lungs.

The positive control used in *in vitro* tests of the products' ability to inhibit the lung surfactant is a PFAS-based product, NFP1, which has been extensively described in previous studies (mentioned in section 8.2.3). NFP1 is an example of the PFAS-based impregnating agents which have been shown to have a significant health effect and which have been subject to restriction of use at EU level from 1 January 2021. The inhibitory dose given in the table is the ratio between the inhibitory dose of the products and the inhibitory dose of NFP1; i.e., a low number expresses a relatively high inhibitory effect on the function of the lung surfactant. Inhibition of the lung surfactant can be used as an indicator of a product's hazard potential, as previous studies have shown that inhibition of the lung surfactant in bioassays predicts effects *in vivo* (inhalation in mice) with 86% accuracy.

Due to the high background level of fluorine, it could only be determined for all products that the total content of organic fluorine (TOF) was below 0.3%, except for product no. 45[30], where the content was below 0.7%.

Two products were found to contain a possible perfluorocarboxylic acid (PFCA) precursor: product nos. 100 and 102. Data from the chemical analyses indicate that it is a polymer or oligomer containing fragments of perfluorohexylethyl methacrylate (6:2 FTMA). The samples showed the presence of 6: 2 fluorotelomeric alcohol (6:2 FTOH) after hydrolysis and C4-C7 perfluorocarboxylic acids after oxidation. The concentration of the polymer (calculated as 6:2 FTMA) was calculated to be 0.53% in one product and 0.27% in the other, but these concentrations must be considered as minimum concentrations with the method used. Product no. 100 could not be tested for the ability to inhibit the lung surfactant as the product destroyed the laboratory equipment. The inhibitory dose for product # 102 was 6 times the inhibitory dose of the positive control. The only product labelled "PFOA-PFOS-free" (product # 100) contained PFAS components but was not found to contain PFOA, PFOS or their related substances.

Based on the test of product no. 102, there is nothing in the results to indicate that products based on PFAS have a stronger inhibitory effect on the lung surfactant than products based on other chemicals.

Of the 12 products that could be tested for inhibition of the function of the lung surfactant, 10 had an inhibitory effect on the lung surfactant. The two products where no inhibitory effect was observed were product nos. 45 and 54. Product nos. 45 and 54 showed traces and actual content of methylsiloxanes in the chemical content analyses, respectively. Product no. 45 is a water-based product, whereas product no. 54 has a chemical composition similar to product nos.

[30] Product No. 45 was not selected for specific analysis as the substance in the *in vitro* test did not have an inhibitory effect on the lung surfactant. The product is water-based and the result is in accordance with previous studies that have shown that water-based products have less inhibitory effect than products based on organic solvents.

27 and 40 in the initial screening. The three products all contained methyl siloxanes, isopropanol, butyl acetate and hydrocarbons (36-43%).

Product nos. 27 and 40 both had inhibitory effects on the function of the lung surfactant with an inhibition factor of 8 and 7 times the positive control (NFP1), respectively. Product no. 27 was selected as the product was from a supplier who has marketed a similar product that has previously led to cases of poisoning.

The lowest inhibitory dose was found for product no. 88, which had an inhibitory factor of 2 times the positive control (NFP1). Product no. 88 was an aerosol spray which stated to be used for impregnating outdoor textiles against water and dirt, where it would be expected that the user could be exposed to relatively large amounts of the impregnating agent. This product, as well as three other products with an inhibitory factor of 4 times the positive control (product nos. 9, 35 and 91), all contained methylsiloxanes and hydrocarbons (i.e., based on organic solvents) to approximately the same extent and were presumed to be based on silane/siloxane/silicone chemistry. When comparing chemical content analyses and the effects on the function of the lung surfactant, products which primarily consisted of hydrocarbons (88-98%) and contained methylsiloxanes (product nos. 9, 26, 35, 82, 88, 91, 100, 102) had an inhibition factor of 2-6 times the positive control (except product no. 100, whose inhibition factor is unknown, as the product damaged the laboratory equipment and therefore could not be analysed). Compared with the large group of products consisting primarily of hydrocarbons and methylsiloxanes, product nos. 24, 40 and 54, which contain a smaller concentration of methylsiloxanes and hydrocarbons and contain isopropanol and butyl acetate, differ. Product nos. 100 and 102 were the only products that contained PFAS in such high concentrations that intentional use of these PFASs must be assumed.

Product nos. 9 and 40 were included in the Consumer Council THINK Chemistry's test (Chapter 4), where, consistent with the results of the present project, the analysis results showed traces of siloxanes. Product no. 9 is stated to be an impregnation product containing silicone, with a wide application range from tents to footwear; product no. 40 is an "all-round" product. Product no. 35 is also a product with versatile use, whereas product no. 91 is for leather furniture. Product no. 91 is one of the products that was assessed to have been sold to Danish consumers in high tonnage.

The results indicate that these products, which are not covered by the use restriction per 1 January 2021, may have a significant inhibitory effect on the lung surfactant (*in vitro*) which - albeit slightly less significant - is comparable to the effect observed for products covered by the restriction.

However, it is difficult to draw unambiguous conclusions about the relationship between the ability to inhibit the lung surfactant and the chemistry of the products as one product (no. 54) containing hydrocarbons, methylsiloxanes, isopropanol, butyl acetate and DEHP could not be shown to inhibit the lung surfactant.

The phthalate DEHP was found in low concentrations in the majority of the products. However, the concentrations are considered too high to be caused by contamination (up to 2%). The substance has previously been widely used as a plasticizer in, e.g., paint, but no specific information has been found on the function of the substance in impregnating agents. The function is probably a softening effect in the finished surface film that makes the film more flexible and durable. DEHP is on the list of substances subject to authorization (REACH Regulation, Annex XIV) due to reproductive toxicity. The substance has been identified as an SVHC (Substance of Very High Concern) due to reproductive toxic and endocrine-disrupting properties, and is therefore included in the candidate list. DEHP is also subject to a use restriction under REACH

(entry 51 to Annex XVII), which prohibits the substance in, e.g., surface coatings. But the substance is not banned in mixtures for impregnation.

Emission rates of respirable particles for the analysed impregnation products varied for the aerosol sprays from 0.28 to 3.35 mg/s during use, which would result in highly variable exposure amounts during use (a factor of 10 between the highest and lowest). As can be seen from the calculated scenarios, the emission rate has a significant influence on the exposure of the user. It should be noted that testing the products' abilities to inhibit the lung surfactant was performed using a nebulizer, so the emission rates during the test were independent of the emission rates of the specific sprays. Based on *in vitro* tests for lung surfactant inhibition and estimated emission rates, the greatest risk of spray impregnation products is expected to occur for products with a low inhibitory dose value and a high emission rate for respirable particles. However, this cannot be known with certainty without the products being tested on animals. In this report, the product with the lowest inhibition factor (at 2), product no. 88, has the lowest emission rate for respirable particles of all aerosol sprays tested. In contrast, product no. 9 has the highest emission rate for respirable particles (3.35 mg/s) and an inhibition factor of 4 compared to the positive control.

The emission rates for respirable particles compared to the effects on the lung surfactant examined in this report show that the specific product nozzles that cause different emission rates have a great influence on the exposure of the consumer and thus also the potential acute respiratory risk. Other factors such as the pressure in the can also affect the exposure, but this has not been investigated in this study.

The emission rate of the only pump-spray product analysed (product no. 45) resulted, as expected, in the lowest emission rate for respirable particles. The product was water-based and without a proven inhibitory effect on the lung surfactant. The result shows that products are available that would likely have significantly fewer potential health effects than the majority of impregnation products based on organic solvents and applied by aerosol spray.

