

ANNEX XV REPORT

PROPOSAL FOR A RESTRICTION

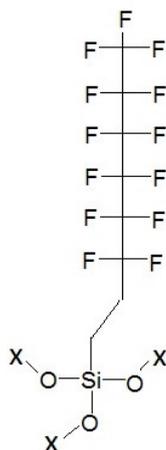
SUBSTANCE NAME(S): (3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanetriol and any of its mono-, di- or tri-O-(alkyl) derivatives

IUPAC NAME(S): N.A. (group entry)

EC NUMBER(S): N.A. (group entry)

CAS NUMBER(S): N.A. (group entry)

INDEX NUMBER(S): N.A. (group entry)



Where X = alkyl groups or hydrogen

CONTACT DETAILS OF THE DOSSIER SUBMITTER:

Danish Competent Authority for REACH
Danish Environmental Protection Agency
Strandgade 29
DK-1401 Copenhagen K
mst@mst.dk, tel.: +45 72544000
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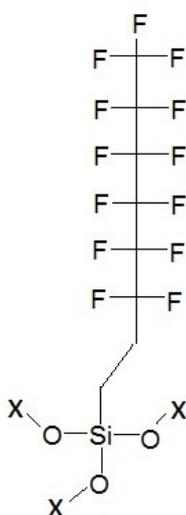
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A. Proposal

A.1 Proposed restriction(s)

A.1.1 The identity of the substance(s)

Substance name	(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanetriol and any of its mono-, di- or tri-O-(alkyl) derivatives
IUPAC name	N.A. (group entry)
EC number	N.A. (group entry)
CAS number	N.A. (group entry)



Where X = alkyl groups or hydrogen

Examples of (3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanetriol mono-, di- or tri-O-(alkyl) derivatives addressed by the proposal for restriction are listed in B.1.1.

A.1.2 Scope and conditions of the restriction

The restriction is a ban on the use of (3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanetriol and any of its mono-, di- or tri-O-(alkyl) derivatives in mixtures containing organic solvents placed on the market or used in spray products for consumers (aerosol dispensers, pump and trigger sprays and mixtures marketed for spray application).

Proposed restriction

Column 1. Designation of substance	Column 2. Conditions of restriction
<p>(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanetriol and any of its mono-, di- or tri-O-(alkyl) derivatives, including among others:</p> <p>(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)trimethoxysilane CAS No. 85857-16-5 EC No. 288-657-1</p> <p>(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)triethoxysilane CAS No. 51851-37-7 EC No. 257-473-3</p> <p>(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)triisopropoxysilane CAS No. 1240203-07-9</p>	<ol style="list-style-type: none"> 1. Shall not be used in formulation of mixtures with organic solvents in spray products intended for supply to the general public 2. Shall not be placed on the market, in a concentration equal to or greater than 2 ppb by weight, in spray products containing organic solvents for supply to the general public. 3. Spray products should in this context be understood as aerosol dispensers, pump and trigger sprays and mixtures marketed for spray application by any means. 4. Organic solvents mentioned in paragraph 1 and 2 include organic solvent used as aerosol propellants.

The (3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanetriol tri-O-(alkyl) derivatives mentioned in the proposed restriction will in this dossier be abbreviated TDFAs. TDFAs belong to the group polyfluorooctyl trialkoxysilanes.

Please see the section "Definition of terms used" for other definitions of the used terms.

TDFAs are hydrolysed to the 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctylsilanols (mono, di and tri). These hydrolysates will subsequently condensate to polysiloxanes (polymers) with 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl as a side-chain. In the complex mixture of the marketed spray products only a minor fraction (or none) of the original TDFAs will be present. Hydrolysis of TDFAs is a prerequisite for the subsequent condensation reactions, which create the "proofing/impregnation" layer upon application of the product.

A transition period of 18 months is proposed as this should be sufficient for all stakeholders to comply with the restriction, including to deplete any stocks available.

A.2 Summary of the justification

A.2.1 Identified hazard and risk

Mice exposed to aerosolised mixtures containing TDFAs and 2-propanol (hydrolysates and condensates of polyfluorooctyl triisopropoxysilane) levels have been shown to develop serious lung injury following short term exposure. A significant concentration-dependent decrease of the tidal volume (VT) was seen, which was still significantly suppressed in the 18.4 mg/m³ group one day after exposure. 3 out of 20 mice died at 18.4 mg/m³ and 10 out of 10 died at 24.4 mg/m³.

The mechanism behind the observed effects has been studied in mice and is believed to involve inhibition of the pulmonary surfactant in the deeper parts of the lungs by depletion of the pulmonary surfactant protein, SP-B. The SP-B protein is embedded in the phospholipids of the pulmonary surfactant, and it is believed that the solvents (depending on lipophilicity) facilitate contact between hydrolysates and condensates of TDFAs and the SP-B proteins. This can also explain why no effect on the lungs are seen for spray products based on hydrolysed TDFAs with water as a solvent even though the product can reach the deep parts of the lungs. Thus, the toxicity of the products in rats and mice depends on hydrolysates and condensates of TDFAs, the solvents, particle size distribution and particle concentration (application method).

Only limited effects were seen in an inhalation study in rats for the pump spray product "Magic Nano Bath & WC" at high doses. However, a risk assessment for mixtures containing TDFAs and 2-propanol shows a risk that is not adequately controlled for these mixtures applied by aerosol dispenser or pump spray. The risk for trigger sprays is expected to be similar to the risk seen for pump sprays.

Evidence of risk to consumers

713 incidents investigated in the EU during the past three to four decades have demonstrated a relationship between short-term exposure to certain proofing/impregnation sprays and development of respiratory illness which has required hospitalisation. Incidents have often occurred as outbreaks which have been linked to use of specific spray products on the market. In several cases the identified sprays have subsequently been withdrawn from the market shortly after their introduction.

Fluorinated polymers are contained in most of the spray products involved in the identified incidents, see Table 5. However, very little information is generally available on the chemical identity of the polymeric active ingredients, as they usually occur in low concentrations and the product have in general only been classified and labelled according to its content of organic solvent by the producer.

Different types of proofing or impregnation sprays are involved in the identified incidents. They include products for both absorbing surfaces (textile and leather) and non-absorbing surfaces (tile and ceramics). Information is not always available regarding the solvent system, and some products may be water-based, with some content of alcohol.

It is estimated that 20 – 40 % of the 713 incidents reported in the EU were most likely spray product(s) containing mixtures of TDFAs and organic solvents intended for the general public. The products with the highest probability of being "spray product(s) containing mixtures of TDFAs and organic solvents for the general public" are "Magic Nano Glass & Ceramic" and "Magic Nano Bath & WC" that were responsible for 154 incidents in Germany in 2006. No human incidents have been reported for the spray product referred to as NFP 1 (containing TDFAs and 2-propanol) that has been studied intensely in animal studies by Nørgaard et al., before it was removed from the market.

The figure of 713 incidents reported for impregnation products in the EU is considered largely to underestimate the real number as the majority of incidents are not likely to be recorded and as it is not likely that a link between the actual exposure and the effects will be established in all cases. Danish data extrapolated to EU indicates 330 - 660 incidents of spray product containing TDFAs and organic solvents per year.

Since spray products containing TDFAs and organic solvents can only account for a part of the incidents, it is likely that other combinations of fluorinated substances and solvents may cause pulmonary distress by the same mechanism as mixtures containing TDFAs and organic solvents. However, documentation from animal studies is not available for other combinations than TDFAs and organic solvents.

Typical consumer exposure situations involve indoor spraying in small rooms, such as bathrooms, and with poor ventilation. In many of the case descriptions presented in Table 5 and in Appendix 1, Table 1 - 2, it is mentioned that windows and doors have been closed. Although some of these product types, e.g. for leather and textile impregnation, may carry a warning text such as "Use only outdoors or in well-ventilated areas" it is likely that these instructions are not always followed, e.g. if the consumer is living in an apartment building in the city.

Most of the reported incidents, both in the EU and outside, (see Appendix 1), linked to the use of aerosol dispensers. However, one product resulting in two incidents of respiratory problems and additional 14 calls to the poison centre is described as a pump spray were reported in Canada (1992-1993). Additionally two occupational cases with three incidents were reported in Switzerland (2002-2003). In these cases the causative agent belonged to the chemical group of fluoroacrylates. No human incidents are reported for the pump spray product "Magic Nano Bath & WC" and only limited effects were seen in an inhalation study in rats. Risk assessment for mixtures containing TDFAs and 2-propanol demonstrates a risk for these mixtures applied by both aerosol dispensers and pump sprays.

A.2.2 Justification that action is required on a Union-wide basis

The justification for acting on a Union-wide basis originates from the EU-wide distribution of incidents of lung injuries due to use of spray products by consumers (aerosol dispensers, pump and trigger sprays and mixtures marketed for spray application) containing TDFAs and organic solvent to avoid different legislative requirements in Member States with the risk of creating unequal market conditions. In order to adequately protect consumers, a restriction should target imported as well as EU produced spray products intended for use by consumers.

A.2.3 Justification that the proposed restriction is the most appropriate Union-wide measure

The proposed restriction addresses the risk for consumers arising from use of spray products containing mixtures containing TDFAs and organic solvents where lung injuries in animal studies have been identified. Similar effects have been seen in humans exposed to spray products containing fluorinated polymers and solvents.

Based on the limited information available, the parent substances do not fulfil the criteria in CLP, Article 36(1) for proposing a harmonised classification.

Mixtures containing TDFAs and organic solvents may fulfil the classification criteria as acute toxic depending on the organic solvent and the content of TDFAs – a mixture containing 1.1% TDFAs and 2-propanol fulfil the criteria for classification with Acute Toxicity, Category 2.

Producers of the spray products containing TDFAs and organic solvents should classify and label the containers appropriately in accordance with this. However, it seems that in none of the incidents reported, the products were labelled as acute toxic to humans. As only classification

of substances can be harmonised under the CLP Regulation (cf. articles 36-38), it is not relevant to consider this risk management option for mixtures of TDFAs and organic solvent.

Some products carry warning text such as "Use only outdoors or in well-ventilated areas". No risk should occur if these instructions for use of the spray products are followed.

Professional users are covered by occupational health regulation, which is assumed to provide a sufficient level of protection if the products are properly labelled. Even if not labelled properly the product will most likely be labelled according to the hazard of the organic solvent(s). This may include precautionary statements such as "Avoid breathing the dust, fume, gas, mist, vapours or spray", depending on the solvent(s). Incidents of lung injuries among professional users working with proofing/impregnation sprays have been identified. However, none of the identified cases seems to involve TDFAs. Professional uses will therefore not be addressed in this restriction.

For consumers, voluntary agreements between stakeholders and information campaigns are not considered to be sufficiently effective. The General Product Safety Directive is not considered appropriate as the knowledge by importers/producers of the risk when combining TDFAs with organic solvents in spray products may be limited (if existing).

Therefore a restriction under REACH is proposed.

Other spray applications than aerosol dispensers are included since a risk assessment for mixtures containing TDFAs and 2-propanol shows a risk that is not adequately controlled for these mixtures applied by pump spray. Other application methods than spraying are not included, as no cases of injuries have been identified and no risk assessment has demonstrated a risk that is not adequately controlled.

Introduction of a risk-based limit value of e.g. 0.00004% (0.4 mg/kg, 400 ppb) for spray products containing TDFAs and organic solvents has been considered (the analytical detection limit is 2 ppb). This would avoid that other mixtures containing other substances where TDFAs could be found as an impurity would be effected. However, such substances have not been identified so far, and if they should exist it is uncertain as to which extent they would constitute a risk. Furthermore, the enforcement of the restriction would be more costly. It might also take a long time before an adequate analytic standard is developed (unless the Total Oxidisable Precursor Assay (TOP Assay) can be adapted, see E.2.1.2.1). Therefore, this option is not considered feasible.

Effectiveness in reducing the identified risks

The restriction is considered effective in reducing the risks for consumers when applying mixtures based on TDFAs and organic solvents. The potential risk from use of other impregnating agents in spray products will not be addressed, and the restriction is expected to only reduce a part of the incidences of lung injury from the spray applications of impregnating agents. Other impregnation agents are not addressed by the proposed restriction due to lack of a substantial causal relationship between the substances and the effects seen in the exposed humans. Nevertheless, implementation of the proposed restriction may have a multiplying effect on reducing the use of mixtures of other mixtures of fluorinated substances and organic solvents.

Proportionality to the risks

As alternative application methods, water-based spray products with TDFAs and spray products without TDFAs are readily available, negative effects on the market are marginal, and considering the potential health effects of the application of the targeted mixtures in aerosol dispensers, a restriction is considered proportionate.

Practicality, including enforceability

The proposed restriction is considered to be an adequate measure for addressing the risks due to the use of TDFAs and organic solvent in spray products intended for consumers. It is easy to understand that the targeted substances must not be used in mixtures with organic sol-

vents in spray products for supply to the general public. This message is easy to communicate down the supply chain and the restriction can be enforced. A standardised method would ensure reproducible enforcement. A commercial laboratory is currently implementing a method for analysing the targeted substances (the so-called TOP Assay). The detection limit of this method is 2 ppb.

The mixtures in the spray products are highly reactive, which complicates an exact quantification of the substances and makes it more expensive.

Monitorability

The EU Rapid Alert System for Non-Food Products (RAPEX) can be used to monitor compliance with the restriction at EU level. The impact of the restriction may be monitored by examining the trend in EU annual incidences of poisoning due to the use of the targeted substances in spray products for consumers reported to national poisoning centre/hot lines. As the exact composition of the impregnating agent is often not known, the monitoring most probably has to be based on reported incidents of respiratory illness resulting from all types of impregnating agents applied by spray. As the reported number of incidents is small, only some of the incidents are due to the targeted substances, and as the annual variation is high, the statistical "noise" would be high. Most probably, years of monitoring would be needed before the direct impact of the restriction could be evaluated on the basis of the monitoring data.

A.2.4 Summary

In summary, TDFAs (polyfluorooctyl trialkoxysilanes) have been shown to cause serious acute lung injury in mice exposed to aerosolised mixtures containing TDFAs and organic solvent at certain concentration levels. The relevance of these findings to humans is supported by numerous cases where consumers have experienced acute pulmonary distress following exposure to proofing/impregnation spray products containing fluorinated substances. Most of the reported incidents are for aerosol dispensers and only five are for pump spray (of these three were occupational). However, a risk assessment for mixtures containing TDFAs and 2-propanol shows a risk that is not adequately controlled for these mixtures applied by both aerosol dispensers and pump sprays.

Detailed information on the fluorinated constituents is typically not available as the fluorocarbon monomers alone do not require hazard classification under CLP¹ and are contained in low concentrations. Mixtures containing TDFAs and organic solvents may fulfil the classification criteria as acute toxic depending on the organic solvent. However, it seems that in none of the incidents reported, the products were labelled as acute toxic by inhalation. At present, the provisions on chemicals and consumer protection legislation are insufficient to protect consumers from acute respiratory distress when using spray products containing TDFAs and organic solvents and, therefore, a restriction seems necessary in order to address and prevent this serious effect.

Alternatives are available and a restriction is considered to have limited negative economic and social impacts.

A.3 Main uncertainties

This restriction proposal is based mainly on effects seen in experiments with mice that have been exposed to aerosolised mixtures containing TDFAs and organic solvent at certain concentration levels.

¹ Regulation (EC) No 1272/2008 of The European Parliament and of the Council of 16 December 2008 on classification, labelling and packaging of substances and mixtures, amending and repealing Directives 67/548/EEC and 1999/45/EC, and amending Regulation (EC) No 1907/2006

As supporting evidence these results are compared to incidents seen in humans that have been using certain spray products. It is not possible to directly relate the incidents with the actual composition of the spray products as such data do not exist. However, the two aerosol products "Magic Nano Glass & Ceramic" and "Magic Nano Bath & WC" that were responsible for 154 incidents in Germany in 2006, were most likely based on a fluorosilane, Koch et al. (2009). The polyfluoroalkyl chain length of the fluorosilane is not known, but it could though very well be TDFAs.

The major uncertainties of importance for the socioeconomic assessment are (for further details see chapter F):

- The number of the reported poisoning incidents that the targeted mixtures have actually been responsible for.
- The annual number of poisoning incidents and the trend in incidents caused by the targeted mixtures. It is uncertain to what extent the market has already changed as a reaction to the reported poisoning incidents and the research regarding the effects of the substances.
- The total number of aerosol dispensers, pump and trigger sprays and mixtures marketed for spray application with the targeted mixtures sold within the EU.
- To what extent alternative substances and mixtures are manufactured within the EU, or imported into EU, respectively.
- To what extent the proposed action would target mixtures based on other polyfluorinated trialkoxysilanes due to trace levels of TDFAs in the mixtures.
- The threshold of 2 ppb is derived from the so-called TOP Assay that is expected to be used for enforcement of the PFOA and PFOA precursor restriction. This method has not yet been tested for fluorinated silanes, silanols and siloxanes.

Several of the uncertainties are related to lack of information from industry. This is not necessarily unwillingness from stakeholders to provide data or information but is considered to be a general lack of knowledge of how the substances are used downstream. It appears that the downstream supply chain is very diffuse, where the substances are sold to distributors and then to downstream users that might even sell to others. This means that the producer or importer loses overview of the uses. This lack of knowledge might be reduced following the public consultation of this proposal.

The substances are only referred to as "fluorinated substance" or "polyfluorinated substance" to the end-producers; this implies that the actual substances are not known; concentrations of parent substances are so low that the producers do not classify the final products.

It was also clear from the consultations that several contacted organizations did not know the exact use of the TDFAs, including possible previous uses or present as well as future uses regarding products for the general public. This underlines also the lack of knowledge regarding previous uses by the downstream users described above.

B. Information on hazard and risk

B.1 Identity of the substance(s) and physical and chemical properties

B.1.1 Name and other identifiers of the substance(s)

Substance name: (3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanetriol and any of its mono-, di- or tri-O-(alkyl) derivatives

EC Number: See table below

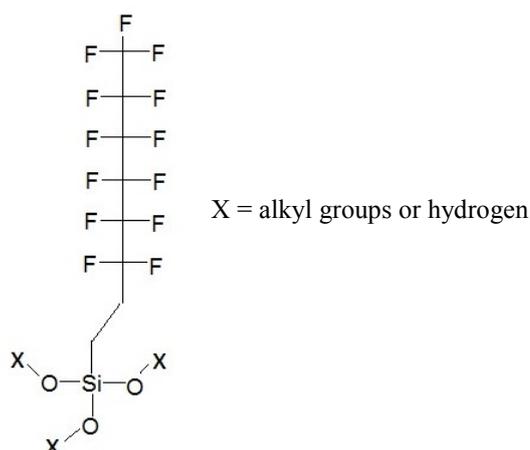
CAS Number: See table below

IUPAC Name: See table below

Synonym: See table below

The restriction targets spray products for consumers (aerosol dispensers, pump and trigger sprays and mixtures marketed for spray application) containing mixtures of TDFAs and organic solvents. TDFAs and its reaction products with organic solvent are hydrolysed to the silanols (mono, di and tri) of 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl. These hydrolysates will subsequently be condensed to siloxane-polymers with 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl (polyfluorooctyl) as a side-chain. In the complex mixture of the marketed spray products only a minor fraction (or none) of the original TDFAs will be present. Hydrolysis of TDFAs is a prerequisite for the following condensation reactions, which creates the "proofing/impregnation" layer upon application of the product. It should be noted that the marketed spray products can include solvents (such as alcohols) that can react with TDFAs. In these products, only a minor fraction (or none) of the original TDFAs will be present. The resulting TDFAs derivatives can instead be expected to be the subject of the hydrolysis/condensation reactions leading to the "proofing/impregnation" layer.

A general formula for the targeted group of substances can be given as:



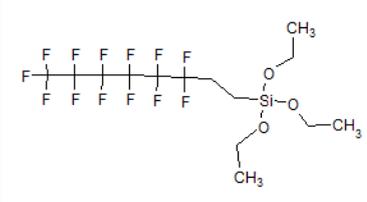
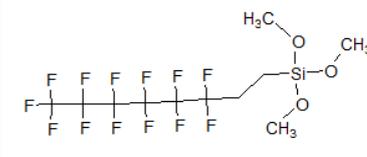
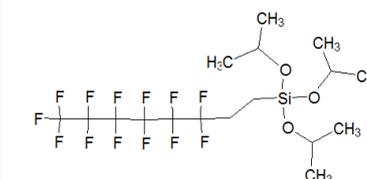
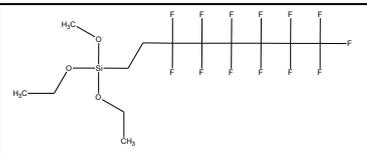
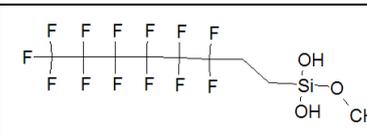
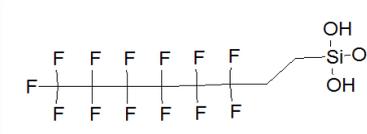
In theory, variations in the alkoxy chain can give rise to a very large number of parent compounds. In practice, only few such substances have been positively identified to be used in impregnation spray products. It is important to note, however, that the restriction should apply to all substances which are covered by the general formula in order to avoid substitution to other polyfluorooctyl alkoxy silanes.

Only two substances meeting the general formula are pre-registered under REACH (see Table 1) (ECHA, 2015a). According to the REACH Reconsile Consortium, polyfluorooctyl trimethoxysilane and polyfluorooctyl triethoxysilane are planned to be registered by its members by 31 May 2018 (Reconsile, year not indicated).

Analysis of the composition of commercial spray products have shown that other TDFAs are present in the spray products e.g. the polyfluorooctyl triisopropoxysilane (Nørgaard et al., 2010b). None of these substances are registered yet.

In the Classification & Labelling (C&L) Inventory under REACH, the polyfluorooctyl triethoxysilane, EC No 257-473-3 is notified by 57 companies, whereas polyfluorooctyl trimethoxysilane is notified by four companies. Further details on the classification are included in B.3.2

TABLE 1 EXAMPLES OF SUBSTANCES TARGETED BY THE PROPOSED RESTRICTION

EC No	CAS No	IUPAC name	Synonyms	Molecular formula
257-473-3	51851-37-7	Triethoxy (3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)-silane (preregistration name)	Polyfluorooctyl triethoxysilane (synonym used in this dossier) 1H,1H,2H,2H-perfluorooctyl triethoxy-silane T1770; Triethoxy-1H,1H,2H,2H-tridecafluoro-n-octylsilane; Triethoxy-1H,1H,2H,2H-perfluoro-n-octylsilane	
288-657-1	85857-16-5	Trimethoxy (3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)-silane (preregistration name)	Polyfluorooctyl trimethoxysilane (synonym used in this dossier) 1H,1H,2H,2H-perfluorooctyl trimethoxysilane	
N.A.	1240203-07-9	Triisopropoxy(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)-silane	Polyfluorooctyl triisopropoxysilane (synonym used in this dossier) 1H,1H,2H,2H-perfluorooctyl triisopropoxysilane	
N.A.	152992-47-7	diethoxy(methoxy)(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silane	Silane, diethoxymethoxy(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)- diethoxy(methoxy)(1H,1H,2H,2H-perfluorooctyl)silane	
N.A.	1531633-11-0	Methoxy(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)-silanediol		
N.A.	185911-29-9	(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)-silanetriol		

B.1.2 Composition of the substances and mixtures

No data on the exact composition of the substances have been obtained from manufacturers.

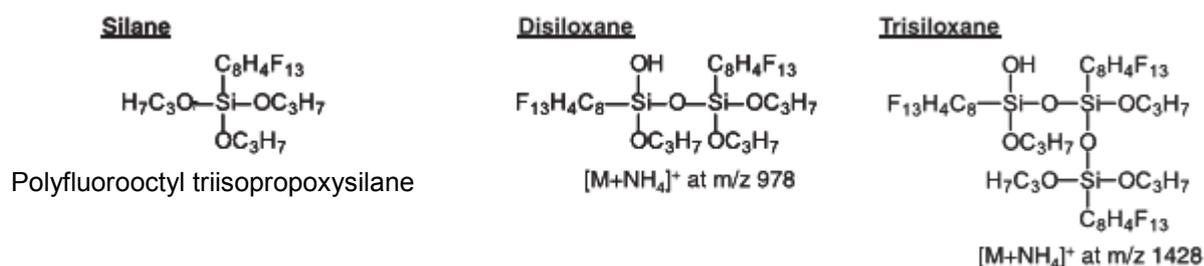
According to the SDS for one of the commercial polyfluorooctyl triethoxysilanes, the product contains approximately 3% tetraethyl silicate (CAS No 78-10-4; EC No 201-083-8).

According to the information from manufacturers of the substances, polyfluorooctyl triethoxysilane can be dissolved to a proportion of about 25% (w/w) in ethanol and various other organic solvents, e.g. n-hexane, xylene, acetone and ethyl acetate. As indicated in B.1.3 polyfluorooctyl triethoxysilane cannot be dissolved in water.

In the presence of water, the ethoxy groups of the polyfluorooctyl triethoxysilane hydrolyse to ethanol and form reactive silanol groups which can bond to a variety of inorganic substances. Hydrolysis is fastest and most complete when an acid or base catalyst is employed.

In mixtures containing organic solvent (alcohols), TDFAs may be present as other substances than the parent compound.

Examples of the chemical form in mixtures of commercial spray products - Nørgaard et al. (2010b) characterised a commercial spray product based on fluorosilanes in 2-propanol. The constituents were identified as polyfluorooctyl triisopropoxysilane and di-, tri- and tetrasiloxane condensates from this compound. The polyfluorooctyl triisopropoxysilane is not available from major chemical suppliers and is not preregistered under REACH. Nørgaard et al. (2010b) hypothesize that most likely the parent substances for the mixture is the commercial polyfluorooctyl triethoxysilane and that the ethoxy groups are replaced by isopropoxy groups, since the commercial polyfluorooctyl triethoxysilane is dissolved in slightly acidic 2-propanol. If this hypothesis is correct, the alkoxy groups on silicon depend on the solvent alcohol. The hydrolysed silanes in the spray products would in any case meet the general formula of the substances targeted by this proposal whereas the disiloxane, trisiloxanes and siloxanes with longer chains would not meet the formula.



Hydrolysates and condensates identified by ESI/MS (electrospray ionisation/mass spectrometry) spectra of commercial fluorosilane spray products (Nørgaard et al., 2010b)

The concentrations of the individual constituents were not quantified by Nørgaard et al. (2010b). The total content of hydrolysates and condensates of polyfluorooctyl triethoxysilane and 2-propanol (polyfluorooctyl triisopropoxysilane, mono-, di- and tri silanols and siloxanes) in the commercial spray product was determined to be $1.1 \pm 0.1\%$.

It is not known to which extent the parent compounds are present as condensates in the commercial spray products.

Water-based mixtures derived from TDFAs - Nørgaard et al. (2014) studied the effects of seven commercially available water-based impregnation mixtures. It is not indicated whether the mixtures were provided in aerosol spray cans or trigger/pump sprays, but the authors have

for this dossier informed that the spray products were all pump sprays. According to the authors, analysis of the spray products by electrospray ionization mass spectrometry (ESI-MS) revealed that they all contained hydrolyzed forms of TDFAs. The authors concluded that the mixture contained TDFAs similar to the substances present in organic solvent-based spray products.

According to the available information on the marketed mixtures, the substances present in some water-based mixtures are different from the substances in the organic solvent-based mixtures. Weißenbach *et al.* (2008) describe the chemistry of various water-based fluoroalkylsilanes based on polyfluorooctyl triethoxysilane. The oligomeric water-based fluoroalkylfunctional siloxanes include reactive silanol moieties combined with hydrophilic groups that are responsible for solubility in water and chemical reactivity. The applications range from easy-to-clean to permanent anti-graffiti coatings. The substances are further described by Standke *et al.* (year not indicated) providing the example of a water-based fluoralkylsilane system shown below.



Structural formula and model of a water-based fluoroalkylsilane system. R_f are fluoroalkyl groups and X are hydrophilic groups (Standke *et al.*, year not indicated))

The substance shown above is in Degussa (2001) identified as "siloxanes and silicones, 3-[[2-[(2-aminoethyl)amino]ethyl]amino]propyl hydroxy, hydroxyl 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl, hydroxy-terminated, formats (salts)" (CAS No 273737-91-0, EC No not identified). The substance is not pre-registered under REACH, but registered in the Swedish Product Register until 2012 (SPIN, 2014). The reason, why the substance is not pre-registered may be that it is considered a polymer. The substance is one example of the water-based impregnating agents, but as described by Weißenbach *et al.* (2008) various impregnating agents are used.

As the commercial spray products are water-based, they would, however, not be targeted by the proposed restriction and are discussed further as possible alternatives.

Presence of TDFAs in other mixtures - TDFAs could likely be present at low concentrations in mixtures based on polyfluoroalkyl trialkoxysilanes with polyfluoroalkyl chain different from octyl.

Five polyfluoroalkyl trialkoxysilanes with polyfluoroalkyl chain different from octyl, respectively, have been pre-registered (see Table 2). Three of the pre-registrations with different EC numbers in fact address the same substance with a heptadecafluorodecyl chain. One of the EC numbers has been registered by an individual submission, but with a confidential tonnage and without any information on uses (EC No 435-230-4).

None of the substances are on the list of silicon-based substances planned to be registered by the REACH Reconcile Consortium (Reconcile, year not indicated).

The heptadecafluorodecyl trimethoxysilane is marketed by the Chinese manufacturer Nanjing SiSiB silicones for anti-sticking for anti-reflective coating, release coating and soil-repellent coating. (SiSiB, 2014) and by Momentive Performance Materials Inc for water and oil repellents for glass and cloth (Momentive, 2014).

Furthermore, a substances with a nonafluorohexyl chain is pre-registered, but not registered. The nonafluorohexyl triethoxysilane is marketed by the chemical manufacturer Tokyo Chemical Industry Co., Ltd. (TCI) and the Chinese manufacturer Nanjing SiSiB Silicones. The substance has to some extent substituted for the polyfluorooctyl triethoxysilane in impregnation sprays in the EU (confirmed by one manufacturer of mixtures for impregnation sprays).

TABLE 2 PRE-REGISTERED AND REGISTERED POLYFLUOROALKYL TRIALKOXYSILANES OTHER THAN TARGET SUBSTANCES

EC Number	CAS Number	Chemical name (as indicated in the pre-registration)	Synonym (as indicated in the pre-registration)	Registered tonnage
435-230-4	-	triethoxy(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)silane	-	Confidential Individual submission
-	101947-16-4	Silane, triethoxy(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)-	Heptadecafluorodecyl triethoxysilane	Not registered
-	83048-65-1	Silane, (3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)trimethoxy-	-	Not registered
-	102390-98-7	Silane, triethoxy(3,3,4,4,5,5,6,6,6-nonafluorohexyl)-	Nonafluorohexyl triethoxysilane	Not registered
207-059-3	429-60-7	trimethoxy(3,3,3-trifluoropropyl)silane	-	Not registered

The composition of commercial substances with polyfluoroalkyl chain different from octyl is not known.

The polymers from mixtures based on polyfluoroalkyl alkoxysilane are quite similar to side-chain-fluorinated polymers used in impregnating agents for textiles, leather, stone, etc. with the difference that the carbon backbone is replaced with a siloxane backbone. The fluorinated intermediates used in the production of the two types of mixtures may likely be the same. As an example, the raw material polyfluorohexyl ethyl iodide (DuPont™ Capstone™ 62-I) used in producing high performance repellents and surfactants is both used for various side-chain-fluorinated polymers and for water- and oil-repellent fluorine-modified silicones (Dupont, 2008). It should be noted that raw materials for manufacture of short-chained fluorine chemistries are mixtures of different chain lengths and in the case of the Capstone™ 62-I, the product consist of polyfluorohexyl ethyl iodide (85.0% min), polyfluorobutyl ethyl iodide (5.0 % max), polyfluorooctyl ethyl iodide (2.0–10.0%), polyfluorodecyl ethyl iodide (6.0% max) and other polyfluoroalkyl ethyl iodides (1.0 % max) (Dupont, 2008). This variation in chain lengths is reflected in variations in chain lengths of the side-chains of the final mixtures and the residual content of perfluoroalkyl and polyfluoroalkyl substances (PFAS), as has been demonstrated in many studies of impregnated textiles (e.g. Knepper et al., 2014; SFT, 2006; Herze et al., 2009).

If the same is the situation for the polyfluoroalkyl trialkoxysilanes, the commercial mixtures may consist of a mixture of different chain lengths and mixtures based on polyfluoroalkyl trialkoxysilanes with polyfluoroalkyl chain different from octyl would be targeted by the proposed restriction. No data on the composition of the commercial mixtures are available.

B.1.3 Physicochemical properties

TABLE 3 PHYSICO-CHEMICAL PROPERTIES OF TWO PRE-REGISTERED TDFAS

	Polyfluorooctyl triethoxysilane EC No 257-473-3	Polyfluorooctyl trimethoxysilane EC No 288-657-1
Molecular weight	510.36 [2]	468.29 [3]
Density	1.334 g/cm ³ (20 °C) [1]	1.457 [3]
Physical state (at ntp)	colourless liquid [1]	clear colourless liquid[3]
Melting point	- 38 °C [1]	-
Boiling point	220 °C (1013 hPa), [1]	226°C (760 mmHg) [2] 88° (13 mm Hg) [3]
Flash point	85 °C [1]	-
Relative density	1.334 g/ml [1]	1.457 g/l [2]
Vapour pressure	7.1 hPa (20 °C) [1]	<1mm (25°C)
Water solubility	Insoluble slow decomposition by hydrolysis [1]	-
pH	5.5 (1000 g/l) (20 °C) [1]	
n-Octanol-water partitioning coefficient	not determined	-
Viscosity, dynamic	5 mPa*s (20 °C) [1]	-

[1]: SDS of commercial polyfluorooctyl triethoxysilane.

[2]: Chemspider, Royal Society of Chemistry

[3]: SDS of commercial polyfluorooctyl trimethoxysilane [supplied outside the EU]

B.1.4 Justification for grouping

As described above, the commercial spray products contain various forms of TDFAs. The composition will depend on the parent compound and the solvents, as the alkoxy moieties may be exchanged with the alkoxy moieties of the solvent, if the solvent is an alcohol. In mixtures based on polyfluorooctyl triethoxysilane and 2-propanol, analysis has demonstrated that the substance is present as polyfluorooctyl trisopropoxysilane.

For the enforcement of a restriction, grouping of all the TDFAs is consequently a pre-requisite for an adequate enforcement of the restriction.

It may be considered to target all polyfluoroalkyl trialkoxysilane as a precautionary approach. However, so far animal studies have only demonstrated the effects of mixtures containing TDFAs and organic solvents. No data are available on the effects of mixtures based on polyfluoroalkyl trialkoxysilanes with other polyfluoroalkyl chain lengths and thus there is no justification for including these substance in the target group.

To the extent that future studies demonstrate that other substance groups/mixtures result in similar effects as the demonstrated effects of the target group, it may be considered to also restrict these substances/mixtures.

B.2 Manufacture and uses

B.2.1 Manufacture, import and export of the substances

B.2.1.1 Manufacture of TDFAs in the EU

Information on the manufacture of TDFAs in the EU has been obtained from the Reconcile REACH Consortium for joint registration of silicones and siloxanes (Appelman, 2014). Within

the two first deadlines of REACH registrations, none of the TDFAs have been registered. As the substances are not registered, no data indicating whether the substances are manufactured or imported by companies outside the consortium are available.

Two substances meeting the general formula for the substances addressed by this dossier have been pre-registered and are included in the list of substances to be registered by 31 May 2018 by the Reconcile Consortium members: polyfluorooctyl triethoxysilane (EC No. 257-473-3) and polyfluorooctyl trimethoxysilane (EC No. 288-657-1).

According to the information from the Reconcile REACH Consortium, polyfluorooctyl triethoxysilane is manufactured by less than four manufacturers in the EU. The total manufactured volume is 10-100 t/y. According to information from industry, approximately 10 % of the manufactured volume is sold via distributors where the further use of the substances is unknown. A part of this is considered to be used in spray products. As a maximum, 1-10 t/y polyfluorooctyl triethoxysilane is used in spray products.

Polyfluorooctyl trimethoxysilane is not manufactured in the EU by members of the Reconcile REACH Consortium. The Consortium holds no information on the manufacture of polyfluorooctyl trimethoxysilane. However, as the registration band for pre-registered substances are 1-10 tonnes, the same level as for polyfluorooctyl triethoxysilane is assumed.

As part of the stakeholder consultation, the international Fluorocouncil has stated that it does not hold any information on the substances. The Fluorocouncil has not indicated whether the substances are produced by its members.

B.2.1.2 Manufacture of TDFAs outside the EU

Outside the EU, polyfluorooctyl triethoxysilane is marketed by the chemicals manufacturers Tokyo Chemical Industry Co., Ltd. (TCI) and Nanjing SiSiB Silicones.

Polyfluorooctyl trimethoxysilane is marketed by the Chinese manufacturers Nanjing SiSiB Silicones and ShinEtsu Silicone and in the USA marketed by Momentive Performance Materials Inc. (Momentive, 2014). Others could manufacture or place the substances on the market, as the list is not exhaustive.

B.2.1.3 Import and export of TDFAs

The statistics on external trade from Eurostat (Comext database) do not include specific commodity entries for TDFAs and consequently no data on import and export of the substances on their own can be obtained from the statistics.

According to information from industry, the import of polyfluorooctyl triethoxysilane into the EU is most likely small compared to the manufacture within the EU. Possible use of polyfluorooctyl trimethoxysilane, is assumed to be based on import, as no production is reported.

B.2.2 Uses of the substances in mixtures in spray products for the general public

B.2.2.1 Formulation of mixtures to be used in spray products

TDFAs are formulated into impregnation/proofing formulations by mixing (suspending) the active substance with water or organic solvents and other constituents. This is either done by the manufacturers of the substances or by downstream formulators. The number of downstream formulators are not known, however, approximately 60 notifications have been received in the C&L Inventory.

According to manufacturer of substances the mixtures typically contain 0.5 – 2.0 % of the polyfluorooctyl triethoxysilane for ready-to-use impregnating agents. The same level is assumed for polyfluorooctyl trimethoxysilane in ready-to-use impregnating agents.

According to information from industry, approximately 10 % of the manufactured volume is sold via distributors where the further use of the substances is unknown. A part of this is considered to be used in spray products. This means that less than 2-20 t/y polyfluorooctyl triethoxysilane and polyfluorooctyl trimethoxysilane are used in spray products.

B.2.2.1.1 Application and mechanism of the mixtures in spray products

The main use of mixtures containing TDFAs and solvent applied by aerosol dispensers, pump or trigger spray is to provide water and oil repellence properties to different non-absorbing surfaces such as stone, glass and enamels. The mixtures based on TDFAs are marketed as mixtures with an "easy to clean" effect.

The active substances of the mixtures are hydrolysed TDFAs monomers dissolved in a solvent. After spraying, the solvent vaporizes and the TDFAs remains on the treated surface by forming a polysiloxane-based (polymer) coating with polyfluorooctyl as a side-chain providing water and oil-proofing. The process is described as follows by one of the manufacturers of fluorsilane-based mixtures (the exact substance not indicated).

"Inorganic-organic hybrid nano-composite materials with unique properties can be prepared by the sol-gel-technology.... The hydrolysis of organically modified silanes leads to the formation of nano-scaled polysiloxane particles. Upon coating of this dispersion the particles agglomerate by forming a gel film on the substrate. During the gel formation a first "self-organization" into a perfluorinated polymer rich and a silicate rich layer structure is taking place. In the following curing step the formation of a tight bonding to the surface of the substrate is achieved via the silicate layer (silicate bonding layer). The silicate layer is also giving a high mechanical strength to the coating. The perfluoroalkyl layer organizing on the top of the coating results in an extremely hydrophobic and oleophobic surface (non-stick layer). (Clariant, 2006)

The unique water and oil repellency properties of these mixtures are in other words derived from the polyfluoroalkyl side-chain that is attached to the polysiloxane backbone. Being nonpolar, the polyfluoroalkyl side-chains will orient away from polar forces, thus forcing themselves toward the air interface. As a result, a tufted surface is formed with thread-like structures of hydrophobic and oleophobic side-chains. The mechanism is basically the same as known for side-chain-fluorinated polymers (with a carbon backbone) used as impregnating mixtures for textiles, paper, stone, etc.

Some of the spray products are marketed as "nano products", as also indicated by the quote above, even though they might not contain nanomaterial as such but are creating a "nanothin" protective layer.

The consumption of the mixtures for spray coating is indicated to be about 10 – 70 ml/m² depending on application.

Hydrophobicity and oleophobicity (water and oil repellency) are associated with the affinity of a substance for water and oils. The hydrophobic and oleophobic properties of the mixtures can be differentiated by the surface tension. According to the US producer of (fluoro)silane-based impregnation mixtures, Gelest (2014), at critical surface tensions of 20-30 dynes/cm², surfaces are wetted by hydrocarbon oils and are water repellent. At critical surface tensions below 20, hydrocarbon oils no longer spread and the surfaces are both hydrophobic and oleophobic. With a surface tension of 12 dynes/cm² the fluorinated long-chain alkyl silanes and (non-fluorinated) methylated medium chain alkyl silanes are the most oleophobic silane surface treatments (Gelest, 2014). The fluorinated silanes also have the highest contact angle of water on smooth surfaces (indication of hydrophobicity).

B.2.2.1.2 Mixtures of TDFAs and organic solvents

Mixtures containing TDFAs and organic solvents seem to account for a minor part of the total consumption of impregnation sprays.

In general, organic solvent-based impregnating agents are used for non-absorbing surfaces (such as glass, tiles and enamels) whereas the water-based impregnating agents may be used for absorbing surfaces (such as leather and textiles).

Typical organic solvents are volatile petroleum distillates, short chain alcohols, xylene, hexane and heptane. Hydrocarbons (i.e. propane, butane) and sometimes compressed air or CO₂ are used as propellants (FOPH, 2008).

Typical impregnating compounds (active substances) for water-proofing are silicones (i.e. poly-siloxanes), fluorocarbon and melamine resins, beeswax and woolwax (FOPH, 2008).

According to Weissenback et al. (2008), a ready-for-use formulation of polyfluorooctyl triethoxysilane in 2-propanol was created for glass and ceramic applications, especially windshields, facades and shower cabins. The identified commercial products with polyfluorooctyl triethoxysilane are all indicated to be diluted with an appropriate organic solvent and used on surfaces of inorganic substrates. Dynasylan F 8261 from Evonik (2014) is indicated to be used for treatment of automotive glass, coating of float glass, and easy-to-clean coatings on ceramics (besides some uses as intermediates). Other substrates indicated are silica, quartz powder, sand, sandstone, cristobalite, wollastonite, mica, kaolin, talc and other silicate surfaces. The Fluowet ETC 100 and ETC 140 from Clariant are specifically marketed for ceramic tiles in kitchens, glass doors of shower cabins, ceramic sanitary ware, wash basins, bath tubes and enamel. These are all inorganic substrates and the impregnating agents with polyfluorooctyl triethoxysilane and organic solvent are in particular marketed as suitable for non-absorbing substrates such as glass, enamel, and ceramic sanitary ware. The products are marketed for professional use only.

Mixtures containing TDFAs and organic solvents have typically not been used for textiles (predominantly side-chain-fluorinated polymers with a carbon-backbone or other types of fluorine-silane compounds) or for building applications where only hydrophobicity is required (predominantly silanes/siloxane-based mixture or other types of mixtures).