TABLE 15. Summary of the project results for 14 selected impregnation products

	Field of application and application method	General information from the dealers' websites and the survey	Inhibitory dose of product (C) compared to a positive control (*in vitro* test) $C_{product}$ / $C_{control}$	Identified ingredients [b]	Emission rate for respirable particles, (mg/s)
9	"All-round" Aerosol spray	Listed on the dealer's website for use on leather, suede and textiles. More specifically, footwear and tents are mentioned. Supplied by a major DIY store chain. Found as online sale by general search, and was not found in physical store. The product was included in the Consumer Council Think Chemistry's test, which showed that the product contained traces of siloxanes.	4	Hydrocarbons, methylsiloxanes, and DEHP.	3.35
26	"All-round" Aerosol spray	Listed on the dealer's website for use on leather, suede and textiles. Supplied in a major DIY store chain. Found as online sale at the general search, and was not found in physical store.	6	Hydrocarbons, methylsiloxanes, and DEHP.	2.40
27	"All-round" Aerosol spray	Listed on the dealer's website for use on leather, suede and textiles etc. Found as an online sale by searching for products that have previously caused cases of poisoning and have not been found in a physical store. The specific product has not caused cases of poisoning, but the same brand has marketed a similar product which has led to a registered case of poisoning in DK. Listed to contain nano.	8	Hydrocarbons, methylsiloxanes, isopropanol, butylacetate and DEHP.	0.71
35	"All-round" Aerosol spray	Listed on the dealer's website for use on skins, footwear and textiles. Found as online search by general search and was not found in physical store. Selected as the supply is primarily for use on prams and children's items.	4	Hydrocarbons, methylsiloxanes and DEHP (0.9%).	0.39

	Field of application and application method	General information from the dealers' websites and the survey	Inhibitory dose of product (C) compared to a positive control (*in vitro* test) $C_{product}$ / $C_{control}$	Identified ingredients [b]	Emission rate for respirable particles, (mg/s)
40	"All-round" Aerosol spray	Listed for use on suede, textiles and shoes, etc. Containing nano. Found as online search by general search, and was not found in physical store. Sold in a larger business chain with outdoor/sports equipment. The product was included in the Consumer Council Think Chemistry's test, which showed that the product contained traces of siloxanes.	7	Hydrocarbons, methylsiloxanes, isopropanol, butylacetate and DEHP.	0.90
45	"Indoor hard surfaces" Pump spray	A product for sealing masonry. Found by the general search, and not found in physical store. Containing nano.	None	Traces of ethanol, hydrocarbons and methylsiloxane; 0.7% total fluorine.	0.05
54	"Footwear" Aerosol spray	An impregnation product for footwear. Found as an online sale by searching for products that have previously caused cases of poisoning, and have not been found in a physical store. The specific product has not caused poisoning cases, but the same brand has marketed a similar product which has led to poisoning cases (NL).	None	Hydrocarbons, methylsiloxanes, isopropanol, butylacetate and DEHP.	1.04
70	"Outdoor equipment (skis)" Aerosol spray	An impregnation product for skis. Found by general search, and not found by visiting physical stores.	14	Dihexylether and ethanol.	0.82
82	"Outdoor equipment (tents and the like)" Aerosol spray:	Listed on dealer website for use on tents, tarpaulins and stitching. Contains silicone. Found by the general search, and also identified in physical store. The product was selected as it is considered to constitute a larger share of the market of the impregnation product in this area of application.	6	Hydrocarbons, methylsiloxanes and DEHP.	0.95

	Field of application and application method	General information from the dealers' websites and the survey	Inhibitory dose of product (C) compared to a positive control (*in vitro* test) $C_{product}$ / $C_{control}$	Identified ingredients [b]	Emission rate for respirable particles, (mg/s)
88	"Outdoor equipment (tents and the like)" Aerosol spray:	Listed on the dealer's website for use on outdoor textiles, e.g. umbrellas and cushions. Found by the general search, and is also identified in physical store. Traded in a major DIY store chain.	2	Hydrocarbons, methylsiloxanes and DEHP.	0.28
89	"Furniture" Aerosol spray	Listed on the dealer's website for use on furniture with leather and leather look.	Could not be analysed	Hydrocarbons, dimethylether, methylethylketone and DEHP.	Not determined
91	"Furniture (leather)" Aerosol spray	Listed on the dealer's website as an impregnation product for rough leather surfaces. The product is from a brand that is considered to make up a larger proportion of waterproofing products for furniture available to the Danish consumers.	4	Hydrocarbons, methylsiloxanes and DEHP.	0.32
100	"Textiles" Aerosol spray	An impregnation product which is stated to be applicable to outerwear and equipment. Found as online sale by the general search, and was not found in physical stores. The product is sold in a larger retail chain with outdoor/sports equipment.	Could not be analysed	Hydrocarbons, isopropylacetate, DEHP, and PFAS. Sum of PFCA: 0.2% [a]	Not determined
102	"Outdoor equipment (tents and the like)" Aerosol spray	No product description on the dealer's website. Based on the image of the product, the product is used for i.a. tents, parasols, outerwear and shoes. Found by a specific search for products on the European market available to the Danish consumer, and was chosen as a representative of products from another country in the EU - in this case the Netherlands.	6	Hydrocarbons, methylsiloxanes, isopropylacetate, DEHP, and PFAS. Sum af PFCA: 0.3%[a].	1.25

[a] It is a polymer or oligomer based on perfluorohexylethyl methacrylate (6:2 FTMA).

[b] All products, except product no. 45 had a total fluorine concentration of less than 0.3% by weight

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Appendix 1. Identified impregnation products

Product no.	Geography	Field of application	Specific scope	Application method (spray, pump, wash)	Quantity used	Type (PFAS-based, siloxane - based, etc.)	Label/web information	SDS information	SDS reviewed
1	DK	All-round: leather, suede and textile	Textile and leather	Pump spray	30-40 mL/m²	Nano			No
2	DK	Other things	Liquid for fishing tackle	Not informed	Does not appear	Silicon "Nano"			No
3	DK	Other things	Dogs and cats	Pump spray	Does not appear	Does not appear			No
4	DK	Other things	Frying pan	Other things	Does not appear	Lard			No
5	DK	Other things	Liquid for fishing tackle	Other things	Does not appear	Does not appear			No
6	DK	Other things	Liquid for fishing tackle	Pump spray	Does not appear	Does not appear			No
7	DK	Footwear	Footwear (leather)	Other things	Does not appear	Wax, leather grease and silicone oil			No
8	DK	Footwear	Leather	Other things	Does not appear	Bi-wax		2 substances	Yes
9	DK	All-round: leather, suede and textile	leather, suede and textiles - tents and footwear are highlighted	Aerosol spray	Does not appear	Silicone		8 substances	Yes (via product link)
10	DK	Footwear	Leather footwear	Not informed	Does not appear	Does not appear	PFOA-PFOS free	-	No
11	DK	Outdoor equipment (Ski)	Ski	Other things	Does not appear	Does not appear		Propan-2-ol	Yes
12	DK	Footwear	Footwear	Pump spray	Does not appear	Siloxane		Poly [3 - ((2-aminoethyl) amino) propyl] methyl (dimethyl) siloxane, hydroxy-terminated	Yes
13	DK	Footwear	Rubber footwear	Pump spray	Does not appear	Siloxane			No

Product no.	Geography	Field of application	Specific scope	Application method (spray, pump, wash)	Quantity used	Type (PFAS-based, siloxane -based, etc.)	Label/web information	SDS information	SDS reviewed
14	DK	Footwear	Footwear	Pump spray	Does not appear	Siloxane	Environmentally friendly. Used indoors! Marked with Good Environmental Choice.	PFC free	No
15	Dk	Outdoor equipment (Ski)	Ski	Not informed	Does not appear	Does not appear		No	Yes
16	Dk	Outdoor equipment (Ski)	Ski	Other things	Does not appear	Does not appear		No	Yes
17	Dk	Outdoor equipment (Ski)	Ski	Other things	Does not appear	Does not appear	Biodegradable		No
18	DK	Outdoor equipment (Ski)	Ski	Pump spray	Does not appear	Does not appear	Environmentally friendly		No
19	DK	Outdoor equipment (tents and the like)	Tents	Pump spray	Does not appear	Does not appear	Does not contain solvents	None	Yes (via product link)
20	DK	Outdoor equipment (tents and the like)	Car (Caleche)	Pump spray	Does not appear	"Nano"		Naphtha	Yes
21	DK	Outdoor equipment (tents and the like)	Barbecue cover	Pump spray	Does not appear	Does not appear			No
22	DK	Outdoor equipment (tents and the like)	Tent	Other things	Does not appear	Does not appear			No
23	DK	Outdoor equipment (tents and the like)	Tent	Other things	Does not appear	Does not appear			No
24	DK	Indoor hard surfaces (tiles, stones, etc.)	Attacks e.g. Cement, masonry, bricks, concrete, wood cladding, wood panels, plas-	Pump spray	3.7-7.5 m²/L	Not informed	Frost free. Does not contain solvents. Does not harm people, animals or plants	None	Yes

Product no.	Geography	Field of application	Specific scope	Application method (spray, pump, wash)	Quantity used	Type (PFAS-based, siloxane -based, etc.)	Label/web information	SDS information	SDS reviewed
			ter, drywall, white-washed surfaces, etc.						
25	DK	Indoor hard surfaces (tiles, stones, etc.)	Natural stone (e.g. kitchen table)	Pump spray	Does not appear	Does not appear	It is stated on the SDS website that it will not be sold in DK! - and that it is food contact -approved.		No
26	DK	All-round: leather, suede and textile	Textiles, leather and suede	Aerosol spray	Does not appear	Does not appear		8 substances	Yes (via product link)
27	DK	All-round: leather, suede and textile	All round	Aerosol spray	Does not appear	"Nano"			No
28	DK	All-round: leather, suede and textile	Shoes, tents and everything in between	Aerosol spray	Does not appear	Does not appear		6 substances	Yes (via product link)
29	DK	Outdoor equipment (tents and the like)	Textiles (clothing) and outdoor equipment	Other things	1 litre covers 18 m²	Silicone		2 substances	Yes
30	DK	All-round: leather, suede and textile	Leather, footwear, tents and textiles	Aerosol spray	Does not appear	Does not appear	Without silicone	8 Fabrics	SDS available via product link
31	DK	Indoor hard surfaces (tiles, stones, etc.)	Tiles, clinker, granite, vinyl floors, etc.	Other things	Does not appear	Does not appear		2- (2-ethoxyethoxy) ethanol and ammonia	Yes