For these purposes water-based products like Dynasylan® F 8815 from Evonik may be used. This product is an example of a fluoroalkylfunctional water-based oligosiloxane, which acts as a surface modification agent on oxidic, carboxy- and hydroxyfunctional substrates, for example ceramic and natural fibres like cotton or leather. The product can be mixed with water to any desired concentration. According to the manufacturer Dynasylan® F 8815 can be used in a great variety of applications. The applications are not further specified. Most likely, the formulations based on the product may be used for various spray applications; including consumer spray applications. In another example Weißenbach et al. (2008) describes the chemistry of various water-based fluoroalkylsilanes based on polyfluorooctyl triethoxysilane. One of the agents is indicated as Protectosil® Antigraffiti, a commercial product marketed by Evonik for professional applications. The product is applied to surfaces of concrete, brick, concrete masonry units and natural stone to allow easy removal of a wide variety of graffiti.

B.2.2.1.3 Mixtures of TDFAs and organic solvents in spray products

The mixtures might be sold in:

- Ready-to-use spray products (aerosol dispensers, pump and trigger sprays etc) or

- cans where the mixture is meant to be applied by alternative application methods as brushes, rollers or cloth².

No information is available on the share of the mixtures sold in the two groups

B.2.2.1.4 Mixtures of TDFAs and organic solvents in spray products for the supply to the general public.

Professionals are expected to be the main group of users of the mixtures. For mixtures in spray products, consumers are expected to account for a higher share of the use than for mixtures in general.

Mixtures based on TDFAs are considered high-end, relatively expensive mixtures for the more demanding applications where both hydrophobicity and oleophobicity is required and the surface is non-absorbing.

The available information indicates that water-based fluoroalkyl oligosiloxanes are used for natural fibres like cotton or leather whereas the organic solvent-based impregnating agents are used for surfaces of inorganic substrates. It cannot be ruled out that some users could use the organic solvent-based agents for textiles and leather but these products are in general not marketed for such applications.

In conclusion, it is estimated that approximately 1 % of the amount of TDFAs, corresponding to 20-200 kg at EU level, indicated as "unknown uses" ends up in ready to use spray products in combination with solvents and sold to the general public. If each spray on average contains 250 ml with a density of 0.79 g/ml (density of 2-propanol) and the average concentration of polyfluorooctyl triethoxysilane is 1.0-1.5%³, the total number of spray products can be estimated to approximately 6 800⁴ – 100 000 units at EU level.

B.2.2.2 The supply chain in general

Apart from the number of manufacturers in the EU (less than 4), the number of downstream users at each step is not known. According to information from manufacturers, the majority of polyfluorooctyl triethoxysilane is used for professional applications and the substances are supplied to large professional users either by the manufacturers of the substances (who also manufacture the final formulations) or by downstream formulators and their agents.

For use in aerosol dispensers, the mixtures are further filled into aerosol containers by aerosol producers. The aerosol producers are either contract producers (private label manufacturing) or they manufacture their own labels. The number of producers of aerosol dispensers with TDFAs is not known, but based on industry information it may likely be in the range of tens to several hundreds.

The number of formulators for the professional and consumer market is not known

One of the producers of end-consumer products contacted states that it is common practice to obtain more or less ready-formulated impregnating agents from large chemical producers. The formulators may then just make some minor modifications to the formulations, e.g. adding some water or other solvent, before filling the formulation in spray products or containers for the consumer.

² It is noted that Consumers themselves might fill the mixtures in spray pumps. However, the supplier may not place the mixtures on the market for such uses.

³ According to a manufacturer the concentration range the products is 0.5-2.0 %. The range average concentration is then considered to be the middle third

⁴ $20/0.79*4/(1.5/100)$: 6751 = rounded 6800

The European Aerosol Federation has stated that TDFAs in aerosol dispensers are not an issue for its members, and this may indicate that the majority of producers of the aerosol dispensers concerned are small companies not organised in the national trade associations. Some of the brands identified in earlier studies and identified by internet searches are small companies specialised in providing impregnating agents (mixtures) or "nanoproducts". Many of the spray products are sold to consumers via internet shops.

B.2.2.2.1 Data from trade organisations on the actual use of the mixtures

According to The European Aerosol Federation (FEA), the organisation does not have any specific information on the use of the concerned substances in aerosol dispensers.

Danish Aerosol Industry Association (AIB) has provided the information that polyfluorooctyl triethoxysilanes are used in some aerosol dispensers with other organic solvents than heptane, butylacetate or ethylacetate. Alternatives used by the members are silanes/siloxanes (without fluorine) or fluorine-based impregnation mixtures (without silane).

B.2.2.2.2 Examples of spray products from the literature with the demonstrated effects

Nørgaard et al. (2010b) tested 10 impregnation spray products ("nanofilm spray products") from three Danish suppliers and found TDFAs with 2-propanol solvent in two spray products for "non-absorbing floor materials" and "rim coating", respectively. Analysis of the content of product for "non-absorbing floor materials" showed that the spray products contained poly-siloxanes (disiloxanes, trisiloxanes and tetrasiloxanes) of polyfluorooctyl triisopropoxysilane (CAS No 246234-80-0, No EC Number). As the polyfluorooctyl triisopropoxysilane is not available from major chemicals suppliers (and not preregistered today) the authors hypothesized that polyfluorooctyl triethoxysilane was used in the production of the spray product and that the ethoxy groups were replaced by isopropoxy groups, since the commercial spray product was dissolved in slightly acidic 2-propanol. The remaining eight spray products were based on alkylsilanes/siloxanes (e.g. hexadecyl trimethoxysilane, EC No 240-465-9) and abrasive/non-ionic tensides.

Other studies of effects of impregnation sprays do not specifically describe spray products with TDFAs.

Danish survey of textile impregnation spray products

A Danish survey of textile impregnation spray products (Feilberg et al, 2008), reviewed product information for 26 impregnation (proofing) spray products on the Danish market for consumer use. Sixteen of the spray products were provided in aerosol spray cans, the latter ten in pump sprays (type not further specified). The active substances were indicated for seven of the products but only at overall type level (fluorocarbon resin, paraffins/wax, silicone, etc.). For none of the spray products it was indicated that they were based on fluorosilane substances. The study thus clearly demonstrates the difficulties in obtaining exact information on the active substances in the spray products.

B.2.2.2.3 Examples of spray products marketed by September 2014

Water and oil-repellent mixtures based on TDFAs are marketed by several of the major manufacturers of chemicals in the EU. The mixtures are marketed for different types of application techniques as described in section C.2.

It has, however, not been possible to identify actual spray products with TDFAs currently marketed, but it seems to be common not to indicate the presence of the active substances of the aerosol dispensers (or pump/trigger sprays) in the SDSs, technical data sheets or on the label. As the parent substances (TDFAs) are typically not classified by the manufacturers (see Table

4) or contained in the mixtures below the general concentration limit, disclosure is not required.

The producer of the TDFAs-containing spray products analysed by Nørgaard et al. (2010b, 2014) informs that polyfluorohexyl triethoxysilane has substituted for polyfluorooctyl triethoxysilane in the impregnation agents of the company. The products are marketed as nanoproducts for paved areas and flooring and are, according to the SDSs, based on fluorosilanes (not further specified) and >20% 2-propanol. The products are supplied as pump sprays and in cans. The mixtures may be supplied to other companies and filled on aerosol containers, but no specific examples have been identified.

A few aerosol dispensers with "nanotechnology" with application areas identical to the TDFAs-containing spray products have been found on the market, but it has not been possible from the suppliers to obtain a confirmation that the mixtures contain TDFAs.

B.2.2.2.4 Notifications to the C&L inventory

The number of notifications to the Classification & Labelling Inventory (C&L) published on ECHA's website may indicate how widespread the use of the substances are (ECHA, 2015b). As indicated in Table 4, polyfluorooctyl triethoxysilane has been notified to the C&L inventory (ECHA, 2015b) by 56 manufacturers and importers whereas the polyfluorooctyl trimethoxysilane has been notified by four notifiers. The notifications do not indicate the application of the substances.

B.2.2.2.5 SPIN data

A search in the SPIN (2014) database with data from the Nordic Product Registers showed that polyfluorooctyl triethoxysilane was registered in Denmark and Sweden in 2012, but the quantities and information on applications are confidential. The only registered non-confidential application is 0.9 tonnes used in nine mixtures for "general repair shops" in Denmark in 2007. The same year the total registered use in Denmark was 3.4 tonnes, but for all other years the quantity is confidential. In the Swedish Product Register the products are registered for "consumer preparations". For other TDFAs, no use in the Nordic Countries is recorded.

B.2.2.2.6 Trend in the use of the substances for the mixtures concerned

Very limited information is available on the use of the targeted mixtures in aerosol dispensers. Most impregnation products described in Nørgaard et al. (2009, 2010a, 2010b, 2014) with the targeted mixtures were delivered in pump sprays. The producers of the products described by Nørgaard et al. inform that the polyfluorosilane mixtures are delivered in pump sprays or in cans for application with a cloth. The overall pattern for all application methods (mainly other than aerosol dispensers), is that the consumption seems to be rather stable.

B.2.2.2.7 Other uses of the substances

Other uses of the substances mentioned in technical data sheets are:

- Intermediates in synthesis of fluorosilicones
- Coating of pigments (e.g. in cosmetics)
- Chemical Vapour Deposition (CVD) processes
- Adhesion promotor between inorganic materials and fluorinated polymers (PFTE, fluorosilicones, etc.)

B.2.3 Uses advised against by the registrants

The substances are not registered.

The MSDS from one manufacturer indicate that for spray application polyfluorooctyl triethoxysilane must not exceed 2% in the product.

B.2.3 Description of targeting

The restriction targets mixtures of TDFAs and organic solvents in spray products (aerosol dispensers, pump and trigger spray) for consumer use.

B.3 Classification and labelling

B.3.1 Classification and labelling in Annex VI of Regulation (EC) No 1272/2008 (CLP Regulation)

The substances are not listed in Annex VI of Regulation (EC) No 1272/2008 (CLP Regulation).

B.3.2 Classification and labelling in classification and labelling inventory/ Industry's self-classification(s) and labelling

The classification and labelling information on notified and registered substances received from manufacturers and importers and reported in Classification & Labelling (C&L) Inventory at ECHA's website is shown in the table below.

About half of the notifiers to the C&L inventory considers the substances to be not classified. The other half classifies the substances as skin irritant and serious eye irritant and possibly respiratory irritant (STOT SE 3; H335).

TABLE 4 SELFCLASSIFICATION OF THE SUBSTANCES ACCORDING TO THE C&L INVENTORY (ECHA, 2015B)

EC No	Name	Hazard Class and Category Code(s)	Hazard Statement Code(s) *	Number of Notifiers
257-473-3	polyfluorooctyl triethoxysilane	Not Classified		30
		Skin Irrit. 2	H315	23
		Eye Irrit. 2	H319	
		STOT SE 3	H335	
		Skin Irrit. 2	H315	3
Eye Irrit. 2	H319			
288-657-1	polyfluorooctyl trimethoxysilane	Not Classified		2
		Skin Irrit. 2	H315	2
		Eye Irrit. 2	H319	
		STOT SE 3	H335	

* H315: Causes skin irritation; H319: Causes serious eye irritation; H335: May cause respiratory irritation.

As the toxicity observed in relation to the impregnation sprays is related to hydrolysates and condensation products of TDFAs and not the parent constituents, classification based on the individual constituents will not reflect the hazard. The Danish EPA has calculated that the product NFP 1 (see B.8.1.2) based on the information on inhalation toxicity in mice provided in Nørgaard et al., (2010a), should be classified as Acute Tox 2, H330 (Fatal if inhaled) (Danish EPA, 2010).

B.4 Environmental fate properties

The targeted substances are highly reactive substances which shortly after application will form polymers, and the releases of the parent substances to the environment is considered negligible.

The environmental issues are related to the possible release of per- or polyfluoroalkyl substances present either as trace content of raw materials and intermediates or released from breaking the bond between the polyfluorinated side-chains and the siloxane backbone. See section B.7.

B.5 Human health hazard assessment

B.5.1 Toxicokinetics (absorption, metabolism, distribution and elimination)

No specific information available for polyfluorooctyl trialkoxysilanes.

B.5.2 Acute toxicity

B.5.2.1 Acute inhalation toxicity - Animal studies

Nørgaard et al. (2010) investigated two types of nanofilm products (NFP 1 and NFP 2) delivered in pump spray bottles. NFP 1 was intended for coating of non-absorbing floor materials and NFP2 for coating of ceramic tiles. NFP 1 contained unspecified fluorosilane and 2-propanol as solvent. NFP 2 contained unspecified alkylsilane and ethanol and methanol as solvents. Mass spectral analysis showed that NFP 1 and NFP 2 contained TDFAs⁵ and 2-propanol (hydrolysates and condensates of polyfluorooctyl triisopropoxysilane) and hexadecyl trimethoxysilane, respectively. The concentration of silanes in NFP 1 and NFP 2 were estimated to $1.1 \pm 0.1\%$ and $1.5 \pm 0.1\%$ silane by weight, respectively. In order to verify the effects observed for NFP 1 and the role of free hydroxyl groups, a synthetic version of NFP 1 was prepared from polyfluorooctyl triethoxysilane with addition of different amounts of water (0.5, 0.75, and 1.0 mol water per hydrolysable group), formic acid and ethanol. The presence of formic acid and the very controlled amounts of water means that polyfluorooctyl monosilanol (synth NFP 1: 0.50 mol), polyfluorooctyl disilanol (synth NFP 1: 0.75 mol) and polyfluorooctyl trisilanol (synth NFP 1: 1.0 mol) are formed.

Particle number size distribution spectra of vehicle controls (peak at ~ 10 nm and ~ 34 nm), NFP 1, (peak at 60.4 nm) NFP 2 (peak at 124 nm), synth NFP 1: 0.75 mol and bis(polyfluorooctyl)tetramethyldisiloxane at an inlet flow of 0.05 ml/min showed that almost all the generated particles can reach the bronchi and bronchioles ($< 10 \mu\text{m}$) and that a large fraction of these also can reach the alveolar region of the lung ($< 4 \mu\text{m}$).

BALB/cJ mice were exposed for 60 min to aerosolised NFP 1, NFP 2, synthetic NFP 1, solutions of polyfluorooctyl triethoxysilane, and bis(polyfluorooctyl)tetramethyldisiloxane in ethanol. 2-propanol and ethanol were used as vehicle controls for NFP 1 and NFP 2 respectively. Exposure to the aerosolised products was measured at $3.3\text{--}60 \text{ mg/m}^3$ ($10^5\text{--}10^6$ fine particles/ cm^3) in the breathing zone of the mice. All test materials were aerosolised by continuous injection of the solutions from a glass syringe to a jet nebulizer by means of an infusion pump followed by homogenous mixing and then direction into a 20 L exposure chamber with an air exchange rate of 1.5 min^{-1} (Nørgaard et al., 2010).

BALB/cA mice were exposed for 60 minutes at concentrations of NFP 1 ranging from 3.3 to 42.4 mg/m^3 and of NFP 2 from 33.2 to 60 mg/m^3 , followed by a 30 minute recovery period in clean laboratory air. Exposure to NFP 1 resulted in a significant concentration-dependent de-

⁵ In the articles by Nørgaard et. al. TDFAs are abbreviated POTS (1H,1H,2H,2H-Perfluorooctyl trialkoxysilanes)

crease of the tidal volume (VT: the volume of inhaled or exhaled air in a single breath during regular breathing) which was still significantly suppressed in the 18.4 mg/m³ group one day after exposure. Several mice in the 24.4 and 42.4 mg/m³ groups were euthanized in a moribund state few hours after exposure and respiratory data are therefore not available one day after exposure. Effects on VT after exposure to vehicle control (2-propanol) were weak and reversible.

Exposure to the highest concentration of NFP 2 (60 mg/m³) resulted in effects on VT which were significantly different from the vehicle control (ethanol), but relatively weak and reversible. Little or no effects on pulmonary function were observed following exposure to the non-hydrolysed polyfluorooctyl triethoxysilane and bis(polyfluorooctyl)tetramethyldisiloxane in ethanol. Reduction in VT did, only to a limited extent, differ from the 95 % confidence interval for the solvent (ethanol) control group. Exposure to the synthetic NFP 1 with 0.5, 0.75, and 1.0 mol of added water per hydrolysable group showed a gradual decrease in VT. Exposure to synth NFP 1: 0.5 mol resulted in a ~40% reduction in VT, whereas synth NFP 1: 0.75 mol resulted in a reduction of VT by ~55%. For both synth NFP 1: 0.5 mol and synth NFP 1: 0.75 mol, the effect on VT was partly reversible. Exposure to synth NFP 1: 1.0 mol resulted in a significant depression in the VT almost immediately after the onset of exposure. The exposure was discontinued for ethical reasons after 30 minutes as the exposed mice were severely affected (Nørgaard et al., 2010).

Bronchoalveolar lavage fluid (BALF) cytology, protein in BALF, and histology were studied in order to assess lung inflammation and lung damage caused by the exposure. Exposure to NFP 1 concentrations from 18.4 mg/m³ (2.3×10^6 fine particles/cm³) gave rise to significant increases of protein level in BALF and reduced body weight, and histological examination showed atelectasis (collapsed alveoli), emphysema, and hemorrhages in the alveoli and bronchioles. No significant increase in macrophages were observed in the lowest exposure group. The results showed that there was a narrow interval between the no-effect level (16.1 mg/m³) and the lethal concentrations (18.4 mg/m³). NFP 2 had no effect on BAL cell numbers at the concentrations studied. Exposure to non-hydrolysed polyfluorooctyl triethoxysilane in ethanol caused an increase in the number of lymphocytes and exposure to synthesised NFP 1 (at 0.75 and 1.0 mol water) induced increased number of neutrophils, lymphocytes, and macrophages. No effects were observed after exposure to bis(polyfluorooctyl)tetramethyldisiloxane in ethanol. Concentration-dependent decreases in body weights were observed following exposure to NFP 1 and significant increases following exposure to synthesised NFP 1 (at 0.75 and 1.0 mol water) but no changes from exposure to NFP 2. With regard to morphological changes of lung tissue, the most extensive damage was observed following exposure to NFP 1 where particles from inhaled NFP 1 were observed in the lumen of the alveoli or taken up in alveolar or interstitial macrophages (Nørgaard et al. 2010).

In conclusion, when aerosolised the particle size distribution shows that all the tested substances has a large fraction that can end up in the bronchioles and alveoli. Effects on VT in mice after exposure to non-hydrolysed polyfluorooctyl triethoxysilane in ethanol, bis(polyfluorooctyl)tetramethyl-disiloxane in ethanol and to vehicle control (ethanol and 2-propanol) were weak and reversible. At the concentrations tested NFP 2 resulted in effects that were relatively weak and reversible.

Exposure to NFP 1 resulted in significant decrease of VT, significant increases of protein level in BALF, atelectasis, emphysema, hemorrhages in the alveoli and bronchioles and death from 18.4 mg/m³. Exposure to the synthetic NFP 1 showed that these toxic effects were not ascribed to polyfluorination alone, but that also the number of free hydroxyl groups (i.e. degree of hydrolysis/condensation) is critical for the toxicity.

Nørgaard et al. (2014) investigated the solvent dependency of pulmonary toxicity of nanofilm spray products (NFPs) based on hydrolysates and condensates of polyfluorooctyl triethoxysilane (TDFAs). Seven commercially available water-based NFPs based on hydrolysates and condensates of TDFAs were included in the study representing both products to be applied on hard and absorbing surfaces. The study also included solutions of hydrolysed TDFAs prepared in methanol, ethanol and 2-propanol, respectively. All test materials (water-based NFPs, water-based NFP concentrate, TDFAs solutions and solvent control (methanol)) were aerosolised

at a flow rate of 0.4–0.6 ml/min by infusion from a glass syringe into a jet nebulizer by means of an infusion pump, mixed and then directed into a 20 L exposure chamber with an approximate air exchange rate of min^{-1} .

BALB/cA mice were exposed head only for 60 minutes followed by a 15 minutes recovery period in laboratory air. To further study the effects of organic solvents mice were exposed to hydrolysed TDFAs in methanol admixed with vaporised methanol, 2-propanol and acetone, respectively. Methanol admixed with vaporised 2-propanol were used as solvent control. Admixture of vaporised methanol, 2-propanol or acetone imitates the effect of aerosol propellant (personal communication with author). Respiratory parameters were collected and inhibition of the pulmonary surfactant was investigated *in vitro* by incubation of lung surfactant (Alveofact) with solvent alone (2-propanol) and hydrolysed TDFAs in 2-propanol with added methanol, ethanol, and 2-propanol (equal volumes of TDFAs solution and solvent), respectively.

Particle number size distribution spectra were presented for two of the commercially available water-based NFPs. They show that the generated particles can reach the bronchi and bronchioles ($< 10 \mu\text{m}$) and that a large fraction of these also can reach the alveolar region of the lung ($< 4 \mu\text{m}$). The particle size distributions spectra of hydrolysed TDFAs in organic solvents showed that these particles can also reach both the bronchioles and alveolar region. The spectra also shows that particle size were unaltered in different organic solvents and addition of vaporised solvent did not change distribution of particles. Particle size were therefore ruled out as responsible for the mechanism behind the toxicity.

Reductions in VT of 40-60 % were observed in mice exposed to the 3 alcohol solutions (methanol, ethanol, and 2-propanol) of hydrolysed TDFAs and it appeared that the increase in chain length of the alcohols increased the initial rate of reduction in tidal volume. No effect on VT were seen by the water-based commercially available NFPs. Incubation of lung surfactant (Alveofact) with water or organic solvent alone did not inhibit the surfactant whereas hydrolysed TDFAs in methanol, ethanol and 2-propanol, respectively, increased inhibition of the surfactant with increasing chain length of the alcohols. Addition of vaporised methanol, 2-propanol and acetone, respectively, to hydrolysed TDFAs in methanol significantly decreased the time to reach a 25% reduction in VT when compared with hydrolysed TDFAs in methanol only. Effect on VT from the vaporised non-alcohol solvent, acetone, were almost identical to the effects on VT from the vaporised 2-propanol. Mice exposed to solvents alone (methanol admixed with vaporised 2-propanol) only showed transient reduction in VT, indicating that the observed toxicity is not attributed to solvents per se.

Based on the observed lower airway irritation (time of pause, TP, elongation) which developed at the end of the study after exposure to hydrolysed TDFAs and 2-propanol Nørgaard et al., 2014 concluded that the effect did not correlate with the reduction in VT and the mechanism behind TP elongation was ruled out as the cause of VT reduction.

In conclusion, when aerosolised the particle size distribution shows that both water-based and solvent-based mixtures containing hydrolysed TDFAs generates a large fraction of particles that can end up in the bronchioles and alveoli. However, only the mixtures containing hydrolysates and condensates of TDFAs in organic solvent had an effect on VT. The effect increased with increasing carbon chain length of the solvent and the *in vitro* experiments demonstrated that the carbon chain length/lipophilicity of the solvent determined the toxicity of hydrolysates and condensates of TDFAs on the surfactant function. The authors, therefore, speculate that the solubility of hydrolysates and condensates of TDFAs in the lung lining fluid increases with the quantity and lipophilicity of the solvent, and thereby facilitates contact between hydrolysates and/or condensates of TDFAs and lung surfactant components. Addition of vaporised acetone to hydrolysed TDFAs in methanol showed that other organic solvents than alcohols can affect the toxicity. Based on the study results, the authors conclude that respiratory toxicity of an impregnation spray product does not only depend on the toxicity of the active agents but also on the amount and properties of the solvents used, and they further suggest that water as a solvent may reduce the toxicity of an impregnation product (Nørgaard et al., 2014).

Sørli et al. (2015) studied whether disruption of the pulmonary surfactant film can be used as a predictor of the toxic effects *in vivo*. Nine impregnation products (including NFP 1, tested in

Nørgaard et al. 2009, 2010 and 2014) with various chemical compositions were selected for testing and the main constituents of each product, e.g., solvents, co-solvents and film-forming compounds, were identified by mass spectrometry. A capillary surfactometry method was used to assess disruption of pulmonary surfactant function *in vitro* and the same mouse model as in Nørgaard et al. (2010a) was used to evaluate acute respiratory toxicity during inhalation. Concentration-response relationships were successfully determined both *in vitro* and *in vivo*. The true positive rate of the *in vitro* method was 100%, i.e., the test could correctly identify all products with toxic effects *in vivo*, the true negative rate was 40%.

Two of the impregnation products, NFP 1 and Rim sealer, contained mixtures of TDFAs and organic solvents. NFP 1 is as described based on TDFAs and 2-propanol whereas Rim sealer is based on TDFAs and a mixture of 2-propanol, 1-methoxy-2-propanol and ethylacrylate. Dry weight concentration of the reaction product (hydrolysates and condensates of polyfluorooctyl alkoxysilanes) in Rim sealer is found to be approximately 27 times smaller than the concentration in NFP 1 (personal communication with author). Based on reduction in VT, wet weight LOAEC for Rim sealer were found to 591 mg/m³. This is approximately 6 times below the wet weight LOAEC for NFP 1 that were found to 3380 mg/m³ (18.4 mg/m³ dry weight) which indicates that Rim sealer are more potent than NFP 1. This change in potency seems to be due to the change in organic solvent. However, Rim sealer has not been investigated as thoroughly as NFP 1 and it cannot be ruled out that Rim sealer contains other substances that contributes to the reduction in VT.

The two products Footware protector and Wood impregnation, contained a mixture of a 8:2 polyfluoracrylate co-polymer, water and glycolethers (personal communication with author). Dry weight concentration of the two products Footware protector and Wood impregnation were 6.3 % and 5.7 % respectively. Based on reduction in VT, wet weight LOAEC for Footware protector and Wood impregnation were found to 103 mg/m³ and 114 mg/m³ respectively. It should be underlined that Footware protector and Wood impregnation has not been investigated as thoroughly as NFP 1.

In conclusion change in organic solvent seems to have made Rim sealer more toxic than NFP 1. At the same time the *in vivo* study showed that a 8:2 polyfluoracrylate in (non-alcohol) organic solvent seemed to have the same pulmonary effect on mice as TDFAs in organic solvent.

As a consequence of what was referred to as "the Magic Nano" conundrum, Pauluhn et al. (2008) performed a comparative assessment in Wistar rats of the acute inhalation toxicity of two aerosol spray products, "Magic Nano Glass & Ceramics" and "Magic Nano Bath & WC" and with a pump spray product, "Magic Nano Bath & WC". The background was a series of severe incidents of pulmonary health impairment observed in Germany in 2006 after normal use of the two aerosol spray products, whereas the use of the previously marketed "Magic Nano Bath & WC" pump spray did not result in the same effects. Symptoms caused by the aerosol spray exposure included strong cough, dyspnoea, and in 13 severe cases also lung oedema (Appendix 1, Table 1 - 2). The study investigated the acute inhalation toxicity, the usefulness of lung function measurements and bronchoalveolar lavage for characterisation of the relationship of functional indicators and lung injury, and to analyse if the findings in consumers could be duplicated in rat studies carried out according to OECD Guideline 403 and GLP. Tests were performed on the products which had been on sale and with a silane content of less than 1 % according to product distributor. The "Magic Nano Glass & Ceramics" spray was specified to contain a corrosion inhibitor. The aerosol sprays were tested in their commercialised technical configuration and the pump spray was nebulized using conditioned, pressurised air (15 L/min; dispersion pressure approximately 400 kPa) into the inhalation chamber. Nominal concentrations were calculated for both spray types, as the calculated actual concentrations could not meet the prerequisites required by the OECD guideline. Particle size analyses were based on sample collections from the breathing zone of animals'.

Results showed that the particle size distributions in the breathing zone samples were in the moderately to low respirable size range. Mortality in rats exposed to a single nose-only exposure occurred within 2 hours after onset of exposure up to the fourth postexposure day in all groups exposed to the "Magic Nano Glass & Ceramic Spray". At the lowest dose tested 2 269

mg/m³ 1/10 rats died. The 4-hour standard LC₅₀ was calculated to 5 098 mg/m³. No mortalities were observed with the aerosol spray "Magic Nano Bath & WC" at the highest dose tested 28 100 mg/m³. One rat exposed to the pump spray at the highest dose tested 81 222 mg/m³ was killed in a moribund state on postexposure day 4. Male rats appeared to be more susceptible than female rats. Clinical findings in rats exposed to the "Magic Nano Glass & Ceramic" and pump sprays included bradypnea, tachypnea, laboured and irregular breathing patterns, red nostrils, and serous nasal discharge, cyanosis, piloerection, reduced motility, flaccidity, uncoordinated gait, and prostration. Reflexes (grip strength, tonus, startle reflex, and righting response) were reduced or impaired. Body weights and rectal temperatures were significantly decreased following exposure to the aerosol spray "Magic Nano Glass & Ceramic" and to the pump spray. Neurobehavioral changes were noticeable particularly in the pump spray group. All signs waned within the first half of the first postexposure week. No effects were observed in rats exposed to the aerosol spray "Magic Nano Bath & WC". Analysis on the first postexposure day demonstrated increased lung weights and inflammatory endpoints (LDH, protein, γ -glutamyl-transaminase, and neutrophilic granulocytes) in bronchoalveolar lavage (BAL) in the Magic Nano Glass & Ceramic spray groups. No changes in total cell counts were observed. A similar but less pronounced pattern was observed in rats exposed to the "Magic Nano Bath & WC" pump spray. No toxicologically significant changes occurred in rats exposed to the aerosol spray "Magic Nano Bath & WC". Changes in breathing pattern were observed in rats exposed to the aerosol spray "Magic Nano Glass & Ceramic" and to the pump spray. The authors noted that pump spray atmospheres appear to trigger marked "upper respiratory tract sensory irritation," although some "lower respiratory tract sensory irritation" cannot be ruled out (Pauluhn et al, 2008).

Overall, the authors conclude that assessment of acute inhalation toxicity of complex end-use products is challenging and that it is not sufficient to rely on data for individual components only. The study does not identify the causative agents resulting in the observed toxicity but speculate whether the mechanism of toxicity is mediated through phagocytosis of inhaled material or dysfunctional lung surfactant. With regard to analytical characterisation of exposure atmospheres, the authors conclude that proper characterisation of these complex vapour and aerosol phase products where all constituents are not known was not possible (Pauluhn et al., 2008).

As a follow up study of "the Magic Nano" conundrum, Koch et al., 2009 investigated the physical-chemical properties of the "Magic Nano" spray products. This included a chemical analysis of the products and a characterisation and assessment of the possible exposure during application of the products.

According to the product distributor the formulation of the aerosol spray products "Magic Nano Glass & Ceramic" and "Magic Nano Bath & WC" were: dimethyl ether (52.3 %), ethanol (26.2 %), water (18-20 %), 2-butanon (< 0.5 %), hydrochloric acid (< 0.3 %), silane (0.46 - 2.3 %) and corrosion inhibitor (0.83 %). The formulations of "Magic Nano Bath & WC" pump spray were: ethanol (57.5 %), water (37 - 42 %), 2-butanon (< 1 %), hydrochloric acid (< 1.25 %) and silane (1 - 5 %). In neither of the cases the precise details of the functional silane were provided by the distributor/manufacturer. The aerosol products, as well as the pump spray, "Magic Nano bath & WC" were studied by electron microscope and X-ray spectroscopy.

Exposure to the non-volatile components of the spray products were determined by spraying and measuring parallel in a model room with a volume of 60 m³. The time-averaged concentration were determined gravimetrically after collection on filters. The release of the content of the aerosol dispensers were carried out over 5 minutes. The sampling equipment were operated for 60 minutes to obtain sufficient material on the filters.

X-ray emission spectrum of samples of the aerosol spray products "Magic Nano Glass & Ceramic" and "Magic Nano Bath & WC" showed that the both products contained Sodium and Phosphorus belonging to the corrosion inhibitor. Besides that both formulations showed pronounced peaks of Silicon and Fluorine. The pump spray "Magic Nano bath & WC" also showed peaks belonging Silicon and Fluorine whereas no peaks were seen from elements belonging to the corrosion inhibitor. This is in line with the information given by the distributor that the two aerosol sprays contained corrosion inhibitor whereas the pump spray formulation did not. In

Pauluhn et al., 2008 only the aerosol spray "Magic Nano Glass & Ceramic" was specified to contain a corrosion inhibitor. Based on the use of the three products for hard non-absorbing substrate surfaces, the pronounced peaks of Silicon and Fluorine in the X-ray emission spectra and the fact that Silicon were always displayed in conjunction with Fluorine electron microscopic analysis, the author's finds it likely that the active substance referred to as silane by the product distributor are in fact a fluorosilane.

Release of one can (approximately 120 g) of the aerosol spray "Magic Nano Glass & Ceramic" in a model room with a volume of 60 m³ resulted in a exposure concentration of non-volatile components (corrosion inhibitor and hydrolysates and condensates of (fluoro)silane) in the inhalable fraction (< 100 µm) of 41.5 mg/m³. Of these approximately 11.5 mg/m³ were able to reach the bronchioles and/or alveoli (< 10 µm). Under the same test conditions (release of approximately 80 g) the exposure concentration of non-volatile components (corrosion inhibitor and hydrolysates and condensates of (fluoro)silane) of the aerosol spray "Magic Nano Bath & WC" were 9 mg/m³ in the inhalable fraction of which approximately 5 mg/m³ were able to reach the bronchioles and/or alveoli. For the pump spray "Magic Nano bath & WC" the inhalable fraction of non-volatile components (hydrolysates and condensates of (fluoro)silane) were found to 0.67 mg/m³. Of these 0.27 mg/m³ were able to reach the bronchioles and/or alveoli. From quantification of non-volatile components by filter sampling it was found that the content of the aerosol sprays were between 1 and 3 %, and that it were 0.2 % for the pump spray. By comparing with the distributor formulation and taking in to account that the aerosols "Magic Nano Glass & Ceramic" and "Magic Nano Bath & WC" contains 0.86 % corrosion inhibitor, it can be speculated that the content of hydrolysates and condensates of the parent (fluoro)silane is approximately 2 % and 0.5 % for "Magic Nano Glass & Ceramic" and "Magic Nano Bath & WC", respectively.

The authors speculated that the inconsistency for the pump spray between the mass fractions of (fluoro)silane compounds specified by distributor (1-5 %) and the mass fraction measured on filter samples (0.2 %) were due to vaporisation of the (fluoro)silanes (Koch et al., 2009).

When the formulation contains non-volatile compound like the corrosion inhibitor there is enough aerosol surface area available the (fluoro)silane molecules can bind to. This is the case for the aerosols "Magic Nano Glass & Ceramic" and "Magic Nano Bath & WC", and therefore a relative high amount of hydrolysates and condensates of (fluoro)silane is found in the filter samples. For the pump spray (no corrosion inhibitor) this surface area is not available and the aerosolized (fluoro)silane evaporates and is only found in small amounts in the filter samples (personal communication with author).

For the aerosol "Magic Nano Glass & Ceramic" approximately 0.2 % of the total released mass (including propellant) were non-volatile respirable aerosol. This means that the nominal concentration of the LOAEL of 2 269 mg/m³ and the LC₅₀ of 5 089 mg/m³ (Pauluhn et al. 2008) of total spray compound corresponds to approximately 4.5 mg/m³ and 10 mg/m³ non-volatiles in the respirable size range, respectively. For the aerosol "Magic Nano bath & WC" approximately 0.007 % of the total released mass (including propellant) that were non-volatile respirable aerosol. This means that the nominal concentration of the NOAEL of 28 100 mg/m³ (Pauluhn et al. 2008) of total spray compound corresponds to approximately 2 mg/m³ non-volatiles in the respirable size range (personal communication with author). This may explain why no toxicologically significant changes occurred in rats exposed to the aerosol spray "Magic Nano Bath & WC".

The relationship between total released mass and non-volatile respirable aerosols are not available for the pump spray "Magic Nano bath & WC".

In conclusion, the active substance in the three "Magic Nano" product is likely to be a fluorosilane. The length of the polyfluoroalkyl chain is unknown but it is possible that the substance belongs to the group of TDFAs.

The dry weight LOAEL and LC₅₀ of "Magic Nano Glass & Ceramic" were estimated to 4.5 mg/m³ and 10 mg/m³, respectively. This estimate is based on the measured non-volatile aerosols in the respirable range. Besides hydrolysates and condensates of (fluoro)silane these non-volatiles also contain corrosion inhibitor which could have an effect on both toxicity and spray pattern of the product since the hydrolysates and condensates can bond to the corrosion inhibitor. Besides the difference in solvent this may explain the difference in spray pattern (amount

of particles with size < 10 µm) when comparing particle size distribution of the aerosols "Magic Nano Glass & Ceramic" and "Magic Nano bath & WC" with the product NFP 1 studied by Nørgaard et al.

Human incidents were reported for the aerosol "Magic Nano Bath & WC" even though no toxicologically significant changes occurred in rats exposed to the aerosol spray at the highest dose tested 28 100 mg/m³ (2 mg/m³ dry weight).

No human incidents were reported for the pump spray "Magic Nano Bath & WC". Toxicologically changes only occurred in rats exposed to the highest dose tested 81 222 mg/m³.

Based on the fractions able to reach the alveoli Koch et al. (2009) estimated that risk of exposure to respirable aerosol are approximately 20-fold lower for the pump spray "Magic Nano bath & WC" than for the aerosol "Magic Nano Glass & Ceramic". Taking in to account the fraction that can also reach the bronchioles (< 10 µm) this number should be adjusted to 20-45 times lower.

In Duch et al. (2014) the toxicological effects of the tile coating product, Stain Repellent Super (SRS), were studied. SRS were reported to cause respiratory and systemic symptoms in 39 persons in Greenland in 2010 (Appendix 1, Table 1 - 2). The product was analysed chemically, and the toxicological properties of the product were studied *in vitro* by surfactometry and *in vivo* in a mouse inhalation model.

Chemical analysis by mass spectrometry revealed that SRS contained the non-fluorinated alkylsilane isooctyl trimethoxysilane and an unknown non-fluorinated alkylsilane as active substances and C₉-C₁₃ (hydrogenated naphta) as solvent.

Using a nose-only inhalation chamber BALB/cA male mice (10/group) were exposed to an aerosol of SRS until effects on the respiratory parameters were observed (10–60 min). Prior to exposure, a 15-min baseline period was recorded for each mouse. To assess exposure-related effects, the respiratory parameters during exposure were compared to baseline levels, that is, each mouse served as its own control. To study how SRS may interfere with pulmonary surfactant components *in vitro*, a Langmuir technique was applied and HL10, extracted from pig lungs, was used as model of pulmonary surfactant. With this technique the dynamic properties of a film surfactant-SRS complex were studied by repeatedly expanding and compressing the film while measuring the surface pressure. As a reference a mixture of surfactant and solvent (n-decane) were used.

Results of mouse inhalation model were that no effect was seen on VT after 60 min of exposure to 59 mg/m³, a 35% reduction was observed after exposure to 76 mg/m³ for 60 min and a 50% reduction was seen after a 30-min exposure to 103 mg/m³. The reduction in VT was associated with a reduction in expiratory flow rate and with an increase in the respiratory frequency.

Results of the *in vitro* test showed that addition of SRS to the HL10 surfactant film to form a surfactant-SRS complex significantly inhibited the pulmonary surfactant function (Duch et al., 2014).

In conclusion, a steep concentration–effect curve with respect to VT and expiratory flow rate of the SRS product was observed. Thus, 30 min of exposure to 76 mg/m³ (LOAEL) gave rise to a 35% reduction in VT, whereas no effect was observed on this breathing parameter after 60 min of exposure to 59 mg/m³ (NOAEL). This suggests that the *dose rate* rather than the *total inhaled dose* of substance is critical for the toxic effect. *In vitro test* with HL10 pulmonary surfactant showed that SRS could significantly inhibited the surfactant function. The authors speculate that, upon inhalation, the SRS product may react with components in the pulmonary surfactants leading to inactivation of these. It could be speculated that the higher dose rate exceeds the production of new surfactant components which therefore gives rise to toxic effects (Duch et al., 2014).

Because of the similarities in respiratory effect, it is likely that the SRS product may possess similar mode of action as the nanofilm product albeit different chemical compositions, that is fluorinated silanes in 2-propanol (NFP 1, Nørgaard et al., 2010a and 2014) and alkylsiloxanes in naphtha for the nanofilm product and SRS product, respectively (Duch et al., 2014).

The lowest dose tested in the mouse inhalation study for SRS (Duch et al., 2014) 59 mg/m³ is approximately the same as the highest dose tested for the product called NFP 2 in Nørgaard et al. 2010a. Even though NFP 2 contained a mixture of another alkylsilane and another solvent than SRS it can be speculated if effects on VT from NFP 2 would have been more pronounced if tested at a higher exposure concentration.

B.5.2.1.1 Mechanism

As hydrolysed TDFAs in methanol, ethanol and 2-propanol, respectively, increased inhibition of the pulmonary surfactant with increasing chain length of the solvents, Nørgaard et al. (2014). Larsen et al. (2014) have investigated the mechanism behind this effect. Pulmonary surfactant is a fluid film covering the inside of the terminal bronchioles and the alveoli. Pulmonary surfactant is composed of phospholipids (90%) and surfactant proteins (SP)-A, -B, -C and -D (10%). The surfactant proteins are embedded in the phospholipids. The function of the surfactant is to decrease surface tension, thus reducing the effort needed to inflate the lung during inspiration. Surfactant function in the terminal bronchioles is vital. If the surfactant is damaged, inactive surfactant liquid will flow into the narrow section of the bronchiole and form liquid plugs, causing reduced lung compliance and labored breathing (Sørli et al., 2015). SP-A and SP-D are not considered to be involved in the reduction of the surface tension (Lopez-Rodriguez and Perez-Gil, 2014).

In Larsen et al. (2014) the toxicological effects and the underlying mechanism of action of lung damage caused by the nanofilm spray product NFP 1 (studied in Nørgaard et al., 2010a) in a mouse inhalation model with BALB/cA male mice were investigated. NFP 1 was intended for application on non-absorbing flooring materials and contained TDFAs and 2-propanol (hydrolyses and condensates of polyfluorooctyl triisopropoxysilane). The toxicological effects and their underlying mechanisms of this product were studied using a mouse inhalation model, by *in vitro* techniques and by identification of the binding interaction.

In the mouse inhalation model NFP 1 was aerosolised and supplied into the 20 L exposure chamber with a flow rate of 20 L/min through the chamber resulting in an air exchange rate of ~1 min⁻¹. Mice were exposed for 60 minutes to 18.4 mg/m³ NFP 1 or an equivalent concentration of 2-propanol (vehicle control group) followed by a 30 minute recovery period. The exposure concentration was the Lowest-Observed-effect-Level found by Nørgaard et al. (2010a). Respiratory parameters were measured during exposure and recovery. Results of the mouse inhalation model with NFP 1 demonstrated a reduction in expiratory flow rate indicating an increased airway resistance. A statistically significant reduction was reached after 10 minutes of exposure. The flow rate did not return to normal during the 30 minute post-exposure recovery period, where the animals were exposed to clean air. A reduction in the expiratory flow rate may be due to bronchoconstriction. Narrowing of the bronchi gives rise to an increased resistance that reduces the expiratory flow. Also, inhibition of the pulmonary surfactant system will lead to increased airway resistance, which may reduce the expiratory flow, Larsen et al. (2014).

NFP 1 was tested *in vitro* in a capillary surfactometer with exogenous pulmonary surfactant preparation, HL10, extracted from pig lungs, containing phospholipids, SP-B, SP-C and cholesterol. *In vitro*, the percent of time with an open passage (low resistance) through the capillary during the 2-min sample period may be used to quantify the pulmonary surfactant function when NFP1 or 2-propanol (vehicle control) is added. Results of the capillary surfactometer test showed that the solvent itself had a minor inhibitory effect of the surfactant function. Replacing a part of the 2-propanol with NFP 1 gave rise to a concentration-dependent decrease in time open, clearly showing an inhibitory effect of NFP 1 on the surfactant. The physiological

consequences of this inhibition have been shown to be liquid blocking of the terminal airways, leading to increased airway resistance, Larsen et al. (2014).