Product no.	Geography	Field of application	Specific scope	Application method (spray, pump, wash)	Quantity used	Type (PFAS-based, siloxane -based, etc.)	Label/web information	SDS information	SDS reviewed
32	DK	Indoor hard surfaces (tiles, stones, etc.)	Steel surfaces in chrome and stainless steel.	Pump spray	10-25 mL/m²	Nano		Ethanol	Yes
33	DK	Indoor hard surfaces (tiles, stones, etc.)	Tiles, clinker and stone surfaces	Not informed	Does not appear	Does not appear		Ethoxylated alcohols and naphtha	Yes
34	DK	Indoor hard surfaces (tiles, stones, etc.)	Concrete, plaster, brick fibre cement etc. - indoors	Not informed	Does not appear	Siloxane, "nano"		5-chloro-2-methyl-2H-isothiazol-3-one	Yes
35	DK	All-round: leather, suede and textile	Textiles, leather and footwear	Aerosol spray	Does not appear	Does not appear			No
36	DK	Indoor hard surfaces (tiles, stones, etc.)	Glass and ceramics	Other things	7-10 mL/m²	Not informed			No
37	DK	All-round: leather, suede and textile	Outdoor equipment, clothing, leather and footwear	Aerosol spray	Does not appear	Does not appear			No
38	DK	All-round: leather, suede and textile	Sports shoes and sportswear	Aerosol spray	Does not appear	Does not appear			No
39	DK	Indoor hard surfaces (Touch screens)	Screen protection (touchscreen)	Other things	Does not appear	"Nano"			No
40	DK	All-round: leather, suede and textile		Aerosol spray	Does not appear	"Nano"		-	No
41	DK	Indoor hard surfaces (tiles, stones, etc.)	Plastic surfaces	Pump spray	10-25 mL/m²	Nano			No
42	DK	Fire impregnation	All absorbent materials	Aerosol spray	Does not appear	Does not appear		3 substances	Yes

Product no.	Geography	Field of application	Specific scope	Application method (spray, pump, wash)	Quantity used	Type (PFAS-based, siloxane -based, etc.)	Label/web information	SDS information	SDS reviewed
43	DK	Indoor hard surfaces (Touch screens)	Screen protection (touchscreen)	Other things	Does not appear	"Nano"			No
44	DK	Indoor hard surfaces (Touch screens)	Screen protection (touchscreen)	Other things	Does not appear	"Nano"			No
45	DK	Indoor hard surfaces (tiles, stones, etc.)	Bricks, concrete and joints	Pump spray	25-100 mL/m²	Does not appear	Contains methanol	1 substance	Yes
46	DK	Indoor hard surfaces (Touch screens)	Screen protection (touchscreen)	Not informed	Does not appear	"Nano"			No
47	DK	Indoor hard surfaces (tiles, stones, etc.)	Bathroom and Tiles	Pump spray	10-25 mL/m²	Reported to be alcohol-based and contain citric acid monohydrate		2 substances	Yes
48	DK	Shoe	Leather	Other things	Does not appear	Non-aromatic oils	Does not contain harmful substances for you and contains non-aromatic oils. No CHC		No
49	DK	Textiles (clothing)	Textiles (clothing)	Dosed by washing	Does not appear	Does not appear		Two preservatives	Yes
50	DK	Indoor hard surfaces (tiles, stones, etc.)	Absorbent wood and stone surfaces - both inside and out	Pump spray	Does not appear	Does not appear		2 substances	Yes
51	DK	Indoor hard surfaces (glass)	Self-cleaning glass	Pump spray	10-25 mL/m²	Nano			No
52	DK	Furniture (textile)	Furniture	Pump spray	Does not appear	Does not appear			No
53	DK	Fire impregnation	All absorbent materials (furniture,	Aerosol spray	Does not appear	Does not appear			No

Product no.	Geography	Field of application	Specific scope	Application method (spray, pump, wash)	Quantity used	Type (PFAS-based, siloxane -based, etc.)	Label/web information	SDS information	SDS reviewed
			curtains, rugs, theatre costumes, paper, Christmas trees, etc.)						
54	DK	Footwear	Footwear	Aerosol spray	Does not appear	Does not appear			No
55	DK	Textiles (clothing)	Textiles (clothing) and outdoor equipment	Dosed by washing	Does not appear	Does not appear		3 substances	Yes
56	DK	Textiles (clothing)	Dn clothes	Dosed by washing	50 mL per jacket	Not informed	Without PCF substances. Bluesign ®	3 substances	Yes
57	DK	Textiles (clothing)	Textiles	Dosed by washing	Does not appear	APT (Acrylic Polymer Technology)	Without fluorocarbon	None	Yes
58	DK	Textiles (clothing)	Textiles	Dosed by washing	Does not appear	Does not appear	PFC-free		No
59	DK	Textiles (clothing)	Textile (clothing)	Dosed by washing	100 mL for a jacket	Not informed	PFC-free		No
60	DK	Footwear	Footwear	Aerosol spray	Does not appear	Does not appear	Does not contain PFOA or PCF.		No
61	DK	Textiles (clothing)	Textiles	Dosed by washing	Does not appear	APT (Acrylic Polymer Technology)	Without fluorocarbon		No
62	DK	Footwear	Footwear	Aerosol spray	Does not appear	"Nano"		3 substances	Yes
63	DK	Furniture (textile)	Carpets, textiles and leather	Pump spray	12-14 m²/L	Not informed	Traded in many Danish stores (see website)		No
64	DK	Textiles (clothing)	Textiles (G-1000)	Not informed	Does not appear	paraffin and beeswax			No
65	DK	Footwear	Leather footwear	Aerosol spray	Does not appear	Does not appear	PFOA-PFOS free	_	No
66	DK	Textiles (clothing)	Textile (clothing)	Pump spray	Does not appear	Polyurethane-based active substance		Fluorocarbon free	No
67	DK	Textiles (clothing)	Textiles	Dosed by washing	Does not appear	Does not appear	Free of fluorine, parabens and methyl isothiazolinone	No substances	Yes

Product no.	Geography	Field of application	Specific scope	Application method (spray, pump, wash)	Quantity used	Type (PFAS-based, siloxane -based, etc.)	Label/web information	SDS information	SDS reviewed
68	DK	Textiles (clothing)	Textile (clothing)	Pump spray	Does not appear	Siloxane		2-methylpentane-2,4-diol	Yes
69	DK	Textiles (clothing)	Textiles	Dosed by washing	Does not appear	Does not appear			No
70	DK	Outdoor equipment (Ski)	Ski	Aerosol spray	Does not appear	Does not appear			No
71	Dk	Textiles (clothing)	Textiles	Dosed by washing	Does not appear	Does not appear			No
72	DK	Textiles (clothing)	Textiles	Dosed by washing	Does not appear	Does not appear			No
73	DK	Textiles (clothing)	Jackets	Dosed by washing	Does not appear	Does not appear		Siloxanes and silicone	Yes
74	DK	Textiles (clothing)	Textiles	Dosed by washing	Does not appear	Does not appear	Contains: Contents: Aqua, fatty alcohol, ethoxylated, propoxylated, sodium C14-17 alkyl sec sulfonate, oleic acid, perfume, citric acid, sodium diethylenetriamine pentamethylene phosphonate, sodium chloride, benzisothiazolinone, methylisothiazolinone, formaldehyde	Sulfonic acids, C14-17-sec-alkane, sodium salts	Yes
75	DK	Textiles (clothing)	Textiles and equipment	Dosed by washing	Does not appear	Does not appear	PFOA-PFOS free	-	No
76	DK	Textiles (clothing)	All textiles	Dosed by washing	Does not appear	Does not appear		-	No

Product no.	Geography	Field of application	Specific scope	Application method (spray, pump, wash)	Quantity used	Type (PFAS-based, siloxane -based, etc.)	Label/web information	SDS information	SDS reviewed
77	DK	Outdoor equipment (Ski)	Ski	Wax iron	Does not appear	Does not appear		2 substances	Yes
78	DK	Textiles (clothing)		Dosed by washing	Does not appear	Does not appear	PF C -free. Biodegradable		No
79	DK	Rugs	Carpets, upholstery and car seats	Not informed	25 m² per litre	Siloxanes	Phosphate-free	2 substances	Yes
80	DK	Textiles (clothing)	Textile (outdoor clothing)	Pump spray	Does not appear	Does not appear	Without PF C		No
81	DK	Outdoor hard surfaces	Stones and tiles	Other things	Does not appear	Does not appear		1.2 Ethanediol	Yes
82	DK	Outdoor equipment (tents and the like)	Outdoor equipment	Aerosol spray	3-9 m ² per spray (600 mL)	Silicone		2 substances	Yes
83	DK	Outdoor equipment (Ski)	Ski	Wax iron	Does not appear	Does not appear			No
84	DK	Textiles (clothing)		Pump spray	Does not appear	Does not appear	PCF-free. Biodegradable		No
85	DK	Outdoor equipment (tents and the like)	Textiles, tents and leather etc.	Aerosol spray	Does not appear	Does not appear			No
86	DK	Outdoor hard surfaces	Composite/non- wood	Not informed	Does not appear	Does not appear		1,2-benzisothiazol-3 (2H) -one, 2-methyl-2H-isothiazol-3-one	Yes
87	DK	Outdoor hard surfaces	WPC/Composite	Other things	23 m²/L	Not informed		Naphtha	Yes (via product link)
88	DK	Outdoor equipment (tents and the like)	Outdoor textiles	Aerosol spray	25 m²/L	Not informed		2 substances	Yes
89	DK	Furniture (leather)	Leather, e.g., taxi seats, chairs and outdoor use such as hoods	Aerosol spray	3-4 m² per bottle (200 mL)	Not informed			No

Product no.	Geography	Field of application	Specific scope	Application method (spray, pump, wash)	Quantity used	Type (PFAS-based, siloxane -based, etc.)	Label/web information	SDS information	SDS reviewed
90	DK	Textiles (clothing)	Textiles	Pump spray	Does not appear	Does not appear	PFC -free.	Propan-2-ol	Yes
91	DK	Furniture (leather)	Leather - suede and the like.	Aerosol spray	Does not appear	Does not appear		Diethanolamine	Yes
92	DK	Furniture (leather)	leather: suede, nubuck, polished leather and the like.	Aerosol spray	Does not appear	Does not appear	Listed for indoor		No
93	DK	Outdoor hard surfaces	Sealing tile cleaner	Not informed	100 m² per 2.5 l.	Silicone		3 substances	Yes
94	DK	Furniture (textile)	Textiles (furniture)	Aerosol spray	Does not appear	Does not appear			No
95	DK	Outdoor equipment (tents and the like)	Tents, umbrellas and footwear	Aerosol spray	Does not appear	Does not appear		7 substances	Yes
96	DK	Furniture (textile)	Textiles - furniture	Aerosol spray	Does not appear	Does not appear	New formula 2020	3 substances	Yes
97	DK	Outdoor hard surfaces	Outdoor surfaces	Pump spray	Does not appear	Does not appear			No
98	DK	Outdoor hard surfaces	Stone, tile and concrete	Not informed	25 m² per bottle (2.5 l)	Not informed		Potassium silicate	Yes
99	DK	Outdoor hard surfaces	Composite	Other things	10 m² per l.	Not informed			No
100	DK	Textiles (clothing)	Outerwear and equipment	Aerosol spray	Does not appear	Does not appear	PFOA-PFOS free	-	
101	DK	Outdoor hard surfaces	Composite/WPC	Other things	25m $^{2/L}$	Not informed		3-iodo-2-propynyl-butylcarbamate	Yes
102	NL	Outdoor equipment (tents and the like)	Outdoor - universal	Aerosol spray	Does not appear	Does not appear			No
103	DK	Outdoor hard surfaces	Tree	Other things	20-30 m²/L	Not informed		No substances	Yes
104	DK	Outdoor hard surfaces	Composite	Not informed	Does not appear	Siloxane, silicone		3 substances	Yes (via product link)

Product no.	Geography	Field of application	Specific scope	Application method (spray, pump, wash)	Quantity used	Type (PFAS-based, siloxane -based, etc.)	Label/web information	SDS information	SDS reviewed
105	DK	Footwear	Shoes, boots and clothes	Aerosol spray	Does not appear	Does not appear	Free of fluorine, parabens and methyl isothiazolinone	No substances	Yes
106	DK	Outdoor hard surfaces	plush garden furniture, polyrattan garden furniture and fences	Pump spray	Does not appear	Silicone		No substances	Yes
107	THE	Textiles (clothing)		Dosed by washing	Does not appear	Does not appear			No
108	UK	All-round: leather, suede and textile	Does not appear	Aerosol spray	Does not appear	Does not appear		5 substances	Yes
109	DK	Footwear	Leather cream	Cloth					
110	DK	Footwear	Leather cream	Cloth					

Appendix 2. Product information for analysed products

Product no. 9

The product is listed under the application category "All-round: leather, suede and textiles" with aerosol spray. On the supplier's website it is identified as a waterproofing product containing silicone for leather, suede and textiles. Application examples are given for "*outside on tents"* and "*footwear"*.

Product no. 9 was included in the Consumer Council Think Chemistry's test, which examined 11 impregnation products for textiles (described in more detail in section 3). The chemical analyses showed that the product contained traces of siloxanes.

Safety data sheet:
Prepared 2015. Was found for the specific product via the dealer's website, from which the following relevant information was retrieved.

CLP (1272/2008) classification of the mixture based on the manufacturer's self-classification: Aerosol 1, Skin Irrit. 2, STOT SE 3, Aquatic Chronic 2.

CLP Hazard Statements: "Extremely flammable aerosol" (H222), "Pressurized container: may burst if heated" (H229). "Causes skin irritation" (H315), "May cause drowsiness or dizziness" (H336), "Toxic to aquatic life with long lasting effects" (H411).

Additional hazard information (EUH):
"Repeated exposure may cause skin dryness or cracking" (EUH066).

The product is stated to contain 99.2% organic solvents.

TABLE 16. Ingredients listed in the safety data sheet, product no. 9

Ingredients	CAS / EC -nr.	w/w (%)
Isobutane	75-28-5 /200-857-2	20-25
Hydrocarbons, C5-C7, n- alkanes, isoalkanes, <5% hexane	- / 922-114-8	10-20
Pentane	109-66-0 / 203-692-4	10-20
Propane	74-98-6 / 200-827-9	10-20
Hydrocarbons, C6, isoalkanes, <5% hexane	- / 931-254-9	10-20
Hydrocarbons, C6-C7, isoalkanes, cycloalkanes, <5% hexane	- / 926-605-8	10-20
Butane	106-97-8 / 203-448-7	2.5-10

Ingredients	CAS / EC -nr.	w/w (%)
Naphtha (petroleum), hydrodesulfurized heavy	64742-82-1 / 265-185-4	0.1-1.0

Product no. 26

The product is listed under the application category "All-round: leather, suede and textiles" and applied by aerosol spray. On the supplier's website it is identified as an impregnation product for protection of textiles against moisture and dirt. It appears from the product image that the product can be used for textiles, leather and suede. According to product information obtained, the product contains silicone.

Safety data sheet:
Prepared in 2016. Consequently obsolete with regard to legislation (CLP and REACH Annex II). The safety data sheet for the specific product was identified via the retailer's website, from which the following relevant information was retrieved. Therefore, there is some uncertainty about the information below taken from the data sheet.

Manufacturer's CLP-classification of the mixture: Aerosol 1, Skin Irrit. 2, STOT SE, 3, Aquatic Chronic 2.

CLP Hazard Statements: "Extremely flammable aerosol" (H222), "Pressurized container. May burst if heated" (H229), "Causes skin irritation (H315)", "May cause drowsiness or dizziness" (H336) and "Toxic to aquatic organisms., with long lasting effects" (H411).

It is stated that the product contains 99.2% organic solvents and 611.4 g/L VOC.

TABLE 17. Ingredients listed in the safety data sheet, product no. 26

Ingredients	CAS / EC -no.	w/w (%)
Isobutane	75-28-5 / 200-857-2	20-25
Hydrocarbons, C5-C7, n- alkanes, isoalkanes, <5% hexane	- / 922-114-8	10-20
Pentane	109-66-0 / 203-692-4	10-20
Propane	74-98-6 / 200-827-9	10-20
Hydrocarbons, C6, isoalkanes, <5% hexane	- / 931-254-9	10-20
Hydrocarbons, C6-C7, isoalkanes, cycloalkanes, <5% hexane	926-605-8	10-20
Butane	106-97-8 / 203-448-7	2.5-10
Naphtha (petroleum), hydrodesulfurized heavy	64742-82-1 / 265-185-4	0.1-1.0

Product no. 27.

The product is listed under the application category "All-round: leather, suede and textiles" and applied by aerosol spray. On the supplier's website it is stated that the product contains "nano" and can be used on all kinds of material, where it provides moisture and stain repellency.