To study how NFP 1 (hydrolysates and condensates of TDFAs) may interfere with pulmonary surfactant components, including SP-B and SP-C, a Langmuir technique was applied and HL10 was used as model of pulmonary surfactant. With this technique the dynamic properties of a film of surfactant, surfactant-NFP 1 complex and surfactant-NFP 1 complex with SP-B and/or SP-C were studied by repeatedly expanding and compressing the film while measuring the surface pressure. Results showed that addition of NFP 1 to the HL10 surfactant film to form a surfactant-NFP 1 complex dramatically changed the shape of the pressure area isotherm. This suggested a reduced mechanical strength of the HL10 surfactant film. By adding synthetic SP-B peptide (SP-B₁₋₂₅), mimicking the natural SP-B, the impaired film could partly be restored. In contrast, addition of SP-C peptide (SP-C₃₃), a model peptide of the natural SP-C, did only change the initial part of the pressure area isotherm, whereas no effect was seen at higher compression state compared with the surfactant-NFP 1 complex isotherm. This suggests that SP-C₃₃ only to a minor degree affected the surfactant properties of the impaired HL10 film.

The interaction between SP-B and NFP 1 observed *in vitro* was confirmed in a Histology examination. Lungs from mice exposed to NFP 1 and solvent control respectively were fixated in formalin immediately after end of the inhalation study, and tissue sections were stained with SP-B-specific antibodies. In lungs of mice only exposed to 2-propanol the presence of native SP-B was apparent, whereas no SP-B could be detected in the lungs of NFP 1 exposed mice. This suggests that the hydrolysates and/or condensates of TDFAs can physically or chemically modify one or more epitopes on SP-B essential for binding to the SP-B-specific antibodies. The SP-B depletion was most prominent in the bronchioles.

The physico-chemical consequences of the interaction between NFP 1 and the SP-B₁₋₂₅ peptide were studied using water in chloroform two-phase system. This system has an interface that to some degree models the water/air interface of the lung. Whereas SP-B₁₋₂₅ in absence of NFP 1 was located exclusively at the interface, addition of NFP 1 led to distribution of SP-B₁₋₂₅ into the organic phase, i.e., SP-B₁₋₂₅ is removed from its site of action.

The interaction of SP-B₁₋₂₅ and NFP 1 (hydrolysates and condensates of TDFAs) were studied by mass spectrometry. Complexes of SP-B₁₋₂₅ and the condensates tetra-, tri-, di- and mono-hydrolyzed tetrasiloxanes of polyfluorooctyl triisopropylsilane were identified. From the mass of these complexes it can be concluded that the tetrasiloxanes do not bond covalently to SP-B₁₋₂₅. A covalent binding of the siloxanes to SP-B₁₋₂₅ would imply a condensation reaction, which would lead to complexes with a lower molecular mass than those observed in the experiment (Larsen et al., 2014).

In conclusion, the investigation of the pulmonary surfactant demonstrated a clear inhibition of the surfactant which has been shown to result in liquid blocking the terminal airways and leading to increased airway resistance. The authors compare this condition with effects seen in humans suffering from acute respiratory distress syndrome which is related to the pulmonary surfactant function. Chemical analysis showed a non-covalent interaction between condensates of hydrolysed TDFAs and the peptide SP-B₁₋₂₅, forming stable complexes and thereby inactivating the pulmonary surfactant protein, SP-B.

Larsen et al. (2014) refer to speculations that polyfluorosilanols with their hydrophobic polyfluoroalkyl chain in combination with hydrophilic silanol groups in some way can mimic the structure of the phospholipids and facilitate both hydrophobic and hydrophilic interactions with proteins, as it has previously been shown for per- and polyfluoroalkyl substances. They have studied the physico-chemical consequences of the interaction between the NFP 1 (hydrolysates and condensates of TDFAs) and the SP-B₁₋₂₅ peptide in a system with an interface that to some degree models the water/air interface of the lung. It was shown that addition of NFP 1 to this system with SP-B₁₋₂₅ caused the peptide to be removed from its site of action and to be distributed into the organic phase. The authors also highlight that binding or adsorption of hy-

drolysates and condensates of TDFAs to the SP-B₁₋₂₅ peptide may hinder proper functioning of the peptide by the steric blocking of active sites of the molecule.

Inhibition of SP-B and SP-C which are small hydrophobic proteins embedded in the phospholipid layer requires that the inhibiting chemical can penetrate into the phospholipid layer. This is only possible for solvents with a certain degree of lipophilicity. The authors conclude that this phenomenon may be an explanation of why toxicity of a waterproofing substance increased with increasing lipophilicity of the solvent (Larsen et al. 2014, Nørgaard et al. 2014).

The authors also emphasize that the toxicity of the products depends both on the active coating substance and the solvents used and that minor changes in either of these components may have significant impact on the toxicity of the whole product (Larsen et al., 2014).

It is not clear to what extent the pulmonary toxicity of the hydrolysed compounds is affected by the length of the polyfluoroalkyl chain of the polyfluoroalkyl trialkoxysilanes.

B.5.2.1.2 Summary of effects seen in animal studies

Larsen et al. (2014) showed that hydrolysates and condensates of TDFAs can inactivate the pulmonary surfactant protein, SP-B, if the hydrolysates and condensates can get in to contact with the protein. The study also showed that the SP-B depletion was most prominent in the bronchioles. Particle number size distribution spectra of all the aerosolised substances tested in Nørgaard et al. (2010a and 2014) i.e. solvents, NFP 1, NFP 2, synthetic NFP 1 (hydrolysates and condensates of polyfluorooctyl triisopropoxysilane), commercial water-based products containing TDFAs, polyfluorooctyl triethoxysilane and bis(polyfluorooctyl)tetramethyldisiloxane showed that almost all the generated particles can reach the bronchi and bronchioles (< 10 µm) and that a large fraction of these also can reach the alveolar region of the lung (< 4 µm). Koch et al. (2009) showed that for the two aerosol products "Magic Nano Glass & Ceramic" and "Magic Nano Bath & WC" there were also a large fraction of the inhalable particles generated that were able to reach the bronchioles and/or alveoli.

The SP-B protein is embedded in phospholipids layer in the pulmonary surfactant and it therefore requires that the inhibiting substance can penetrate into the phospholipid layer. This requires the presence of an organic substance. For this reason no effects are seen on the tidal volume (VT) from the commercial water-based products containing hydrolysates and condensates of TDFAs when tested in a mouse inhalation model, despite that they can reach the bronchioles and/or alveoli when aerosolised (Nørgaard et al., 2014).

In a mouse inhalation model Nørgaard et al. (2014) showed that the effect on VT increased with increasing carbon chain length/lipophilicity of the alcoholic solvents methanol, ethanol and 2-propanol when mixed with hydrolysed TDFAs. However, this is not only true for alcoholic solvents, since addition of vaporised acetone to hydrolysed TDFAs in methanol increased the VT (Nørgaard et al., 2014). This is also indicated by the human incidents with impregnation products containing mixtures of non-alcoholic organic substances (in many cases paraffinic hydrocarbons) and fluorinated substances (in many cases fluoroacrylates) presented in Appendix 1, Table 1 - 2.

The fact that addition of vaporised methanol, 2-propanol or acetone to hydrolysed TDFAs in methanol increases the VT (Nørgaard et al., 2014) shows that it is relevant to take organic solvent aerosol propellants in to account when hydrolysed TDFAs is applied by an aerosol dispenser. Methanol, 2-propanol and acetone are not used as aerosol propellants but the lipophilicity (logKow) of dimethyl ether (DME), that can be used as propellant in aqueous aerosols, is almost identical to that of 2-propanol. Lipophilicity of hydrocarbon propellants (blends of propane, n-butane and isobutene), that can be used as propellants in organic solvent aerosols or in combination with DME in aqueous aerosols, are higher than that of 2-propanol.

Nørgaard et al. (2010) showed that effects on VT in mice after exposure to vehicle control solvents (ethanol and 2-propanol), non-hydrolysed polyfluorooctyl triethoxysilane in ethanol and

bis(polyfluorooctyl)tetramethyl-disiloxane in ethanol were weak and reversible, despite that they can both reach the bronchioles and/or alveoli when aerosolised. Neither of these two substances contains functional chemical groups that can participate in a polymerisation reaction. However, when polyfluorooctyl triethoxysilane (TDFAs) is hydrolysed to its corresponding mono-, di- or tri-silanol, it can subsequently polymerize by a condensation reaction to siloxane-polymers with polyfluorooctyl as side chain. These siloxanes will also contain one or more hydroxyl groups that can participate in a condensation reaction. Nørgaard et al. (2010) have shown that the number of free hydroxyl groups (i.e. degree of hydrolysis/condensation) is critical for the toxicity. The interaction of the pulmonary surfactant protein SP-B and NFP 1 (hydrolyses and condensates of TDFAs) were studied by mass spectrometry (Larsen et al., 2014). Complexes of SP-B and the condensates tetra-, tri-, di- and mono-hydrolyzed tetra-siloxanes of polyfluorooctyl triisopropylsilane were identified. From the mass of these complexes it can be concluded that the tetrasiloxanes do not bond covalently to SP-B.

Larsen et al. (2014) refer to speculations that polyfluorosilanols with their hydrophobic polyfluoroalkyl chain in combination with hydrophilic silanol groups in some way can mimic the structure of the phospholipids and facilitate both hydrophobic and hydrophilic interactions with proteins, as it has previously been shown for per- and polyfluoroalkyl substances. Moreover both the 8:2 fluoroacrylate tested in Sørli et al. (2015) and the hydrolyses and condensates of alkylsilane tested in Duch et al. (2014) seems to have the same effects on VT og expiratory flow rate as hydrolyses and condensates of TDFAs. Both of these two substances contain functional chemical groups that can participate in a polymerisation reaction.

It is not clear to what extent the pulmonary toxicity of the hydrolysed compounds is affected by the length of the polyfluoroalkyl chain of the polyfluoroalkyl trialkoxysilanes.

Inhalation of aerosolized NFP 1 and "Magic Nano Glass & Ceramic" by mice and rats, respectively, has shown to lead to an irreversible reduction in tidal volume (Nørgaard et al., 2010; Pauluhn et al., 2008) and in expiratory flow rate (Nørgaard et al., 2014). These effects have been proposed to be driven by interaction between the impregnation product and the pulmonary surfactant. The disrupted pulmonary surfactant may lead to liquid blocking of the terminal airways, which increases airway resistance. Furthermore, disruption of pulmonary surfactant may lead to development of atelectasis (Nørgaard et al., 2010). Atelectasis may progress to tissue damage and edema, and product testing may cause lethal lung damage as seen in mice in Nørgaard et al. (2010) and in rats in Pauluhn et al.(2008), Sørli et al. (2015).

Overall, the pulmonary effects following short-term exposure to aerosolised mixtures containing polyfluorooctyl trialkoxysilane seem to depend on the concentration of polyfluorooctyl trialkoxysilane, the type and concentration of the solvent and the application method (droplet size and concentration).

B.5.2.2 Acute inhalation toxicity - Human incidents with impregnation spray products

Over the past more than three decades the use of different commercial products with water-proofing impregnation agents has been linked to acute lung injury. Symptoms often reported are: cough, dyspnea, pulmonary oedema, nausea, fever, shivers and headache. Respiratory symptoms have been reported to appear shortly after exposure or with some delay. Symptoms usually resolve within a few days, but sometimes supportive treatment with oxygen, bronchodilators or corticosteroids is needed.

The common characteristic of the products producing the observed lung effects is typically the presence of substances/monomers for polymers with per- or polyfluoroalkyl side-chains as ingredients in mixture with organic solvents. Detailed information about the specific ingredients is, however, seldom available.

The observed incidents have been described as outbreaks, as they have typically occurred in serial waves of incidents, which have subsided when possible causative products have been

removed from the market. Problems have reappeared when new formulations containing similar ingredients have been introduced on the market, e.g. in relation to change of solvents.

Incidents with impregnation products are most often seen with aerosol dispensers. However, one product resulting in two incidents of respiratory problems and additional 14 calls to the poison centre is described as a pump spray were reported in Canada (1992-1993). Additionally two occupational cases with three incidents were reported in Switzerland (2002-2003). In this cases the causative agent belonged to the chemical group of fluoroacrylates, Vernez et al. (2004). In Table 5 the European case stories collected from Poison Centers or available in the open literature and attributed to exposure to impregnation sprays are presented. Non-European case stories are presented in Appendix 1, Table 1 - 1. More detailed case stories are presented in Appendix 1, Table 1 - 2 for those incidents which are more well described in the literature. Table 1 - 2 is a sub-set of Table 5 and Table 1 - 1. In an answer to a call for evidence, carried out in spring 2015, the German Federal Institute for Risk Assessment (BfR) submitted a list of 19 case stories with impregnation sprays. These case stories are presented in Appendix 1, Table 1 - 3. Unfortunately, no information on product names, solvents and number of incidents were available for these case stories. Therefore they are not included in Table 5.

No human incidents have been reported for the spray product NFP 1 (containing TDFAs and 2-propanol), that have been studied intensely in animal studies by Nørgaard et al., before it was removed from the market. However, the two aerosol products "Magic Nano Glass & Ceramic" and "Magic Nano Bath & WC" have been involved 154 human incidents. According to Koch et al. (2009) the active substances in these two products are likely to be a fluorosilane, were the length of the polyfluoroalkyl chain are not known. It could though very well be TDFAs.

For most cases in Table 5, the detailed composition of the involved impregnation sprays is not known. Some of the incidents can be due to spray products containing mixtures of TDFAs and organic solvents and some are known to be due to other active substances (e.g. fluoracrylates or alkylsilanes). In Table 5 the column "Likely to be TDFAs" it is assessed how likely it is that the product causing the incidents were spray product(s) containing mixtures of TDFAs and organic solvents for the general public. Within the past three to four decades reports of 713 incidents with impregnation sprays in the EU are available. These incidents are the incidents in Table 5 minus cases from Switzerland and Greenland. It is estimated that 20 – 40 % of these 713 incidents were most likely spray product(s) containing mixtures of TDFAs and organic solvents for the general public. The products with the highest probability of being "spray product(s) containing mixtures of TDFAs and organic solvents for the general public" are "Magic Nano Glass & Ceramic" and "Magic Nano Bath & WC".

TABLE 5 OVERVIEW OF REPORTED INCIDENTS OF PULMONARY DISTRESS RELATED TO IMPREGNATION SPRAYS IN EUROPE

Country/ year	Product name	Container type and product use	Active ingre- dients	Solvent	Indi- viduals affect- ed	Source	Likely TDFAs ¹
Germany, 2006	Magic Nano Glass & Ce- ramic Magic Nano Bath & WC	Aerosol dispensers Surface sealants, bathroom	(fluor)silanes	Dimethyl ether, ethanol	154	BfR 2010 Pauluhn et al., 2008 Koch et al. 2009 Appen- dix1 Table 1-2	++

Country/ year	Product name	Container type and product use	Active ingre- dients	Solvent	Indi- viduals affect- ed	Source	Likely TDFAs ¹
Denmark, 1991-2007	Different products, names not available	Spray products (type not specified)	Fluorinated compound (most prod- ucts)	No information	84	Lyngenbo et al. 2008	++ ²
		Furniture, clothes, shoes, ceramic surfaces, carpets, tents, riding equip- ment, car seats , sealing foundation for paint, unknown	Fluoroacrylates (dodecylacry- late) and cy- closiloxanes (16 incidents)			Appendix 1 Table 1-2	
Nether- lands, 2011	No infor- mation	Aerosol dispensers	Fluorocarbon polymer	No information	1	Epping et al. 2011	+
		Rain-proofing spray for shoes				Appendix 1 Table 1-2	
Germany, 2006	Nano HiTech	Aerosol dispensers Use: No information	No information	No information	16	FOPH 2008	+
Sweden, 2001-2015	6 different products, names not available	3 products: Aerosol dispenses	Fluorocarbon resin	n-heptane, butylacetate, 2-propanol and isopropy- lacetate	98	Info from the Swedish Poison Information Centre	+
		3 products: Applica- tion form notn specified	Fluorinated polymer	n-heptane, 2- propanol and ethylacetate			
		Use: Not specified	Fluorinated polymer	2-propanol and metylisobutyl- keton			
			Fluorinated polymer	isoparaffins			
			Fluorocarbons	Tripropyl- eneglykol			
		Fluorinated polymer	Petroelum destilates and aceton				
Germany, 1979-83	Different products, names not available	Spray products Leather impregna- tion	Fluorocarbon polymer	No information	224	FOPH 2008	÷
Nether- lands, 2002-2003	Different products, names not available	Spray products Impregnation sprays	Fluorocarbon resin	n-heptane, mixture of solvents	99	FOPH 2008	÷

Country/ year	Product name	Container type and product use	Active ingre- dients	Solvent	Indi- viduals affect- ed	Source	Likely TDFAs ¹
UK, 2003	No infor- mation	Spray product Waterproofing spray	Fluorocarbon compounds	No information (Solvent change to low- odour solvent mix)	1 (fatal)	FOPH 2008	÷
France, 2003	No infor- mation	Spray product Leather and textile waterproofing spray	No information	No information	1 (fatal)	FOPH 2008	÷
Scotland, 2005	Rucoguard EPF 1610	Spray gun connect- ed to an air com- pressor Textiles	Fluorocarbon polymer (cati- onic fluorocar- bon polymer made by te- lomerisation)	Isopropanol	4	Wallace et al. 2005 Appendix 1 Table 1-2	÷
Nether- lands, 2013-2015	HG protector for untreated wooden fur- niture HG water, oil, fat & dirt proof for leather HG water, oil, fat & dirt proof for textile Scapino trend spray No infor- mation for the other 22 products	Spray products (types not speci- fied) Wooden furniture, leather, textile, unknown	Fluorocarbon polymer	No information	26	Info from National Poisons Information Center	÷
Spain, 2004-205	No infor- mation	Spray products Uses specified as industrial, cleaning and other	Fluorinated silanes or fluor- inated com- pounds	Aromatic or isoparaffinic hydrocarbons	5	Info from National Poisons Information Center	÷
Switzer- land, 2002- 2003	RapiAquaS- top (46% of incidents). K2R (27% of incidents) RapiIntemp (12% of incidents) (Patina-Fala (3 incidents	Aerosol dispensers and trigger sprays (3 incidents) Leather and textiles Stone-tiled walls and floors (3 inci- dents)	Fluorinated acrylate poly- mer	Isoparaffinic hydrocarbons	180	Vernez et al. 2006 Vernez et al. 2004 Appendix 1 Table 1-2	÷ ³
Greenland, 2010	Stain Repel- lant Super®	High pressure air- less spray gun (135 bar)	Non-fluorinated alkylsiloxanes	Hydrogenated naphtha C ₉ -C ₁₃ . (50-100%)	40 (of these 39 were	Duch et al. 2014	÷ ³

Country/ year	Product name	Container type and product use	Active ingre- dients	Solvent	Indi- viduals affect- ed	Source	Likely TDFAs ¹
		Surface coating product used for ceramic tiles			evacu- ated to larger hospital and clinically evalu- ated)	Appendix 1 Table 1-2	
Total number of incidents in EU					713 (100%)		
Know or most likely TDFAs in organic solvents for consumer use					158 (22%)		
Possible TDFAs in organic solvents for consumer use					114 (16%)		

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

² Four of the incidents 84 were due to a product intended for use on ceramic surfaces. These four incidents are counted as ++

³ Not part of EU

"Magic Nano Glass & Ceramic" and "Magic Nano Bath & WC" was pulled from the market in 3 days in 2006 because of the respiratory epidemic in users. Investigations into the composition of the product were considerably complicated by the fact that the distributor had no knowledge of the composition of his products, and the suppliers refused to provide information – they argued to keep trade secrets on three components of their preparations Hahn (2007). Based on the use of the Magic Nano products for hard non-absorbing substrate surfaces, the pronounced peaks of Silicon and Fluorine in the X-ray emission spectra and the fact that Silicon were always displayed in conjunction with Fluorine electron microscopic analysis, Koch et al. (2009) finds it likely that the active substance called silane by the product distributor are in fact a fluorosilane - possibly TDFAs (see B.5.2.1).

Detailed information on the actual use of the two aerosols causing the incidents (room size, ventilation etc.) is not available. The only clinical data is available are from the German Poison Information Centre-Nord (GIZ) who registered more than 10 different incidents in 3 days Groneberg (2010). The symptoms reported were (see Appendix 1, Table 1 – 2):

- Magic Nano Glass & Ceramic (7 incidents): Respiratory symptoms such as, severe dyspnoea, cough and pain by inhalation. Other symptoms reported: Fever, chills, weakness, chest pain, nausea and headache.
- Magic Nano Bath & WC (3 incidents): Respiratory symptoms such as severe dyspnea and cough. Other symptoms reported: Chills. In one person cough persisted for up to 6 weeks after exposure.

No prior knowledge of medical history are available for the humans affected.

According to Pauluhn et al. (2008) the total of 154 persons were intoxicated by "Magic Nano" (including the 10 incidents described by Groneberg, 2010). Cardinal symptoms were strong cough, dyspnea, and in 13 severe cases also severe lung edema. Since description of symptoms are only available for 10 incidents (Groneberg, 2010) it is not possible to evaluate the severity (moderate or mild) of the remaining 141 incidents (154 minus 13). Of the 19 incidents with impregnation sprays submitted by BfR (Appendix 1, Table 1 - 3) two seems to belong to the "Magic Nano" case. In these two incidents symptoms (cough, dyspnoea, laboured breathing, bronchitis) are evaluated as "minor".

No human incidents are reported for the pump spray "Magic Nano Bath & WC". Pauluhn et al. (2008) performed a comparative assessment in Wistar rats of the acute inhalation toxicity of two aerosol spray products, "Magic Nano Glass & Ceramics" and "Magic Nano Bath & WC" and with a pump spray product, "Magic Nano Bath & WC". No toxicologically significant changes occurred in rats exposed to the aerosol spray "Magic Nano Bath & WC". The pump spray were in the beginning lethal range at the highest dose tested 81222 mg/m³. The 4-hour standard LC₅₀ was calculated to 5098 mg/m³ (10 mg/m³ dry weight) for the aerosol "Magic Nano Glass & Ceramics". Clinical findings included bradypnea, tachypnea, laboured and irregular breathing patterns, red nostrils, and serous nasal discharge, cyanosis, piloerection, reduced motility, flaccidity, uncoordinated gait, and prostration. Analysis on the first postexposure day demonstrated increased lung weights and inflammatory endpoints (LDH, protein, γ -glutamyl-transaminase, and neutrophilic granulocytes) in bronchoalveolar lavage (BAL) in the "Magic Nano Glass & Ceramic" spray groups. No changes in total cell counts were observed.

Inhalation of aerosolized NFP 1 (containing TDFAs and 2-propanol) and "Magic Nano Glass & Ceramic" by mice and rats, respectively has shown to lead to an irreversible reduction in tidal volume (Nørgaard et al., 2010; Pauluhn et al., 2008) and in expiratory flow rate (Nørgaard et al., 2014). These effects have been proposed to be driven by interaction between the impregnation product and the pulmonary surfactant. The disrupted pulmonary surfactant may lead to liquid blocking of the terminal airways, which increases airway resistance. Furthermore, disruption of pulmonary surfactant may lead to development of atelectasis (Nørgaard et al., 2010). Atelectasis may progress to tissue damage and edema, and product testing may cause lethal lung damage as seen in mice in Nørgaard et al. (2010) and in rats in Pauluhn et al. (2008) (see B.5.2.1.2). It is likely that interaction between the impregnation product and the pulmonary surfactant in a similar way is responsible for the effects seen in humans.

Eventhough no toxicologically significant changes occurred in rats exposed to the aerosol spray "Magic Nano Bath & WC", at the highest dose tested 28 100 mg/m³, human incidents were reported. This may indicate that humans are more sensitive to these substances than rats.

No human incidents are reported for the pump spray "Magic Nano Bath & WC". Toxicologically changes only occurred in rats exposed to the highest dose tested 81 222 mg/m³. It can be speculated if this is due to the solvent (57 % ethanol and 37-42 % water) not being able to penetrate the phospholipid layer and giving the (fluoro)silane access to the SP-B protein in the pulmonary surfactants or if the dose rate are lower than the production of new pulmonary surfactant components. The chemical composition of the pump spray was different from the aerosol dispenser "Magic Nano Bath & WC", Koch et al. (2009) and the two can therefore not directly be compared (see B.5.2.1).

B.5.2.3 Summary of acute inhalation toxicity

Over the past more than three decades, the use of different commercial products with water-proofing impregnation agents has been linked to acute lung injury. It is estimated that 20 – 40 % of the 713 incidents reported in the EU were most likely spray product(s) containing mixtures of TDFAs and organic solvents intended for the general public. The products with the highest probability of being "spray product(s) containing mixtures of TDFAs and organic solvents for the general public" are "Magic Nano Glass & Ceramic" and "Magic Nano Bath & WC" that were responsible for 154 incidents in Germany in 2006.

Mice exposed to aerosolised mixtures containing TDFAs and 2-propanol (hydrolysates and condensates of polyfluorooctyl triisopropoxysilane) at certain concentration levels have been shown to develop serious lung injury following short term exposure. A significant concentration-dependent decrease of the tidal volume (VT) was seen, which was still significantly suppressed in the 18.4 mg/m³ group one day after exposure. 3 out of 20 mice died at 18.4 mg/m³ and 10 out of 10 died at 24.4 mg/m³. A similar picture was observed for the aerosol spray product "Magic Nano Glass & Ceramics" when tested in Wistar rats where the 4-hour LC₅₀ was

calculated 10 mg/m³ (dry weight). No toxicologically significant changes occurred in rats exposed to the aerosol spray "Magic Nano Bath & WC".

The mechanism behind the observed effects have been studied in mice and is believed to involve inhibition of the pulmonary surfactant in the deeper parts of the lungs by depletion of the pulmonary surfactant protein, SP-B. The SP-B protein is embedded in the phospholipids of the pulmonary surfactant, and it is speculated that the solvents (depending on lipophilicity) facilitate contact between hydrolysates and condensates of TDFAs and the SP-B proteins. This can also explain why no effect on the lungs are seen for spray products based on hydrolysed TDFAs with water as a solvent, even though the product can reach the deep parts of the lungs. Thus, the toxicity of the products in rats and mice depends on hydrolysates and condensates of TDFAs, the solvents, particle size distribution and particle concentration (application method). It is likely that interaction between the impregnation product and the pulmonary surfactant SP-B protein in a similar way is responsible for the effects seen in humans.

Even though no toxicologically significant changes occurred in rats exposed to the aerosol spray "Magic Nano Bath & WC", at the highest dose tested 28 100 mg/m³, human incidents were reported. This may indicate that humans are more sensitive to these substances than rats.

B.5.3 Irritation

B.5.3.1 Skin irritation

As shown under B.3.2, polyfluorooctyl triethoxysilane and polyfluorooctyl trimethoxysilane are classified as skin irritants by those notifiers who have classified the substances.

B.5.3.2 Eye irritation

As shown under B.3.2, polyfluorooctyl triethoxysilane and polyfluorooctyl trimethoxysilane are classified as severe eye irritants by those notifiers who have classified the substances.

B.5.3.3 Respiratory irritation

As shown under B.3.2, polyfluorooctyl triethoxysilane and polyfluorooctyl trimethoxysilane are classified as possible respiratory irritants by those notifiers who have classified the substances.

B.5.4 Corrosivity

Polyfluorooctyl triethoxysilane and polyfluorooctyl trimethoxysilane are not considered corrosive according to the notified self-classifications.

B.5.5 Sensitisation

No information has been identified regarding the sensitisation of alkoxysilanes or polyfluorooctyl alkoxysilanes.

B.5.6 Repeated dose toxicity

No information has been identified regarding repeated dose toxicity of alkoxysilanes or polyfluorooctyl alkoxysilanes.

B.5.7 Mutagenicity

No information has been identified regarding the mutagenicity of alkoxysilanes or polyfluorooctyl alkoxysilanes.

B.5.8 Carcinogenicity

No information has been identified regarding the mutagenicity of alkoxysilanes or polyfluorooctyl alkoxysilanes.

B.5.9 Toxicity for reproduction

No information has been identified regarding the reproductive toxicity of alkoxysilanes or polyfluorooctyl alkoxysilanes.

B.5.10 Other effects

No information has been identified regarding other effects of alkoxysilanes or polyfluorooctyl alkoxysilanes.

B.5.11 Derivation of no-effect concentration (DNEL)

Based on the data from studies of lung damage in mice after inhalation of nanofilm spray products conducted by Nørgaard et al. (2010), a no-effect concentration can be derived. A true no-effect concentration cannot be derived for rats based on the inhalation study by Pauluhn et al. (2008) since the product "Magic Nano Glass & Ceramic" contained a corrosion inhibitor that might affect the result. Despite that, a product specific no-effect concentration will be derived.

The product NFP 1 contained an unspecified fluorosilane and 2-propanol as solvent. Chemical analysis using electrospray ionization mass spectrometry (ESIMS) showed that NFP 1 contained hydrolysates and condensates of polyfluorooctyl triisopropoxysilane (total concentration 1.1 ± 0.1 %). "Magic Nano Glass & Ceramic" contained a silane likely to be a fluorosilane, a corrosion inhibitor and as solvent dimethyl ether (52.3 %), ethanol (26.2 %) and water (18-20 %), Koch et al. (2009). The length of the polyfluoroalkyl chain of the fluorosilane is not known but it could be TDFAs.

Based on the published results (Nørgaard et al., 2010), as well as information from the authors on the number of dead animals (0/10 at 3.3 mg/m^3 , 0/10 at 15.7 mg/m^3 , 0/10 at 16.1 mg/m^3 , 3/20 at 18.4 mg/m^3 , 10/10 at 24.4 mg/m^3 and 8/10 at 42.4 mg/m^3), a 1 hour LC_{50} is estimated to 20.4 mg/m^3 . By using Haber's law, the 4 hour LC_{50} is estimated to 5 mg/m^3 . 1 hour NO-AEC and LOAEC is estimated to 16.1 mg/m^3 and 18.4 mg/m^3 , respectively.

As described in section 5.2.1 pulmonary toxicity also depends on the chain length/lipophilicity of the solvent. Mixtures of TDFAs and solvents that are less lipophilic than 2-propanol (e.g. methanol) are expected to have a higher LC_{50} . Mixtures containing TDFAs and methanol are expected to have a LC_{50} value that are only slightly higher than mixtures containing TDFAs and 2-propanol (as a maximum a factor of 4). This observation is based on comparison of the 25 % and 40 % reduction in the mice Tidal Volume (VT) from an exposure concentration of 24.4 mg/m^3 NFP 1 (Nørgaard et al., 2010) and an exposure concentration of 43 mg/m^3 of a mixture of TDFAs and methanol (Nørgaard et al., 2014). For NFP 1 the 25 % and 40 % reduction in VT were seen at 31 min and 42 min, respectively. For the mixture of TDFAs and methanol it was seen at 27 min and 37 min, respectively. At an exposure concentration of 24.4 mg/m^3 NFP 1 10/10 mice died. The number of dead mice is not known for the mixture of TDFAs and methanol.

Mixtures of TDFAs and solvents that are more lipophilic than 2-propanol are expected to have a lower LC₅₀. This seems to be the case for the product Rim sealer, tested by Sørli et al. (2015). The solvents used in this product is a mixture of 2-propanol, 1-methoxy-2-propanol and ethylacrylate (see 5.2.1).

The dry weight LOAEL and 4 hour LC₅₀ in rats of "Magic Nano Glass & Ceramic" were estimated to 4.5 mg/m³ and 10 mg/m³, respectively. This estimate is based on the measured non-volatile aerosols in the respirable range. Besides hydrolysates and condensates of (fluoro)silane these non-volatiles also contain corrosion inhibitor which could have an effect on both toxicity and spray pattern of the product since the hydrolysates and condensates can bond covalently to the corrosion inhibitor (see B.5.2.1).

LOAEL or LC₅₀ could not be estimated for the two other "Magic Nano" products studied by Pauluhn et al. (2008).

According to ECHA's *Guidance on information requirements and chemical safety assessment Chapter R.8: Characterisation of dose [concentration]-response for human health*, version 2.1 (ECHA, 2012a), an inhalatory DNEL (acute) can be derived by applying a large assessment factor (AF) for severity of effect to the LC₅₀-value. A default AF of 100 is suggested as a starting point. In addition an AF of 3 are used because of the very steep concentration-response curve. The derived 4 hour no-effect concentration (DNEL) for TDFAs and 2-propanol (hydrolysates and condensates of polyfluorooctyl triisopropoxysilane) is calculated using the total assessment factor of 300:

$$DNEL(acute) = \frac{5 \text{ mg/m}^3}{300} = 0.017 \text{ mg/m}^3$$

In the same way the product specific acute 4 hour DNEL for "Magic Nano Glass & Ceramic" can be calculated to 0.03 mg/m³.

B.6 Human health hazard assessment of physico-chemical properties

Not relevant for the present restriction dossier.

B.7 Environmental hazard assessment and PBT and vPvB assessment

The environmental risks of the use of TDFAs is to a large extent related to the possible release of persistent per- and polyfluoroalkyl substances (PFAS) during the entire lifecycle of the mixtures (e.g. Knepper et al., 2014; SFT, 2006; Herze et al., 2009; Buck et al., 2011). When cured, the mixtures form a siloxane polymer with polyfluorooctyl side-chains. The side-chains resemble 6:2 fluorotelomers (with a polyfluorinated part of 6 carbon atoms and two carbon atoms without fluorine).

Due to lack of information on the presence of non-polymer PFAS in the mixtures and final surfaces and the fate of the polyfluorinated side-chains of the polymers, it is not possible to assess to which extent the use of the TDFAs may contribute to the environmental load of PFAS.

B.8 Exposure assessment

B.8.1 General discussion on releases and exposure

This dossier targets consumer exposure by application of mixtures containing TDFAs and solvents in spray products (aerosol dispensers, pump and trigger sprays and mixtures marketed for spray application). The hypothesis regarding the toxicity related to the impregnation sprays is that the observed effects are caused by the presence of both TDFAs and free hydroxyl groups which form the toxic hydrolysates and condensates responsible for the observed toxic effects of the products. The dossier therefore targets both the polyfluorooctyl alkoxysilanes and the hydrolysis products in ready-to-use products.

Since inhalation is the primary exposure route and since animal data are only available for inhalation exposure, this is the only exposure route addressed.

B.8.1.1 Summary of the existing legal requirements

Only two substances (polyfluorooctyl trimethoxysilane and polyfluorooctyl triethoxysilane) meeting the general formula are pre-registered under REACH. No registration dossiers have been submitted yet.

According to the Classification & Labelling (C&L) Inventory under CLP, the two substances are classified for skin, eye and respiratory irritation by industry.

Currently there is no restriction of either the parent compounds or the reaction products in place.

B.8.1.2 Summary of the effectiveness of the implemented operational conditions and risk management measures

The mechanism behind the toxicity related to impregnation sprays containing TDFAs has recently been suggested in the literature. As the toxicity is related to specific reaction products of parent compounds in the product formulation, the classification of the product does not reflect the actual hazard when classification is based only on the individual ingredients. Consumers are therefore not sufficiently warned about the risks from inhalation of the products. Many products will due to the content of solvents carry warnings such as: "Avoid inhalation" or "To be used outdoors". However, many proofing/impregnation products for e.g. bathroom tiles and grout sealants are typically used in small rooms with poor ventilation where exposure can reach levels which may cause serious lung injury. Existing risk management measures do not at present reflect the particular hazard caused by mixtures containing TDFAs and organic solvents. Essentially, Nørgaard et al. (2010a) shows that products containing a mixture of TDFAs and 2-propanol should be classified with Acute Toxicity, Category 1, H330 (Fatal if inhaled) since $LC_{50} \leq 0.05$ mg/l (see B.5.11). Since the content of hydrolysates and condensates of TDFAs and 2-propanol in NFP 1 is 1.1 %, the producers of NFP1 should classify the product with Acute Toxicity, Category 2, H330 (Fatal if inhaled).

B.8.2 Manufacturing

B.8.2.1 Occupational exposure

No data are available from manufacturers regarding the occupational exposure of workers by the manufacture of the substances.

B.8.2.2 Environmental release

No data are available from manufacturers regarding the environmental release by the manufacture of the substances.

B.8.3 Use - spray application

B.8.3.1 Workers exposure

Only very few incidents of occupational exposure to impregnation sprays in aerosol dispensers resulting in respiratory illness are reported (Appendix 1, Table 1 - 2). Incidents involving application using spray guns are more frequently reported. Three of the occupational incidents reported involved pump spray. In these cases, the causative agent belonged to the chemical

group of fluoroacrylates. In general, little or no information is available on the occupational use of and exposure to spray products containing the TDFAs in the EU.

Professionals are covered by occupational health regulation which is assumed to provide a sufficient level of protection provided the hazardous effects of this type of products are well known (i.e. that the product is properly classified and labelled). Even if not labelled properly the product will most likely be labelled according to the hazard of the organic solvent(s). This may include precautionary statements such as "Avoid breathing the dust, fume, gas, mist, vapours or spray", depending on the solvent(s). Therefore, it is expected that it is more likely that professionals are using precautionary measures.

B.8.3.2 Consumer exposure

Several incidents have demonstrated that consumers occasionally use impregnation sprays for e.g. leather, ceramics and tiles indoors in small confined rooms without open windows or doors and without any personal protection.

The possible exposure of consumers is estimated in three scenarios of which the two are subdivided:

- a) Impregnation of flooring/tiles (4 or 7 m²) in a bathroom of 10 or 17.4 m³, respectively. Depending on the size of the floor, the spray duration is assumed to be 40 and 70 sec, respectively, for the aerosol dispenser, and 13 and 23 min, respectively, for the pump spray. The exposure duration is assumed to be 30 min. Scenario a1) describes the spraying of 4 m² in a 10 m³ bathroom and scenario a2) describes the spraying of 7 m² in a 17.4 m³ bathroom.
- b) Impregnation of a sofa⁶ in a living room (58 m³). The surface area of the sofa is based on data from a standard IKEA 3-person sofa, and it is assumed that approximately 6.2 m² of the sofa is impregnated (front and sides of the sofa, as well as all of the cushions). The spray duration is assumed to be 62 sec and 20 min, for the aerosol spray can and pump spray, respectively. The exposure duration is assumed to be 1 hour.
- c) Impregnation of a pair of shoes/boots⁷ in a kitchen (15 m³) (scenario c1) and in a bathroom (10 m³) (scenario c2). According to Engelund et al. (2005), 27.8 g is required for impregnation of a pair of women's boots (including overspray). The spray duration is therefore assumed to be 7.5 sec for the aerosol spray can and 2.5 min for the pump spray. The exposure duration is assumed to be 5 min.

For the calculations, two exposure models are used: The ConsExpo model (v5.0 beta) and the ECETOC Targeted Risk Assessment model. The ECETOC model is used as a secondary model, for comparison of results.

For the estimates, it is assumed that the same version of the NPF 1 formulation is used as both a pump spray and an aerosol dispenser. It is assumed that 40 g product/m² is required (worst case). The ConsExpo model uses mass generation rates instead of applied amount. A mass generation rate of 4 g product/sec is used for the aerosol spray can and 0.2 g product/sec for the pump spray (based on information from Nørgaard, 2015 (personal communication)).

These mass generation rates are used to calculate the spray duration, based on the surface area of the article being sprayed.

⁶ Spray products containing TDFAs in mixtures with organic solvents are normally not used for absorbing surfaces. Sofa is used as an example of a medium exposure scenario.

⁷ Spray products containing TDFAs in mixtures with organic solvents are normally not used for absorbing surfaces. Shoes/boots is used as an example of a small exposure scenario.

Reasonable worst case scenarios are estimated. The three scenarios are based on different critical assumptions regarding duration of exposure and room size in order to see the effect of these parameters on the level of exposure. The effects of changing ventilation rates and exposure duration is also tested.

Information and product specific data on NFP 1 used in the exposure estimation originates from Nørgaard et al. (2009 and 2010) as well as personal communication with A. Nørgaard.

No exact data on average particle diameter is available for the aerosols generated from NFP 1. As a worst case scenario, it is therefore assumed that all generated aerosols have a particle diameter < 10 µm.

The algorithm for calculating inhalation exposure in ECETOC TRA is rather simple and turned out being not useful, for further information see Appendix 2.

For comparison, for scenario a2 concentrations have been estimated from the measured concentrations in exposure chambers used for the toxicity tests with animals. The particle number size distribution was roughly the same in both the animal experiment (Nørgaard et al. 2010a) and in spray chamber experiments with NFP 1 (Nørgaard et al. 2009 and Nørgaard 2010d). However, the number of particles generated by the pump spray in the spray chamber experiments is significantly lower than the number of particles generated the high-pressure nebulization in the animal experiment.

Pump spray

The number of particles generated by the pump spray for NFP 1 was approximately 4×10^2 particles/cm³ per g applied product. For the coating of surfaces, 10 to 40 g/m² of the product is used depending on product type. For the product NFP 1, no specifications or recommendations on the amount to be used are provided. Therefore, it is assumed that the highest recommended amount as a worst case scenario is used.

By using 40 g/m² NFP 1 in the standard room and using pump spray as application form, the concentration of TDFAs and 2-propanol (hydrolysates and condensates) reaches around 1.4 mg/m³ ($\approx 6 \times 10^3$ particles/cm³) immediately after treatment. This concentration may be overestimated, since the high air velocity in the test chamber enhances the external diffusion from the coated surface (Nørgaard 2010d).

No particle concentration measurements are available for NFP 1 in trigger spray, however, it is expected to be comparable to the particle concentrations measured for pump spray.

High-pressure spray (aerosol dispenser)

The high-pressure nebulization of the NFP 1 in the study by Nørgaard et al. (2010a) generated significantly higher particle concentrations ($1.4 \times 10^5 - 4.6 \times 10^6$ particles/cm³) than observed in spray chamber experiments with pump spray products. The particle concentrations correspond to a mass concentration of the hydrolysates and condensates of TDFAs and 2-propanol sampled on the filter in the exposure chamber at 0.5 mg/m³ – 42.4 mg/m³ (dry weight). This is the concentrations that mice are exposed to in the animal study, Nørgaard et al., (2010a). Extrapolating this to the worst case scenario where 40 g/m² NFP 1 is used in the standard room and using high-pressure spray (aerosol dispenser) as application form, the concentration of hydrolysates and condensates reaches around 46.2 mg/m³ (cf. Appendix 2). The mass concentration of the hydrolysates and condensates of TDFAs and 2-propanol sampled on the filter in the mouse inhalation study (Nørgaard et al., 2010) corresponds to on average 0.29 % of the total NFP 1 infused in the exposure chamber (cf. Appendix 2).

No particle concentration measurements are available for NFP 1 aerosolised by an aerosol dispenser. Moreover, the particle concentration that can be generated by an aerosol dispenser depends on the pressure and the type of nozzle used. However, even with the possibility to vary these parameters, it is expected that the particle concentration of NFP 1 generated by use of an aerosol dispenser will be somewhere within the interval of the particle concentrations generated by the high-pressure nebulizer.