Safety data sheet:
Prepared in 2018. A German safety data sheet was found for the product, from which the following relevant information was obtained.

Manufacturer's CLP-classification of the mixture: Aerosol 1, Skin irrit. 2, Eye irrit 2, STOT SE 3, Aquatic Chronic 3.

CLP Hazard Statements: "Extremely flammable aerosol" (H222), "Pressurized container. May burst if heated" (H229), "Causes skin irritation" (H315), "Causes serious eye irritation" (H319), "May cause drowsiness or dizziness"(H336) and "Harmful to aquatic organisms, with long lasting effects" (H412).

TABLE 18. Ingredients listed in the safety data sheet, product no. 27

Ingredients	CAS / EC -no.	w / w (%)
In sopropyl alcohol	67-63-0 / 200-661-7	≥ 20 - < 30
Naphtha, hydrotreated, low boiling point	921-024-6	≥ 20 - < 30
Naphtha, hydrotreated, low boiling point	927-241-2	≥ 10 - < 20
n - hexane	110-54-3 / 203-777-6	≥ 1 - < 5
Butane	106-97-8 / 203-448	≥ 10 - < 20
Propane	74-98-6 / 200-827-9	≥ 5 - < 10
Isobutane	75-28-5 / 200-857-2	≥ 5 - < 10
n- butyl acetate	123-86-4 / 204-658-1	≥ 1 - < 5
2-methylbutane	78-78-4 / 201-142-8	≥ 0 - < 0.1

Product no. 35.

The product is listed under the application category "All-round: leather, suede and textiles" and applied by aerosol spray. On the supplier's website, it is indicated that the product is used for textiles. Product picture shows, however, that the product can be used for fabric, leather and footwear.

It has only been possible to find a safety data sheet from 2006 for the product, which is considered obsolete both in terms of legislation (CLP and REACH Annex II) and chemical content.

Product no. 40

The product is listed under the application category "All-round: leather, suede and textiles" applied by aerosol spray. On the supplier's website it is indicated that the product contains "*Strong nanoparticles"*, which provides a protective effect against moisture and dirt. The product is listed for use on suede, textiles, synthetic clothing and shoes.

Product no. 40 was included in the Consumer Council Think Chemistry's test, which investigated 11 impregnation products for textiles (described in more detail in section 3). In the chemical analyses, the Consumer Council Think Chemistry's study showed that the product did not contain fluorine substances, but contained other environmentally harmful substances.

Safety data sheet:
Prepared in 2013. Consequently obsolete with regard to legislation (CLP and REACH Annex II). There is uncertainty about the information below taken from the data sheet.

Manufacturer's CLP-classification of the mixture: "Highly flammable gas" (H220) or "Flammable gas" (H221), "May cause long-term damage to aquatic organisms" (H413).

TABLE 19. Ingredients listed in the safety data sheet, product no. 40.

Ingredients	CAS / EC -no.	w/w (%)
Distillates (petroleum), hydrotreated light	64742-47-8 / 923-037-2	25-50

Ingredients	CAS / EC -no.	w/w (%)
Butane, chemically pure	106-97-8 / -	25-50
Liquid propane	74-98-6	2.5-10
n-butyl acetate	123-86-4	2.5-10

Product no. 45

The product is listed under the application category "Indoor hard surfaces (tiles, stones, etc.)", and is the only selected product in this category. No products in this category were applied by aerosol spray and this product is applied using a pump spray. The product is described as a wall-sealer, usable both indoors and outdoors, to provide a water and dirt-repellent effect on mineral/absorbent surfaces. The quantity used is stated at 25-100 mL/m². Methanol is listed as ingredients on the packaging of the product.

Safety data sheet:
Prepared in 2020. Available for the specific product via third-party website, but is considered to be valid with respect to the specific product due to the description.

TABLE 20. Ingredients listed in the Safety Data Sheet, product no. 45.

Ingredients	CAS / EC No	w/w (%)
Methanol	67-56-1 / -	<0.5%

Product no. 54

The product is listed under the use category "Footwear". The supplier's website states that it is possible to protect footwear against water and dirt. The treatment should take place every 14 days.

Safety data sheet:
Prepared in 2014. Available for the specific product via third-party website, but is considered to be valid with regard to the specific product due to the description. However, it should be noted that it is obsolete in terms of legislation (CLP and REACH Annex II). There is uncertainty about the information below taken from the data sheet.

Manufacturer's CLP-classification of the mixture: Aerosol 1, Specific target organ toxicity - single exposure 3, chronic aquatic toxicity 3.

CLP Hazard Statements: "Extremely flammable aerosol" (H222), "Pressurized container. May burst if heated" (H229), "May cause drowsiness or dizziness" (H336) and "Harmful to aquatic life with long lasting effects" (H412).

Additional hazard information (EUH):
"Repeated exposure may cause skin dryness or cracking" (EUH066).

TABLE 21. Ingredients listed in safety data sheet, product no. 54

Ingredients	CAS / EC No	w/w (%)
Naphtha (petroleum) hydrotreated heavy	64742-48-9 / 927-241-2	≥ 50 - <75
Isobutane	75-28-5 / 200-857-2	≥ 1 0 - <20
Propane	74-98-6 / 200-827-9	≥ 5 - <10
Butyl acetate	123-86-4 / 204-658	≥ 1 - <5

Product no. 70
The product is listed in the application category "Outdoor equipment (Ski)" and is an aerosol ski-wax spray. On a retailer's website, the product is described as "*biodegradable, and thus it is better for nature*". After application, the layer of ski-wax is retained for only a few days, after which a new layer of impregnating agent must be applied.

Safety data sheet:
Prepared in 2018. Available for the specific product via third party website, but is considered to be valid with respect to the specific product based on the description.

Manufacturer's CL P classification of the mixture: Aerosol 1, Skin Irrit. 2, Eye Irrit. 2.

CLP Hazard Statements: "Extremely flammable aerosol" (H222), "Pressurized container. May burst if heated" (H229), "Causes skin irritation" (H315), "Causes serious eye irritation" (H319).

TABLE 22. Ingredients listed in the safety data sheet, product no. 70

Ingredients	CAS / EC -no.	w/w (%)
Diethyl ether	112-58-3 / 203-987-8	≥ 15 - <20
Ethanol	64-17-5 / 200-578-6	≥ 75 - <80

Product no. 82
The product is listed under the use category "Outdoor equipment (tents and the like)". The product is applied by aerosol spray; it is indicated that a full spray can lasts for 3-9 m², depending on the type of fabric. The active substance is stated to be silicone, the product can be used on all kinds of tents, tarpaulins, stitching and the like.

Safety data sheet:
Prepared in 2016, and therefore obsolete with regard to legislation (CLP and REACH Annex II). Available for the specific product via the manufacturer's website; considered to be valid with respect to the specific product. Therefore, there is uncertainty about the information below taken from the data sheet.

Manufacturer's CLP-classification of the mixture: Aerosol 1, STOT SE 3.

CLP Hazard Statements : "Extremely flammable aerosol" (H222), "Pressurized container. May burst if heated" (H229), "May cause drowsiness or dizziness" (H336).

Additional hazard information (EUH):
"Contains Zirconium butanolate. May produce an allergic reaction" (EUH208).

TABLE 23. Ingredients listed in the safety data sheet, product no. 82

Ingredients	CAS / EC No	w/w (%)
Naphtha (petroleum) hydrotreated heavy (<0.1% benzene).	64742-48-9 / 919-857-5	30-60
Zirconium butanolate	1071-76-7 / 213-995-3	<1%

Product no. 88
The product is listed under the application category "Outdoor equipment (tents and the like)" and applied by aerosol spray. The product is stated to protect outdoor textiles from water and dirt, and the quantity used is stated to be 25 m²/L.

Safety data sheet:
Prepared in 2015, and therefore obsolete with regard to legislation (CLP and REACH Annex II). Available for the specific product via the manufacturer's website; considered to be valid with respect to the specific product.

Manufacturer's CLP-classification of the mixture: Aerosol 1, STOT SE 3.

CLP Hazard Statements: "Extremely flammable aerosol" (H222), "pressurized container. Can be disrupted by heating" (H229), "May cause drowsiness and dizziness" (H336).

Additional hazard information (EUH):
"Repeated exposure may cause skin dryness or cracking" (EUH066).

TABLE 24. Ingredients listed in the safety data sheet, product no. 88

Ingredients	CAS / EC No	w/w (%)
Naphtha (petroleum), hydro-treated heavy	64742-48-9 / 265-150-3	95-100
Carbon dioxide	124-38-9 / 204-696-9	

Product no. 89

The product is listed under the application category "Furniture (leather)" and is applied using an aerosol spray. It is stated that 1 can (200 mL) impregnates 3-4 m². The product is used to prevent colour smearing and as a finisher after applying cover colours.