According to Koch et al. (2009), release of one spray can (approximately 120 g) of the aerosol "Magic Nano Glass & Ceramic" in a model room with a volume of 60 m³ resulted in a exposure concentration of non-volatile components (corrosion inhibitor and hydrolysates and condensates of (fluoro)silane) in the inhalable fraction (< 100 µm) of 41.5 mg/m³. Of these approximately 11.5 mg/m³ were able to reach the bronchioles and/or alveoli (< 10 µm).

This product specific gas phase mass concentration of corrosion inhibitor and hydrolysates and condensates of (fluoro)silane able to reach the bronchioles and/or alveoli (11.5 mg/m³) will be used for characterisation of "Magic Nano Glass & Ceramic" (B 9.1.1.2).

Detailed information on the exposure estimation (input values, resulting exposure estimates, etc.) is given in Appendix 2.

Table 6 shows the exposure estimates made on the basis of above-mentioned assumptions and the input parameters shown in Appendix 2.

TABLE 6 EXPOSURE ESTIMATES FOR NFP 1 ESTIMATED WITH CONSEXPO AND BASED ON MEASURED CONCENTRATIONS IN SPRAY CHAMBERS

Scenario		Mean event concentration (mg/m ³)
a1) Spraying of 4 m ² in a 10 m ³ bathroom	Pump spray	13
	Aerosol dispenser	41
a2) Spraying of 7 m ² in a 17.4 m ³ bathroom	Pump spray (estimated)	11
	Pump spray ('measured')	1.4
	Aerosol dispenser (estimated)	42
	Aerosol dispenser ('measured')	46
b) Impregnation of a 6.2 m ² sofa in a 58 m ³ living room	Pump spray	3.5
	Aerosol dispenser	11
c1) Impregnation of a pair of shoes/boots in a 15 m ³ kitchen	Pump spray	1.6
	Aerosol dispenser	5.4
c2) Impregnation of a pair of shoes/boots in a 10 m ³ bathroom	Pump spray	2.5
	Aerosol dispenser	8.1

Changing the ventilation rate only had a limited effect on the exposure concentrations. Reducing the exposure duration from 30 to 15 min for spraying of 4 m² in a 10 m³ bathroom, had no effect in the aerosol dispenser scenario. This is no surprise, since for this scenario, this just means that the person spraying will leave the bathroom after 15 min instead of after 30 min. When using the same scenario on the pump spray, the time spent in the room is changed from 17 min to 2 min. This will lower the exposure concentration by 27 % (see Appendix 2).

The estimation of the consumer exposure to hydrolysates and condensates of polyfluorooctyl triisopropoxysilane from using the product NFP 1 is based on a number of assumptions, which are all subject to different uncertainties that has an impact on the validity of the resulting estimates. The assumptions that are specific to the product NFP 1, such as mean generation rate, initial droplet (particle) size distribution and airborne fraction, are based on the expert knowledge of A. Nørgaard.

The assumptions regarding room size and room ventilation rates are based on default values from the ECHA guidance document on consumer exposure estimation (ECHA, 2012), the RIVM general fact sheet (Bremmer et al, 2006) and data from Nørgaard et al. (2010b). In ECETOC TRA default room volumes and ventilation are used.

Results in Table 6 should, therefore, be interpreted very carefully, and the results can only be seen as indicative of the expected exposure concentrations.

This is underlined by comparing modeled results from scenario a2 with the measured exposure concentrations for impregnation of 7 m² floor in a 17.4 m³ room. For the aerosol dispenser the results are of the same order of magnitude (calculated 42 mg/m³ and measured 46 mg/m³). For the pump spray the calculated exposure concentrations are one order of magnitude higher than the measured (calculated 11 mg/m³ and measured 1.4 mg/m³). This could indicate that the fraction of active compound airborne of 10 % is slightly overestimated for the pump spray (see Appendix 2).

B 8.3.3 Indirect exposure of humans via the environment

Indirect exposure to TDFAs or hydrolysates and condensates of TDFAs and organic solvents via the environment is not expected to be frequent or to reach high levels of exposure. However,

exposure may occur if bystanders are close to a person performing outdoor spraying with impregnation sprays.

B.8.3.4 Environmental exposure

Environmental exposure to TDFAs or hydrolysates and condensates of TDFAs and organic solvents is considered to be very limited. Products for tiles and ceramics are used indoors with limited release to the external environment. Products for leather and textiles are also used outdoors, but it is not known to which extent these product types contain TDFAs or if other fluorinated polymers prevail. Environmental exposure from soil deposition of overspray can occur but is expected to be limited due to the limited market share for these products.

The main application areas of the substances are mixtures applied by saturated brushes, roller or high-volume-low-pressure (HVLP) guns. The mixtures are mainly based on organic solvents (alcohols). A common professional application area is outdoor spray application (using e.g. HVLP guns) on large building surfaces. Likely, this could be the major source of direct release of the substances to the environment.

B.8.4 Other sources (for example natural sources, unintentional releases)

No data indicating that TDFAs are formed and released from natural sources have been identified. Based on an expert judgment it is estimated that unintentional formation and releases would not contribute significantly to the total releases.

B.8.5 Overall environmental exposure assessment

The overall environmental exposure resulting from the use of impregnation products in aerosol dispensers is considered limited.

B.8.6 Combined human exposure assessment

Combined human exposure is not considered relevant in this context where the effects are a consequence of short term exposure to the aerosol spray. It should, however, be considered that subsequent use of other similar products before onset of symptoms may aggravate the effects.

B.9 Risk characterisation

B.9.1 Use in aerosol dispensers, pump and trigger sprays

B.9.1.1 Human health

B.9.1.1.1 Workers

No data are available from manufacturers regarding the occupational exposure of workers by the manufacture of the substances or for professional use in aerosol dispensers, pump and trigger sprays in order to characterize the risk.

B.9.1.1.2 Consumers

A quantitative risk assessment has been carried out for the reaction product of TDFAs and 2-propanol applied by pump spray and in aerosolised form.

The risk assessment is based on the product named NFP 1 in the articles by Nørgaard et al. The active substances in this product are hydrolysates and condensates of TDFAs in 2-

propanol. Chemical analysis of NFP 1 using electrospray ionization mass spectrometry (ESIMS) showed that it contained 1.1 ± 0.1 % active substances.

The acute 4 hour DNEL was calculated to 0.017 mg/m^3 (see B.5.11).

The risk characterisation ratio (RCR) is calculated by dividing the derived exposure concentration with the derived DNEL:

$$RCR(\text{acute}) = \frac{\text{Exposure concentration}}{DNEL}$$

Table 7 shows the measured and calculated exposure concentrations along with the characterisation ratios. A risk characterisation ratio above 1 shows that the risk is not controlled.

TABLE 7 EXPOSURE ESTIMATES AND RISK CHARACTERISATION RATIOS FOR NFP 1 IN DIFFERENT SCENARIOS

Scenarios		Mean event concentration (mg/m ³)	RCR		
a1	Spraying of 4 m ² in a 10 m ³ bathroom	Pump spray	13	765	ConsExpo
		Aerosol dispenser	41		
a2	Spraying of 7 m ² in a 17.4 m ³ bathroom	Pump spray	11	647	ConsExpo
		Aerosol dispenser	42	2471	
a2	Spraying of 7 m ² in a 17.4 m ³ room	Pump spray	1.4	82	Measured values
		Aerosol dispenser	46	2718	
b	Impregnation of a 6.2 m ² sofa in a 58 m ³ living room	Pump spray	3.5	206	ConsExpo
		Aerosol dispenser	11	647	
c1	Impregnation of a pair of shoes/boots in a 15 m ³ kitchen	Pump spray	1.6	94	ConsExpo
		Aerosol dispenser	5.4	318	
c2	Impregnation of a pair of shoes/boots in a 10 m ³ bathroom	Pump spray	2.5	147	ConsExpo
		Aerosol dispenser	8.1	476	

Table 7 shows that for all of the scenarios there is a risk that is not adequately controlled when applying mixtures containing TDFAs and 2-propanol by both aerosol dispenser and pump spray.

No particle concentration measurements or calculations exist for NFP 1 in trigger spray, however, it is expected to be comparable to the particle concentration measured for pump spray. Therefore the risk is expected to be similar to the risk seen for pump sprays.

Table 7 should be interpreted very carefully, the expected exposure values calculated by ConsExpo are based on a number of assumptions (see B.8.3.2). Moreover, the exposure concentrations are estimated for exposure durations from 5 minutes to 1 hour. The acute DNEL is based on a standard 4 hour LC₅₀. Thus, the RCR may be overestimated. The 4 hour LC₅₀ used for calculating the DNEL is based on TDFAs with 2-propanol as a solvent. As described in section 5.2.1 pulmonary toxicity also depends on the chain length/lipophilicity of the solvent. Mixtures of TDFAs and solvents that are less lipophilic than 2-propanol (e.g. methanol) are expected to have a higher LC₅₀ value and therefore a higher DNEL. Mixtures containing TDFAs and methanol are expected to have a LC₅₀ value that is only slightly higher than mixtures containing TDFAs and 2-propanol (see 5.11). Mixtures of TDFAs and solvents that are more lipo-

philic than 2-propanol are expected to have a lower LC₅₀. This seems to be the case for the product Rim sealer, tested by Sørli et al. (2015). The solvent used in this product is a mixture of 2-propanol, 1-methoxy-2-propanol and ethylacrylate (see 5.2.1).

Even when taking these uncertainties into account it must be expected that there is a risk that is not adequately controlled for both aerosol dispenser and pump spray containing mixtures of TDFAs and organic solvent – at least for the worst case scenario.

This risk characterization ratio shows that the risk is higher for the mixtures containing TDFAs and 2-propanol when the product is applied by aerosol dispenser than when it is applied by pump spray. This is in line with the much bigger number of incidents reported with use of aerosolised products.

If no other parameters are changed a NFP 1-like product with a concentration of hydrolysates and condensates of TDFAs and 2-propanol at 0.0004 % (2718 times less than the NFP 1 concentration of 1.1 %) that is applied on 7 m² in a 17.4 m³ room by an aerosol dispenser would give rise to a RCR equal to 1. Thus, for a NFP 1-like product the risk is controlled if the product is applied by an aerosol dispenser and the concentration of hydrolysates and condensates of TDFAs and 2-propanol is below 0.0004 %.

This result cannot be generalised to other products based on mixtures containing TDFAs and organic solvents since toxicity also depends on the solvent (Nørgaard et al. 2010a). Rim sealer is e.g. more toxic than NFP 1, Nørgaard et al., 2015 (see B.5.2.1). To take this in to account an extra assessment factor should be added when setting an risk-based limit value. An assessment factor of 10 is used for setting the limit value of 0.00004 % (400 ppb) in RMO 2 (see, E.2.2).

A product specific acute 4 hour DNEL for “Magic Nano Glass & Ceramic” was calculated to 0.03 mg/m³ in section B.5.11. Besides hydrolysates and condensates of a (fluoro)silane (that might be TDFAs) the non-volatile part of this product also contained a corrosion inhibitor. Therefore, it is questionable if this DNEL is the true rat DNEL only based on hydrolysates, condensates and solvents (dimethyl ether (52.3 %), ethanol (26.2 %) and water (18-20 %)). For further discussion on this, see B.5.2.1, Koch et al. (2009).

Koch et al. (2009) showed that release of approximately 120 g of the aerosol spray “Magic Nano Glass & Ceramic” in a model room with a volume of 60 m³ resulted in an exposure concentration of non-volatile components of 11.5 mg/m³ which were able to reach the bronchioles and/or alveoli. From this a RCR of 383 can be derived, which shows that a risk exists for this product which is not controlled. This is in line with fact that a number of incidents were reported for this product.

For the aerosol product “Magic Nano Bath & WC” no toxicologically significant changes occurred in rats at the highest dose tested 28 100 mg/m³. However, for this product human incidents were reported. This may indicate that humans are more sensitive to these substances than rats.

Based on the fractions able to reach the alveoli, Koch et al. (2009) estimated that risk of exposure to respirable aerosol is approximately 20-fold lower for the pump spray “Magic Nano bath & WC” than for the aerosol “Magic Nano Glass & Ceramic”. Taking into account the fraction that can also reach the bronchioles (< 10 µm) this number should be adjusted to 20-45 times lower. This would give a RCR of approximately 8, indicating a risk, for the pump spray when used under the same conditions as the aerosol spray “Magic Nano Glass & Ceramic”. No human incidents are reported for the pump spray “Magic Nano Bath & WC”. Pulmonary effects only occurred in rats exposed to the highest dose tested 81 222 mg/m³. It can be speculated if this is due to the solvent (57 % ethanol and 37-42 % water) not being able to penetrate the phospholipid layer and giving the (fluoro)silane access to the SP-B protein in the pulmonary surfactants or if the dose rate are lower than the production of new surfactant components. The

chemical composition of the pump spray was different from the aerosol dispenser "Magic Nano Bath & WC", Koch et al. (2009) and the two can therefore not directly be compared (see B.5.2.1).

B.9.1.1.3 Indirect exposure of humans via the environment

Indirect exposure of TDFAs and hydrolysates and condensates of TDFAs and organic solvents via the environment is not expected to be frequent or to involve high levels of exposure.

B.9.1.1.4 Combined exposure

Exposure leading to the observed pulmonary effects are specifically related to the spray application process and the relevance of combined exposure is not relevant.

B.9.1.2 Environment

See section B.2.4.

B.10 Summary on hazard and risk

Recent research have demonstrated that hydrolysates and condensates of TDFAs and organic solvents can cause serious acute lung injury in mice exposed to aerosolised mixtures. These findings are supported by numerous incidents where consumers have experienced acute pulmonary distress following exposure to impregnation sprays in aerosol dispensers containing fluorinated polymers and free hydroxyl groups. Other polymer/solvent systems with and without fluorinated constituents seem to have caused similar effects. This is, however, not documented in animals studies or verified in humans exposed to products with a known composition. The products with the highest probability of being "spray product(s) containing mixtures of TDFAs and organic solvents for the general public" are "Magic Nano Glass & Ceramic" and "Magic Nano Bath & WC" that are known to have caused human incidents. These two aerosol products were responsible for 154 incidents in Germany in 2006.

Risk assessment, based on the floor sealant product NFP 1 (by Nørgaard et al.), were carried out for the hydrolysates and condensates of TDFAs and 2-propanol. Five different scenarios indicated that pump spray application of NFP 1 presents an unacceptable risk of serious injury.

The risk for trigger sprays is expected to be similar to the risk seen for pump sprays.

Aerosolised NFP 1 generates higher particle concentrations than is generated by pump spray with approximately the same particle size distribution. Aerosolised NFP 1 therefore present an even higher risk, which also needs to be controlled.

Based on the risk assessment of NFP 1 (hydrolysates and condensates of TDFAs and 2-propanol) it must be expected that an adequately controlled risk of serious pulmonary injury exists for all organic solvents in mixture with TDFAs when applied by aerosol dispenser or pump spray – at least for the worst case scenario.

The environmental risk is expected to be very limited due to limited environmental exposure from these products.

C. Available information on alternatives

C.1 Identification of potential alternative substances and techniques

Several alternative options to the use of mixtures containing TDFAs and organic solvent in aerosol dispensers, pump and trigger spray exist:

- Alternative application methods for the mixtures concerned:
 - Brush, roller or cloth
- Aerosol dispensers, pump and trigger spray containing water-based mixtures containing TDFAs
- Polyfluoroalkyl trialkoxysilanes with polyfluoroalkyl chain different from octyl:
 - Aerosol dispensers, pump and trigger sprays with triethoxy(3,3,4,4,5,5,6,6,6-nonafluorohexyl)silane or triethoxy(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)silane (organic solvent-based)
- Products without fluorotrialkoxysilane:
 - Aerosol dispensers, pump and trigger sprays containing side-chain-fluorinated polymers (organic solvent or water-based)
 - Aerosol dispensers, pump and trigger sprays containing silane/siloxane/acrylic-based mixtures (organic solvent or water-based)

Besides these alternatives, an alternative technique is not to use any impregnating or proofing agents, but use more time on the cleaning of the surfaces or accept that surfaces are more stained. Considering that these types of impregnating agents are not common consumer products sold in supermarkets it is based on expert judgment considered that this most likely is the technique applied by most consumers.

C.2 Assessment of alternative application methods for the mixtures concerned

C.2.1 Human health risks associated with alternative application

Among the identified incidents summarised in Table 5, most incidents are related to products described as spray products without specific indication of whether the spray is applied by pump spray, trigger spray or pressurized aerosol spray. One product resulting in two incidents of respiratory problems and additional 14 calls to the poison centre is described as a pump spray. Two occupational cases with three incidents by pump spray application, were also reported. Although information is not available for all products, it is expected based on information search on the Internet that most impregnation products have been marketed as aerosol sprays.

No specific data are available regarding the effect of different spray techniques, and evidence of pulmonary effects related to exposure from the hydrolysed TDFAs aerosols is so far based on the data from Nørgaard et al., 2010 and the specific characterization of the spray, including particle number and size distribution.

In general it is more likely that aerosol dispensers produce a fraction of respirable particles that would reach the alveoli and come into contact with the lung surfactant, compared to pump sprays and trigger sprays. However, the risk assessment shows that the risk for pump and trigger spray is not controlled (see B.9.1.1.2).

Parameters such as application pressure, type of nozzle and volatility of the mixture influence droplet/particle size.

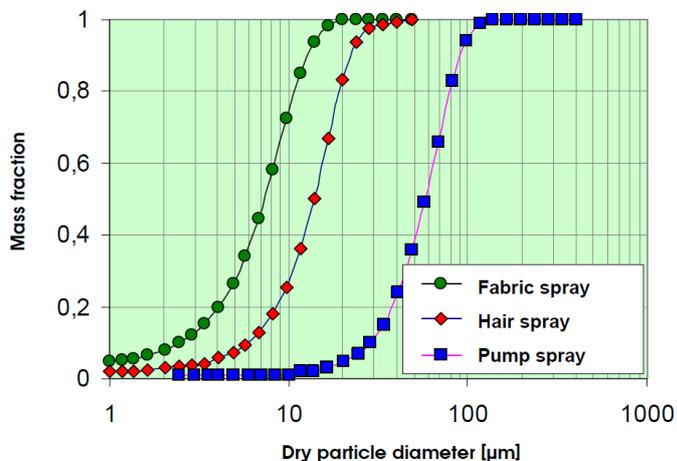
The Cosmetic Ingredients Review (CIR) Expert Panel has issued a document on aerosols (CIR, 2012), describing the typical particles released from a pump spray. According to CIR (2012), the median d_{ae} of the airborne droplets/particles of pump hair sprays range from 60 μm to 80 μm and typically less than 1% of the airborne droplets/particles released from pump sprays are in the range considered to be respirable (i.e., $d_{ae} < 10 \mu\text{m}$). Droplets/particles with $d_{ae} > 15$

μm are expected to be deposited almost exclusively in the nasopharyngeal and bronchial regions of the respiratory tract, from where particles with $d_{ae} > 7 \mu\text{m}$ are typically cleared within 24 hours in healthy individuals through mucociliary action (CIR, 2012).

In comparison, the median d_{ae} of the airborne droplets/particles of propellant hair sprays are mentioned to range from 25 μm to 50 μm . The CIR Expert panel also states that usually, 1% to 2.5% but no more than 5% of the droplets/particles emitted from propellant hair sprays are within the respirable range.

The Swiss Confederation (2008) has in their report on "Toxicology of waterproofing sprays" presented a graphical overview of the mass fraction as a function of dry particle diameter for three types of spray. This overview is presented in Figure 1. The fabric spray and the hair spray are aerosol sprays.

FIGURE 1 MASS FRACTION AS A FUNCTION OF PARTICLE DIAMETER (AFTER COMPLETE EVAPORATION OF THE SOLVENT) FOR THREE TYPES OF SPRAY



No pulmonary risk can be expected from application of mixtures containing TDFAs and organic solvents by cloth, roller or brush, since these application forms will not generate particles in the respirable range.

C.2.3 Environment risks related to alternative application methods

The environmental risks related to alternative application methods, such as brush, roller or cloth, for the mixtures concerned are considered to be similar or lower than the environmental risks of applying the mixtures by aerosol dispensers, pump or trigger spray. Used outdoors, the application by aerosol dispensers may lead to higher releases to the surroundings, because of small droplet size.

The overspray⁸ fraction will depend on both the mixture and the object being sprayed. Spraying on ceramic surfaces and tiles (which usually will be indoors) or grout is likely to result in less overspray compared to objects such as shoes and textiles of varying shape. Hard surfaces are more likely to result in bounce-back. The overspray fraction will in general depend on e.g. nozzle velocity and particle size. Typical values reported for spray paint reach up to 40 % whereas the worst case overspray potential from trigger sprays has been reported at 6 % (EPA, 1987; Jayjock, 2012).

Releases of volatile poly- and perfluoroalkyl substances in the mixtures such as residual content of fluorotelomer alcohols, FTOH, takes place both by the application and during use of the

⁸ Overspray is a function of the pressure exerted by the contents of the container, the nozzle diameter, the size and shape of the target, and the size of the particles.

cured coatings. It is assumed that the application method has very limited influence on the life-time releases of the poly- and perfluoroalkyl substances from the products.

C.2.3 Availability of application methods

Various products based on TDFAs for surface treatments of stone, glass, enamel, etc. are available on the EU market.

Some suppliers have indicated that the mixtures (e.g. the Protectocil® product range from Evonik) offers a high degree of application flexibility. The mixtures can for building applications be applied by either brush, roller or using high-volume-low-pressure spraying techniques. The mixtures are widely used for protection of full facades e.g. for anti-graffiti control and for most professional applications other techniques than aerosol application is the preferred application method.

The Fluowet® ETC product range easy-to-clean (ETC) coating (from Clariant) is indicated to either be applied by manual wiping or via spray coating (exact substance not indicated - may otherwise be included in the list of alternatives with fluorosilanes different from TDFAs). The major application area for the mixtures seems to be for non-absorbing surfaces, but the mixtures are also marketed for ceramic, modification of paints and varnishes and treatment of natural fibres like cotton or leather.