It has not been possible to find a safety data sheet for the product.

Product no. 91

The product is listed under the application category "Furniture (leather)" and is applied using an aerosol spray. The product protects against dirt and has been identified during the survey as a product that is marketed in Denmark in a high tonnage.

Safety data sheet:
Prepared in 2019. Available for the specific product via the manufacturer's website and is considered valid.

Manufacturer's CLP-classification of the mixture: Aerosol 1.

CLP (1272/2008) hazard sentences: "Extremely flammable aerosol" (H222) "Pressurized container. May burst if heated" (H229).

TABLE 25. Ingredients listed in the safety data sheet, product no. 91.

Ingredients	CAS / EC No	w/w (%)
Naphtha (petroleum), hydrotreated heavy (<0.1% benzene)	64742-48-9 / 265-150-3	95-100
Carbon dioxide	124-38-9 / 204-696-9	1-5
Fatty alcohol ethoxylate	68439-46-3-e / -	1-3

Other information from safety data sheet: Repeated exposure may cause skin dryness or cracking.

Product no. 100

The product is listed under the category "Textiles (clothing)" and is the only identified product in this category of use applied by aerosol spray. It is stated on the supplier's website that the product is "PFOA PFOS free".

It has not been possible to identify a safety data sheet for the product.

Product no. 102

The product is listed under the use category "Outdoor equipment (tents and the like.)" and applied by aerosol spray. It is described on the Dutch supplier's website that the product protects against moisture for leather and textile.

Safety data sheet:
A German safety data sheet from the manufacturer, prepared on 13.05.2020, has been found.

Manufacturer's CLP-classification of the mixture: Aerosol 1, Skin Irrit. 2, STOT SE 3", Aquatic Chronic 2.

CLP Hazard Statements: "Extremely flammable aerosol" (H222), "Pressurized container. May burst if heated" (H229), "Causes skin irritation" (H315), "May cause drowsiness or dizziness" (H336), "Toxic to aquatic life organisms, with long lasting effects" (H411).

TABLE 26. Ingredients listed in the safety data sheet, product no. 102

Ingredients	CAS / EC No	w/w (%)
Propane	74-98-6 / 200-827-9	~ 10
Butane	106-97-8 / 203-448-7	~ 20
Hexane (with <5 & n- hexane (203-777-6)	107-83-5 / -	~ 60

Product no. 108

The product was not analysed as it was not received.

The product is listed under the application category "All-round: leather, suede and textiles" and applied by aerosol spray. The product is not found on Danish websites but is available to the Danish consumer via the internet. The supplier is from the UK.

Safety data sheet:
Available for the specific product via third-party website. Information from this source must be considered with some uncertainty. (Dated 19.01.2019).

Manufacturer's CLP-classification of the mixture: Aerosol 1, STOT SE 3.

CLP Hazard Statements: "Extremely flammable aerosol" (H222), "Pressurized container. May burst if heated" (H229).

TABLE 27. Ingredients listed in the safety data sheet, product no. 108

Ingredients	CAS / EC No	w/w (%)
Acetone	67-64-1 / -	37-41

Isopropyl alcohol	67-63-0 / -	31-35
Light alkylate Petroleum Naphtha	64741-66-8 / -	17-21
Carbon Dioxide	124-38-9 / -	2-6
Fluorochemical Urethane	Trade Secret	<3

Appendix 3. Overview of impregnation chemistry and function

In this appendix, we will aim at giving a general overview of the basic chemistry and functions of impregnation products.

Water repellency and other properties
The basis for most impregnation products is to assure water repellency in order not to wet the surface.

The so-called 'contact angle' - Θ - determines whether a surface is considered hydrophilic or hydrophobic. If the contact angle is below 90º, the surface is hydrophilic; if it is above 90º, it is hydrophobic. The higher the contact angle, the more hydrophobic and the more 'droplet-like' the water will appear on the surface (Figure 8). A surface is considered ultra-hydrophobic if the contact angle is above 150 º. Hydrophobic surfaces are characterised by having a low surface free energy. This means that the hydrogen bonds between the water molecules are stronger than the weaker van der Waals forces between the water molecules and the hydrophobic surface. This is what in turn creates the high contact angle and therefore, the droplet-like shape of water on hydrophobic surfaces. Further details on these mechanisms can, e.g., be found in Nørgaard (2010).

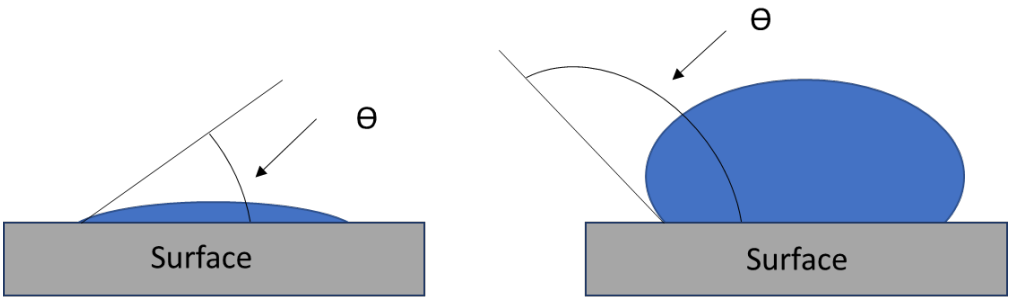

FIGURE 8. Contact angle - Θ - below 90 º (hydrophilic) and above 90 º (hydrophobic), respectively.

Depending on the application, there can be a demand for other properties of the impregnation products. For example, for textile impregnation products, it is often desirable that the textiles are also repellent with regard to other types of dirt (e.g., grease) and/or that such dirt is removed when the textiles are washed. Furthermore, the impregnation product should remain on the textile during use and during wash to the extent possible. For many indoor applications, dirt repellency is the main desired result of the impregnation products applied.

As can be seen from Table 28, alternatives to fluorinated impregnation products generally perform well in terms of water repellency, whereas PFAS-based impregnation products seem superior in terms of oil and alcohol repellency. This finding is in accordance with several studies that note that non-fluorinated repellents generally lack the oil repellency property (Texshield, 2013; Simoncic et al.,2010). The chemistry behind the dirt-repellent properties of PFAS-based impregnation products is further described below.

TABLE 28. Comparison of performance of impregnating agents as described by a presentation by Archroma (2013)

Performance	Water repellency	Oil repellency	Alcohol repellency	Stain release *	Abrasion resistance	Self cleaning
Fluorinated						
F-(Meth)Acrylates	+	+	+	+	+/-	-
F-Urethanes	+	+	+	+	+	-
F-Silicones	+	+	+	+	-	-
F-Particle**	+	+	+	-	+	+
Non-fluorinated						
(Meth)Acrylates/ Urethanes	+	-	-	+/-	+/-	-
Silicones	+	-	-	-	-	-
Waxes	+	-	-	-	-	-
Dendrimers	+	-	-	-	+/-	-
Particle	+	-	-	-	+	+

* Oil and water-based stains. **F-Particle is not explained in original presentation.

Water and grease/oil repellency depends on the surface chemistry as well as the surface roughness. Chu and Seeger (2014) elaborate on this in a tutorial review and go through a range of techniques for modifying surfaces and applying impregnation products. Many of these techniques require special equipment and are therefore only relevant when producing the article with its specific surface and original surface chemistry.

The current project focuses on consumer impregnation products and thereby mainly on how the properties of a given surface can be restored or improved following the application of the impregnation product to the surface of the object be re-impregnated.

Chemistry

A basic property of most impregnation products is to ensure that hydrophobic chemical groups repel water from the surface. One of the oldest techniques is to mechanically incorporate paraffins/waxes into and/or onto the surface, as for example into and onto the fibres on textile surfaces and pores (Texshield, 2013). A disadvantage of this technique is that the impregnation product can wear off due to limited bonding to the surface. A current product on the market, containing paraffins and beeswax, has accompanying consumer instructions that state the need to repeat application at frequent intervals.

The desired chemistry in most impregnation products is therefore to ensure adhesion to the object's surface, preferably via strong chemical bonding, and to ensure the repellency properties via hydrophobic groups pointing away from the surface.

Various chemistries can be used to ensure this 'connecting'/'coupling' role between the object surface and the hydrophobic groups, e.g. the organ silane technology (see e.g. Materne et al., 2012). In that case, the silane can carry the hydrophobic groups (as well as via an alkoxy or acetoxy group), which through a reaction sequence can create hydrogen bonding and eventually covalent 'Si-O-substrate' bonds to the object surface, thereby ensuring strong adhesion.

In order to further strengthen the impregnation and/or improve its properties, these connecting chemistries can sometimes react/crosslink with neighbouring connecting groups, creating a repellent film on the surface (see e.g. Materne et al., 2012). In the case of silane, this would result in siloxanes and with further polymerisation, silicones. Whether this result occurs depends on the functionality/reactivity of the connecting group, e.g., the chemical entities attached to the silicon in the original silane, as well as the circumstances (e.g., temperature) under which the impregnation product is applied. In some situations, consumer impregnation products will already consist of partly polymerised chemistries (oligomers), e.g., siloxane oligomers.

From the available information, it is often not possible to determine whether impregnation consumer products will create adhesion of individual molecules or more complex/polymerised structures. The degree of polymerisation depends both on the chemistry in the product (which can be partly polymerised) and the possible further reaction once the product has been applied to the surface.

From Table 28, it can be seen that the chemical groups are similar for fluorinated and non-fluorinated impregnation products, except for paraffins/waxes, which are only used in non-fluorinated chemistry.

Paraffin/wax emulsions

Paraffin is a synonym for alkanes which are long-chain hydrocarbons with the general molecular formula C_nH_{2n+2}.

Repellent products with this basic chemistry are typically emulsions of paraffins containing metal salts of fatty acids, usually stearic acid. The metals used most are aluminium, zinc and zirconium (Lassen et al., 2015a). The products often appear as waxes.

For example, for impregnation of textiles, the metal ion, e.g., Zr^{2+}, provides fixation onto the fibre and ensures that the water repellent groups have the right orientation on the fibre surfaces (Figure 9). Water repellency also arises from the ability of the metal ions to support the formation of macromolecules, which arrange as a fatty layer around the fibre (see Lassen et al., 2015a referencing Lang, 2014, personal comm.).

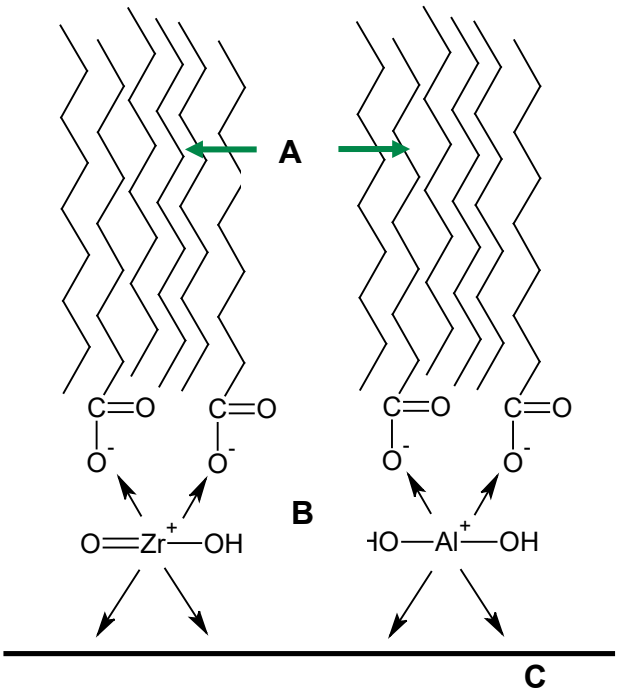

FIGURE 9. Examples of a fatty acid metal salt on a fibre surface. A: hydrophobic interactions; B: polar interactions; C: fibre surface (Taken from Lassen et al., 2015a; based on Schindler and Hauser, 2004)

11.1.1.1 Silanes, siloxanes and silicones

Based on Materne et al. (2012), organosilane molecules have the basic structure X-R-$Si(OR')_3$, where

> X is a non-hydrolysable organic moiety, which can be reactive toward another chemical (e.g., an amino, epoxy, vinyl, methacrylate, sulphur group) or it can be non-reactive.
>
> OR' is a hydrolysable group, like an alkoxy group (e.g., methoxy, ethoxy, isopropoxy) or an acetoxy group that can react with various forms of hydroxyl groups present on the inorganic or organic surface of a substrate/object. The alkoxysilane is hydrolysed (often with acid as a catalyst) to mono-, di- and tri silanoles ($-Si(OH)_3$). The silanoles are extremely reactive and can via a condensation reaction react with each other to create siloxanes/silicones with the hydroxyl groups on the surface of the substrate (Nørgaard et al., 2010a).
>
> R is a spacer which can be an aryl or alkyl chain.

In impregnation products, the 'R' moiety is responsible for hydrophobic properties, whereas one of the OR' group, following a sequence of chemical reactions, secures adhesion to the surface through first creating a hydrogen bond. Following energy input, these can be dehydrolysed (i.e., a condensation reaction where H_2O is removed) to form the strong covalent 'Substance – O – Si' bonds.

Further, depending on the OR' groups and their reactivity properties, the individual silane molecules can react with each other, i.e., polymerise to create siloxanes or polysiloxanes structures (i.e., silicones), thus creating a film structure as discussed above.

Some of these products are marketed as pre-reacted siloxanes or silicones. These types of products can be marketed as fluorinated (R being fluorinated aryl- or alkyl chains) or non-fluorinated (R being not fluorinated aryl- or alkyl chains).

11.1.1.2 Vinyl, (meth-)acrylate and di-isocyanate/polyurethane chemistry

According to Texshield et al. (2013), the more traditional fluorochemical repellents are based on vinyl or acrylic polymers, and the authors give an example of a repellent used for textiles: '*Acrylic acid can be reacted with a perfluoro alcohol to form the corresponding acrylate ester. The acrylate monomer will polymerise to form a high molecular weight polymer that can be converted to an emulsion. The emulsion dries to a continuous film, covering the fibre surface. The perfluoro segment is there as a side chain attached to the polymer backbone. Being non-polar, it will orient away from polar forces, thus forcing itself toward the air interface. Heat facilitates the orientation by increasing molecular motion, hence the need to iron (hot press) treated textiles after laundering to re-orientate the fluorocarbon chains at achieve optimum repellence'.*

Similarly, vinyl, (meth-)acrylate and di-isocyanates can be modified via reaction with alcohols to form polyvinyl, polyacrylate and polyurethane (also called PUR) structures with hydrophobic side chains, which when applied will point away from the surface to which they are attached with the polar forces of the polymer molecules/structures.

The following figure applied from Lassen et al. (2015b) *'illustrates how the PFAS-based polymers are typically composed on the surface of the finished fabric. On a backbone of carbon atoms, which cross-links to form a two-dimensional polymer structure upon curing, both polyalkylfluorinated and non-fluorinated side chains are attached. The fluorinated side chains can be of varying lengths in the individual product. The chains are attached to the backbone by ester bonds. The impregnating agents are applied as a thin film on the surface of the fabrics, usually in combination with other finishing agents, by a process in which the polymerization and curing occurs on the surface of the fabric (Knepper et al., 2014). The side chains of the two-dimensional polymer structure formed during cure protrude as small hairs from the material, and aid in providing the dirt and water repellent effect´*. (cited from Lassen et al., 2015a)

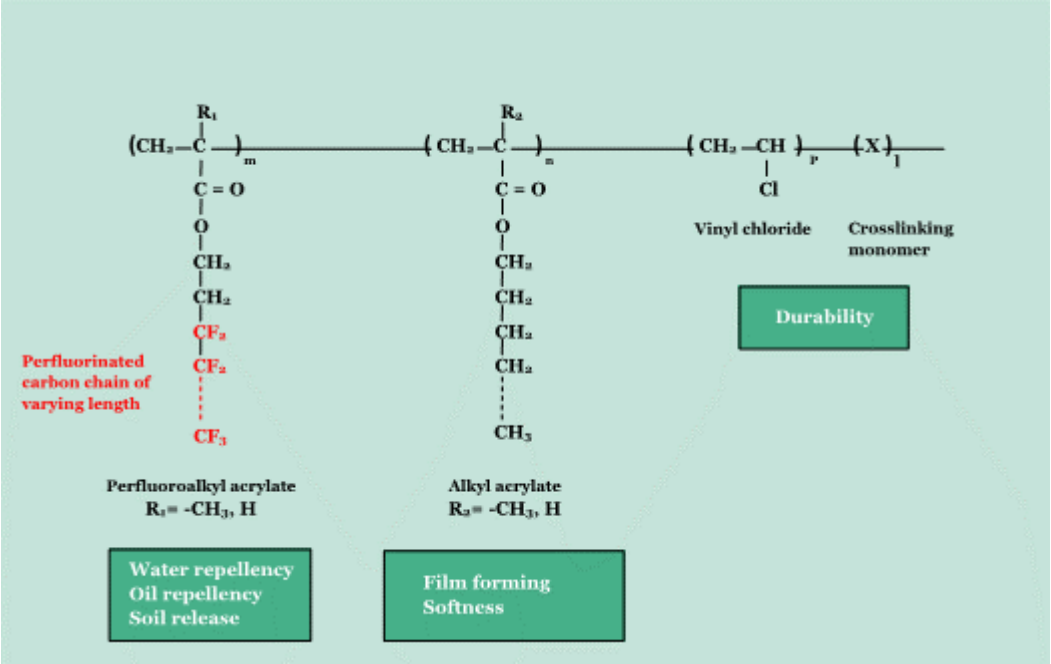

FIGURE 10. Polymer structure of oil and water repellents for textile. The perfluoroalkyl moiety of the polyfluoroalkylated side chain is marked in red. The product is marketed as a fluoroalkyl acrylate copolymer (From Lassen et al., 2015b; based on Daikin 2009).

There is possibly other chemistry involved in the bonding of these types of molecules/polymers to the object surface, but limited evidence for this has been identified within the scope of the current project.

These types of products can be marketed as fluorinated (with fluorinated aryl or alkyl-chains) or non-fluorinated (with not fluorinated aryl or alkyl chains).

11.1.1.3 Dendrimers

According to ZDHC (2012): '*Dendrimer based repellent chemistry is a relatively new field of repellent chemistry. Dendrimers are characterized by regular hyperbranched monomers leading to monodisperse, tree-like structures. The synthesis of monodisperse polymers demands a high level of synthetic control which can be achieved through step by step reaction, building the dendrimer up one monomer layer at a time. The primary components of each dendrimer are the core, internal cavities, branching units and closely packed surface groups'.*

Lassen et al. (2015a) found the following in relation to textile impregnation:

'Depending on the chemical composition, dendrimers can provide water and/or oil repellency. The company Rudolph Group, for example, offers different textile finish products based on dendrimer technology. The oil- and soil-repellent dendrimer finishes include a fluorocarbon resin in their structure, while the fluorocarbon-free dendrimers only provide water repellency. Compared to other PFAS-based repellents, the fluorine content of the oleophobic dendrimer finishes is reduced. The fluorocarbon-free dendrimers provide water repellency through closely packed surface groups, i.e. methyl groups.

Commonly, these finishes are applied as two-component systems consisting of an emulsion containing the dendrimers and a solution containing a crosslinking substance providing the fixation to the fibre. Fluorocarbon-free dendrimers are based on hydrocarbon or polyurethane

chemistry. Crosslinking is commonly achieved by chemical binding of the dendrimers with isocyanates to the fibre (Personal communication with the industry).' (cited from Lassen et al., 2015a)

As appears from this brief introduction, dendrimers can be fluorinated as well as non-fluorinated.

'Nanotechnology' and other chemistries

An increasing number of products, including impregnation products, are claimed to be 'nano'. 'Nano' generally refers to the size of particles or structures in the 1-100 nm range. For example, Nørgård et al. (2010) elaborates on how some impregnation products, e.g., based on organosilanes, can create nanofilms when applied to the product surface. He notes that some products that claimed to be 'nano' do not contain nanomaterials, but create the nanostructure (the nanofilm) after being applied to the object surface.

A model of an oligomeric water-based fluoroalkylfunctional siloxane with reactive silanol moieties combined with hydrophilic groups is shown in the figure below from the Annex XV dossier for polyfluorooctyl trialkoxysilanes (TDFAs) used in spray products (DEPA, 2016). The applications of this product range from easy-to-clean surfaces to permanent anti-graffiti coatings.

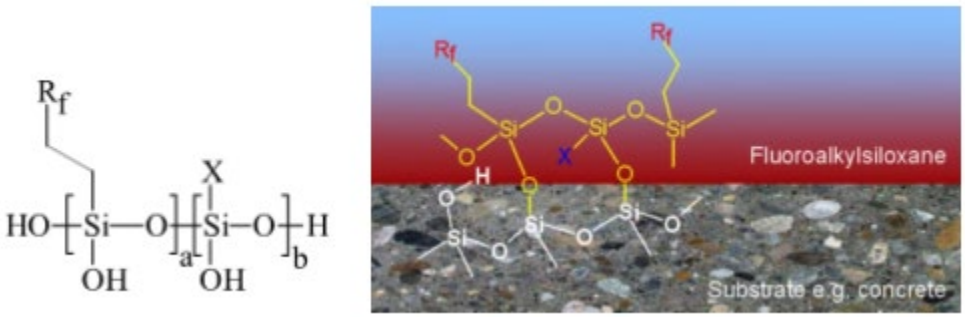

FIGURE 11. Structural formula and model of a water-based fluoroalkylsilane system. Rf are fluoroalkyl groups and X are hydrophilic groups (Standke et al., year not indicated as shown in Annex XV dossier for trisiloxanes))

'Nano' can also refer to nanosized particles being part of the product formulation. Nano-TiO_2 can, for example, be added to products and surfaces to ensure a dirt repellent/self-cleaning effect and nanosilver can be added to textile/textile products for its antibacterial (and thereby anti-odour) properties (see e.g. Larsen et al., 2015).

Repellents based on melamine resins are available on the market[31]. The identified products contain C_6 fluorinated side-chains, and do not contain the longer fluorinated C_8-chains. Information on how these resins bind to the surface is not readily available.

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Appendix 4. CLP Regulation and synergistic effects

Spray products, such as impregnation products, are chemical mixtures that are regulated (i.e., classified and labelled) under the CLP. In addition, the individual substances in a chemical mixture may be regulated under REACH. It is the company that places a substance or a mixture on the EU market that is responsible for CLP compliance, while the Danish Environmental Protection Agency's Chemicals Inspectorate is responsible for checking compliance with the rules in Denmark. CLP includes both chemical substances and mixtures sold to private consumers, and substances and mixtures that are used professionally.

Classification and labelling of impregnation spray products under CLP can be particularly challenging, as the mixture can potentially be acutely toxic by inhalation, although the individual substances in the mixture are not themselves toxic by inhalation. CLP states in Article 12 that this synergistic effect must be taken into account, but in many cases, it can be difficult to determine in advance whether this effect will occur.

Examples of synergistic effects between the active substance and the organic solvents in impregnating agents have been observed. This is the case for the product "Non-absorbing floor materials" (NFP 1) mentioned in Nørgaard et al., 2009, Nørgaard et al., 2010, Nørgaard et al., 2014, Larsen et al., 2014, Sørli et al, 201 8 and ECHA, 2017. When the individual ingredients in NFP 1 (approximately 1% polyfluorooctyl triethoxysilane[32] in 2-propanol and a little acid as catalyst) were tested individually by inhalation in mice, they had no effect. In contrast, when the entire NFP1 mixture was tested under the same experimental conditions, a sharp decrease in Tidal Volume (VT) was observed, as well as several mice that were in a lethal state a few hours after exposure. Based on this experiment, NFP 1 should according to CLP be classified as acutely toxic in category 2 with the hazard statement H330 - "Fatal if inhaled".

However, the manufacturer had not labelled NFP 1 as acutely toxic. On the other hand, according to the old classification scheme, the product was labelled F; R 11 - "Highly flammable", Xi; R36 - "Irritating to eyes" and Xi; R67 - "Vapours may cause drowsiness and dizziness" similar to the then-classification of 2-propanol (under CLP, 2-propanol is harmonized classification as: Flam. Liq. 2; H225 - "Flammable", Eye Irrit. 2; H319 - "Eye irritant" and STOT SE 3; H336 - "May cause drowsiness or dizziness by inhalation").

The example shows that in some cases there is a risk of under-classifying impregnation products if synergistic effects are not taken into account. In such cases, the products are not labelled correctly and consumers and workers do not receive the correct information as to how to handle the product properly.

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Hazard and exposure assessment of do-it-yourself products for impregnation

A large number of do-it-yourself impregnation products are marketed to Danish consumers. The products are typically used for re-impregnation of consumer products (e.g. footware and outdoor clothing) immediately after the products have been purchased or when the water and/or dirt-repellent effect begins to diminish.

The Danish Environmental Protection Agency has chosen to make a survey of the market, where 110 do-it-yourself impregnation products were identified within ten different application categories. Out of these products, 14 were included in initial chemical content analyzes, as well as hazard and exposure analyzes. The main components in the majority of the products were saturated hydrocarbons, but some of the products also contained oxygen-containing solvents (e.g. alcohols, ethers, esters or ketones). The potential hazard of 12 of the 14 selected impregnation spray products was performed by measuring acute respiratory toxicity. Of the 12 products tested, 10 inhibited the function of the lung surfactant and may therefore potentially be harmful by inhalation.

On the basis of this study, it could not be demonstrated that the products with PFAS resulted in an inhibition of the lung surfactant at lower doses as compared to products without PFAS; in fact, the lowest inhibitory doses were seen for impregnating agents based on siloxanes/silicones. The results show that the hazardous properties of an impregnation product cannot be determined solely on the basis of the ingredients, and it is therefore necessary to examine the ability of the individual products to inhibit the lung surfactant in connection with a hazard as-assessment.

The Danish Environmental
Protection Agency
Tolderlundsvej 5
DK - 5000 Odense C

www.mst.dk