C.2.4 Technical and economic feasibility of alternative application methods

The alternative application methods, brush, roller or cloth, are considered to be and economic feasible as these alternatives are available at prices that are comparable to pump and trigger sprays. In terms of price per unit mixture, aerosol dispenser application is a relative expensive method. For the consumer, using small quantities of the mixtures for minor applications, this may be outweighed by the convenience of the method and the fact that the sealed package protects the product and extends its service life. The amount of waste may hereby be reduced.

The technical feasibility of the application methods available for consumers are compared in Table 8.

TABLE 8 COMPARISON OF TECHNICAL FEASIBILITY OF AVAILABLE APPLICATION METHODS FOR CONSUMERS

	Aerosol dispenser	pump or trigger spray	Brush, roller or cloth
Easy to apply to non-absorbing surfaces	+++	+++	+++
Easy to apply to absorbing surfaces	+++	+++	+
Easy to apply to large non-absorbing surfaces	++*	++*	+++
Easy to apply right amount at the right place (smaller surfaces)	+++	++(+)	+
Low risk of leakage	+++	++(+)	+
Long service life	+++	++(+)	+

+++ Represents the highest score

*Large surfaces will in many cases be handled with other spraying equipment (e.g. HVLP-guns) by professionals

For the consumer with limited surface areas to coat, the use of aerosol dispensers is a very convenient application method. For larger surfaces pump or trigger sprays may be preferred. For most professional users aerosol dispensers are not the preferred application method. Other

spray methods or brush and rollers the preferred application methods due to larger surfaces needing treatment. For absorbing surfaces brush, roller or cloth cannot be used as alternative, however, for these surfaces spray application with water-based impregnation agents are usually used (see C 3.4). For some consumer applications, the alternative could likely be not to use any impregnation agents and use more time on cleaning of the surfaces or accept more dirt.

Aerosol dispensers are designed to deliver the right amount of product exactly where it's needed. The same is to a certain extent true for pump and trigger sprays. When using brush, roller or cloth it is more difficult to control the amount of product used.

Aerosol dispensers are hermetically sealed and the mixtures cannot leak. This protects the product and extends its service life. The same is to a certain extent true for pump and trigger sprays, depending of the quality of the sprays. However, working with an open container increases the risk of spillage.

C.3 Assessment of water-based mixtures containing TDFAs

C.3.1 Human health risks associated with water-based impregnating agents

Water-based impregnation products are usually marketed for absorbing surfaces such as concrete, leather, textiles and wood, and although several products are on the market, they are rarely reported as the cause of respiratory illness. Nørgaard et al. (2014) exposed mice to aerosolised water-based NFPs containing TDFAs in addition to seven commercially available products. The results showed that no acute respiratory effects were observed at exposure concentrations up to 110 mg/m³ of the aqueous solution of TDFAs.

Based on these results and the lack of case reports involving water-based impregnation sprays, no specific risk from these water-based products has been identified.

C.3.2 Environment risks related to water-based impregnating agents

The environmental risks related to water-based impregnating agents based on TDFAs applied by aerosol dispensers, pump or trigger spray are considered to be similar to environmental risks of applying mixtures containing TDFAs and organic solvents by aerosol dispensers, pump or trigger spray. The potential environmental effect of most concern is the possible releases of persistent polyfluoroalkyl substances, and this is independent on the solvent used.

Releases of volatile poly- and perfluoroalkyl substances in the mixtures such as residual content of fluorotelomer alcohols, FTOH, takes place both by the application and during use of the cured coatings. It is assumed that the solvent has very limited influence on the life-time releases of the poly- and perfluoroalkyl substances from the products.

C.3.3 Availability of water-based mixtures

Various water-based fluorosilane mixtures are available in pump or trigger spray. It is uncertain to which extent these type of impregnating agents are provided in aerosol dispensers.

Nørgaard et al. (2014) studied the effects of seven commercially available water-based impregnating agents delivered in pump sprays. The impregnating agents were obtained from NanoCover (Denmark), Nanonordisk (Denmark) and Percenta AG (Germany).

According to the Nørgard et al. (2014), analysis of mixtures containing fluorosilanes by electrospray ionization mass spectrometry (ESI-MS) revealed that they all contained hydrolyzed forms of TDFAs. It was by the authors concluded that the mixture contained TDFAs similar to the substances present in organic solvent-based products.

Other information indicates that water-based mixtures containing fluorosilanes are different from the substances in mixtures based on organic solvent. Weißenbach *et al.* (2008) describes the chemistry of various water-based fluoroalkylsilanes based on polyfluorooctyl triethoxysilane. The oligomeric water-based fluoroalkylfunctional siloxanes include reactive silanol moieties combined with hydrophilic groups that are responsible for solubility in water and chemical reactivity. The mixtures are further described in section B.2.1. One of the agents has been described to consist of "siloxanes and silicones, 3-[[2-[(2-aminoethyl)amino]ethyl]amino]propyl hydroxy, hydroxy3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl, hydroxy-terminated, formates(salts)" (CAS No 273737-91-0 (Degussa, 2001)). The SDSs of the commercial mixtures in general do not include information on the composition.

Various water-based mixtures are marketed. As an example, the Dynasytan F 8811 (Evonik) is described as a fluoroalkyl functional water-based oligosiloxane which acts as a surface modification mixture on various substrates such as ceramic and natural fibres like cotton or leather. The reactive silanol groups can bind chemically to an inorganic substrate while aminoalkyl functional groups provide solubility in water. The SDS does not indicate name or CAS number of the active substance.

C.3.4 Technical and economic feasibility of water-based impregnating agents

In general, organic solvent-based impregnating agents are used for non-absorbing surfaces (such as glass and enamels) whereas the water-based impregnating agents may be used for absorbing surfaces (such as tiles, stone and textiles).

For non-absorbing surfaces alternative can be application of organic solvent-based impregnating agents with brush, roller or cloths.

For absorbing surfaces the water-based impregnating agents are considered feasible alternatives. The price of the water-based impregnating agents are according to one manufacturer not much different from the price of the organic solvent-based, but due to differences in application spectra the prices cannot be readily compared.

C.4 Assessment of polyfluoroalkyl trialkoxysilanes with polyfluoroalkyl chain different from octyl

C.4.1 Availability of polyfluoroalkyl triethoxysilanes with polyfluoroalkyl chain different from octyl

Polyfluoroalkyl triethoxysilanes with polyfluoroalkyl chain different from octyl are available on the EU market. The substances are apparently not manufactured within the EU; they are not supplied by major chemical manufacturers in the EU and not planned to be registered by members of the Reconsile Consortium.

Nonafluorohexyl triethoxysilane (C₄ chemistry) is manufactured outside the EU and supplied in the EU for the same purposes in spray products as polyfluorooctyl triethoxysilane. Within the last two years, at least one of the formulators of mixtures which may be used in spray products with polyfluorooctyl triethoxysilanes have replaced the substance with nonafluorohexyl triethoxysilane. Products with this alternative substance are provided in trigger sprays and in cans and may be sprayed on, rolled up or applied by paint brush.

It has been noted by one market actor that replacement of the substance is in line with a general trend in the use of per- and polyfluoroalkyl substances away from the use of C8 chemis-

tries (such as PFOA, PFOS and 8:2 FTOH)⁹ toward the use of C₄₋₆ chemistries, which are considered to be less bioaccumulative. In this terminology, the TDFAs with a chain of six fluorinated carbon atoms, would be considered C6 chemistry. The polyfluoroalkyl chain resemble the chain of the 6:2 fluorotelomers, such as 6:2 FTOH.

According to one formulator, the mixtures typically contain 0.5 and 1.5 % of the nonafluorohexyl triethoxysilane for ready-to-use impregnating agents.

Outside the EU, heptadecafluoredecyl triethoxysilane (C₈ chemistry) is manufactured and marketed for surface coatings, but no information on the availability in the EU has been identified. The general trend in the use of per- and polyfluorinated substances (also per- and polyfluorinated substances without silanes) in the EU and the USA is toward shorter-chain chemistries (as reviewed by Lassen et al., 2013). It is therefore not very likely that producers of aerosol dispensers, pump or trigger sprays would substitute polyfluorooctyl triethoxysilanes for per or polyfluoroalkyl substances based on C8 chemistry. However, it cannot be ruled out that some importers may change to polyfluoroalkyl trialkoxysilanes with longer chain length.

C.4.2 Human health risks associated with polyfluoroalkyl triethoxysilanes with polyfluoroalkyl chain length different from octyl

Only little effect on pulmonary function were seen in mice following short term exposures to aerosolised polyfluorooctyl triethoxysilane. Aerosolised mixtures containing polyfluorooctyl triethoxysilane and organic solvent (2-propanol) showed a significant concentration-dependent decrease on the VT, Nørgaard et al. 2010a. No specific information on pulmonary function is available for aerosolised mixtures containing polyfluoroalkyl triethoxysilanes with polyfluoroalkyl chain length different from octyl and organic solvent.

No specific information on human health endpoints is available for the polyfluoroalkyl triethoxysilanes with polyfluoroalkyl chain length different from octyl. However, given the structural similarity with TDFAs it is not unlikely that these substances in mixtures with organic solvents would have some effect on lung surfactants if aerosolised.

C.4.3 Environment risks related to polyfluoroalkyl triethoxysilanes with polyfluoroalkyl chain length different from octyl

The environmental risks of the use of the substances is to a large extent related to the possible release of persistent per- and polyfluoroalkyl substances (PFAS) during the entire lifecycle of the mixtures.

Data on the content of PFAS in the mixtures are not available. The mixtures are in chemical structure quite similar to side-chain-fluorinated polymers used in impregnating agents for textiles, leather, stone, etc. with the difference that the carbon backbone is replaced with a siloxane backbone. The fluorinated intermediates used in the production of the two types may likely to be the same. As an example, the raw material polyfluorohexyl ethyl iodide, DuPont™ Capstone™ 62-I used in producing high performance repellents and surfactants is both used for various side-chain-fluorinated polymers and for water- and oil-repellent fluorine-modified silicones (Dupont, 2008). Of importance is that most likely the non-polymeric PFAS in the final product contain a mixture of substances with different chain lengths. This is indicated by the fact, that raw materials for manufacture of short-chained fluorine chemistries are mixtures of different chain lengths. In the case of the Capstone™ 62-I, the product consist of polyfluorohexyl ethyl iodide (85.0% min), polyfluorobutyl ethyl iodide (5.0 % max), polyfluorooctyl ethyl iodide (2.0–10.0%), polyfluorodecyl ethyl iodide (6.0% max) and other polyfluoroalkyl ethyl iodides (1.0 % max) (Dupont, 2008). This variation in chain lengths is reflected in variations in

⁹ PFOA: Perfluorooctanoic acid (EC No 06-397-9), PFOS: Perfluorooctane sulfonic acid (EC No 217-179-8), 8:2 FTOH: 8:2 Fluorotelomeralcohol (EC No 211-648-0)

chain lengths of the side-chains of the final products and the residual content of PFAS, as has been demonstrated in many studies of impregnated textiles (e.g. Knepper et al., 2014; SFT, 2006; Herze et al., 2009).

Materials treated with impregnating agents based on side-chain-fluorinated polymers contain low concentration of various per- and polyfluoroalkyl substances. The substances may either be residual substances from the manufacture or application of the impregnating agents or they may be formed by hydrolysis of the bond between the side-chains and the carbon backbone during use. A similar process most probably takes place in the fluorosilane-based mixtures. The dominant substances are in general the volatile fluorotelomer alcohols (predominantly 6:2 FTOH, 8:2 FTOH and 10:2 FTOH) and the perfluoroalkyl carboxylic acids (predominantly PFHxA, PFNA and PFOA) (as summarised in Knepper et al., 2014). The released fluorotelomers may serve as precursors for formation of perfluoroalkyl substances. As an example, while the fluoroalkyl part of 8:2 FTOH is very stable, the 8:2 FTOH is degraded to the persistent perfluorooctanoic acid (PFOA) and perfluoroheptanoic acid (PFHpA) or transformed to perfluorononanoic acid (PFNA) in the environment (Buck et al., 2011). With a similar process the 6:2 FTOH is assumed to be degraded/transformed to the persistent perfluorohexanoic acid (PFHxA), perfluoropentanoic acid (PFPA) and perfluoroheptanoic acid (PFHpA) in the environment.

No data are available, but most likely PFAS released from surfaces treated with mixtures based on short-chain fluorosilanes will tend to be short-chain.

The data on the fate and effects of short-chain PFAS in the environment is more limited than the data on the C₈ PFAS such as PFOA, PFOS and 8:2 FTOH.

PFOS, PFOA and other long-chain per- and polyfluorinated carboxylic and sulfonic acids and their salts, and the long chain homologues, are all extremely persistent in the environment (abiotically and biotically) and they bioaccumulate in particular in mammals and birds, despite not fulfilling the traditional bioaccumulation criteria based on bioconcentration in fish. They are not very toxic to aquatic and other organisms based on standard toxicity endpoints, but there are indications that they have certain endocrine disrupting properties (as reviewed by Lassen et al., 2013).

The short-chain PFAS are as persistent in the environment as the long-chain homologues, but do not bioaccumulate to the same extent as the long-chain PFAS, as they are excreted more rapidly from the organisms studied. No data on the ecotoxicity of the short-chain fluoroalkyl carboxylic and sulfonic acids have been obtained. (as reviewed by Lassen et al., 2013).

As the silane part of the mixtures is the same, possible effects related to the silane part of the mixtures are considered to be the same regardless of the length of the polyfluorinated side chains.

The releases from both the polyfluorooctyl triethoxysilane and the polyfluorohexyl triethoxysilane would mainly be short-chained PFAS (as compared to C₈ chemistry) and it is not possible on the basis of the available data to assess whether the environmental effects would be smaller when nonafluorohexyl triethoxysilane are applied.

C.4.4 Technical and economic feasibility of TDFAs with polyfluoroalkyl chain length different from octyl

According to an identified formulator of consumer products, polyfluorohexyl triethoxysilane has substituted polyfluorooctyl triethoxysilanes in consumer products produced by the company. The change from one polyfluoroalkyl alkoxysilane to another is described as rather unproblematic for the production of impregnating formulations, because the same production facilities can be used for polyfluoroalkyl alkoxysilane with different polyfluoroalkyl chain lengths. However, C₄ polyfluoroalkyl alkoxysilanes are stated to possess a lower performance (ca. 90-95%

of hydrophobic properties and ca. 70-80% of oleophobic properties compared to C6 polyfluoroalkyl alkoxy silanes.

The formulator indicates that the final coating may be slightly less stable when mixtures with shorter polyfluoroalkyl chains is used. This could mean that that amount of substances with shorter polyfluoroalkyl chains used over the years will be higher compared to TDFAs. Formulators of mixtures based on these alternatives have not provided any information on the technical and economic feasibility of the alternatives as compared with mixtures based on TDFAs.

With respect to costs of different polyfluoroalkyl substances, no definite information could be obtained from substance producers or importers. Indicative prices from a German chemical manufacturer, importer and formulator¹⁰ suggest that prices increase with increasing chain length of the polyfluoroalkyl alkoxy silanes. The substances are used in concentrations of <2% in the final spray products. According to the available information, changing the substance to a shorter-chain substance have not influenced the price of the final spray product.

TABLE 9. PRICES ON TDFAs AND FLUORINATED ALTERNATIVES

Substance, purity	CAS	Alkyl chain length **	Price per 25 g (€)
Nonafluorohexyltriethoxysilane; 95%	102390-98-7	C4	116
Nonafluorohexyltrimethoxysilane; 95%	85877-79-8	C4	165.8
1H,1H,2H,2H-Perfluorooctyltriethoxysilane; 97% (TDFAs)	51851-37-7	C6	198
1H,1H,2H,2H-Perfluorooctyltrimethoxysilane; 97% (TDFAs)	85857-16-5	C6	385
(Tridecafluoro-1,1,2,2-tetrahydrooctyl)trichlorosilane; 97%	78560-45-9	C6	60.4*
(Heptadecafluoro-1,1,2,2-tetrahydrodecyl)triethoxysilane; 97%, stabilized with copper	101947-16-4	C8	217
(Heptadecafluoro-1,1,2,2-tetrahydrodecyl)trimethoxysilane; 95%	83048-65-1	C8	207.6
<i>Non-fluorinated alternatives</i>			
Hexadecyltrimethoxysilane; 90%	16415-12-6		13.40

* Price not available for the quantity of 25 g, calculated based on the price for the listed quantities of 10 and 50 g.

** Note the total length of the carbon chain is longer as the substances contain two non-fluorinated carbon atoms .

C.5 Assessment of the use of products without polyfluoroalkyl trialkoxysilanes

C.5.1 Human health risks associated with products without polyfluoroalkyl trialkoxysilanes

Silane/siloxane chemistries

Nørgaard et al. (2010a) exposed mice to a non-fluorinated alkylsilane-based product containing ethanol and methanol as solvents and found no significant effects at the concentrations studied (up to 60 mg/m³).

¹⁰ ABCR GmbH. <http://www.abcr.de/de/produkte/>

In a recent case from Greenland, where 39 people were hospitalized, following exposure to a proofing spray used occupationally and using high pressure spray application (135 bar), the product was analysed and no fluorinated compound was identified. Instead this product contained nonfluorinated alkylsiloxanes (See Appendix 1, Greenland).

It is not clear to what extent the incidents reported in Table 5 involve incidents with non-fluorinated silanes/siloxanes.

Health risks - The silanes and siloxanes is a complex group of substances and information have not been obtained for the specific substances in the silane/siloxane mixtures used for relevant applications. The most well described substances are the cyclic and short chain linear siloxanes (used for other applications), but in this context, data on the linear polydimethylsiloxanes (PDMS, CAS No. 63148-62-9) is more relevant as the PDMS is used as components of the impregnating agents, and the substance may be used as an indicator for the effects of silane/siloxanes.

Linear polydimethylsiloxanes as a type of non-volatile (odourless), fluid (viscous) "silicones", have been evaluated in a comprehensive monograph published by the European Centre for Ecotoxicology and Toxicology of Chemicals (ECETOC, 2011). High molecular weight PDMS have many different applications and may be incorporated into a matrix and become solid e.g. in silicone coatings.

Humans may be exposed to PDMS via oral ingestion and dermal contact. In laboratory animals, PDMS had a low potential for absorption via these routes. Swallowed PDMS is rapidly excreted unchanged in the faeces. Aerosolised PDMS may give rise to inhalation exposure, but there is no indication of any adverse effects. PDMS is not a skin irritant or a skin sensitizer, and it is only mildly to non-irritating to the eyes. Acute and repeated dose toxicity studies conducted in laboratory animals on PDMS of different viscosities do not show any significant adverse effects. Long-term chronic/carcinogenicity and reproductive toxicity studies were also without adverse effects. PDMS is not mutagenic in vitro.

PDMS is used in urology, ophthalmology and dermatology (skin correction). Autoimmune disorders (e.g. scleroderma) cannot be linked to PDMS. Several human diseases (connective tissue, atypical connective tissue, rheumatic and autoimmune diseases, and breast cancer) have been reported after injection of PDMS (for cosmetic purposes) or placement of breast implants (made of high viscosity PDMS). These diseases are, however, not associated with PDMS. In humans, PDMS has no effect on the immune system.

According to the ECETOC assessment, overall, PDMS does not present a risk to the environment or to human health (ECETOC, 2011).

PFAS-based chemistries

Health risks - Only little effect on pulmonary function were seen in mice following short term exposures to aerosolised polyfluorooctyl triethoxysilane. Aerosolised mixtures containing polyfluorooctyl triethoxysilane and organic solvent (2-propanol) showed a significant concentration-dependent decrease on the VT, Nørgaard et al. 2010a. No specific information on pulmonary function is available for mixtures containing PFAS.

Apart from the risk of acute pulmonary effects from spray application of mixtures containing PFAS, the human health risks associated PFAS are associated with the possible releases of the substances during the entire lifecycle of the impregnating agents. PFOA, PFOS and other long-chain per- and polyfluorinated carboxylic and sulfonic acids and their salts, and the long chain homologues, are known to cause serious health effects.

A restriction under REACH has been proposed for PFOA and PFOA-related substances, since PFOA is a persistent, bioaccumulative and toxic (PBT) substance, which means that it persists

in the environment and may have irreversible adverse effects on the environment and human health in the long term. PFOA has the potential for environmental long-range transport, which makes emissions of PFOA a trans boundary pollution problem. In addition, PFOA is toxic for reproduction (category 1B) and has been shown e.g. to affect cholesterol levels in humans (ECHA 2014).

PFOS and derivatives are included in the list of restricted substances under the Stockholm Convention on persistent organic pollutants (POP) and are in the EU restricted via Annex XVII of REACH. PFOS is toxic for reproduction (category 1B).

PFAS-based impregnating agents based on short chain fluorine chemistry (C₄₋₆) is available. Short chained PFAS is as persistent as the long chained PFAS but less bioaccumulative. Toxicity has not been investigated as thoroughly as the long chained.

C.5.2 Environment risks related to products without polyfluoroalkyl trialkoxysilanes

Silane/siloxane chemistries

According to the ECETOC (2011) assessment, PDMS (linear polydimethylsiloxanes) is not considered persistent, bioaccumulative and toxic (PBT) or very persistent and very bioaccumulative (vPvB) as defined in the REACH Regulation. Overall, PDMS does seem not present a risk to the environment or to human health (ECETOC, 2011). As mentioned above, overall, PDMS does not present a risk to the environment or to human health (ECETOC, 2011).

PFAS-based chemistries

PFAS-based impregnating agents based on short chain fluorine chemistry (C₄₋₆) is available and the fluorinated part of the mixtures would resemble the fluorinated parts of the TDFAs. Consequently the environmental effects as concern the fluorinated part is expected to be similar to the effects of the TDFAs.

C.5.3 Availability of products without polyfluoroalkyl trialkoxysilanes

Different chemistries are used in the manufacture of impregnating agents for various applications and several different types of water- and oil-repellents are marketed. According to the Danish Aerosol Industry Association (AIB), aerosol dispensers containing impregnation agents based on siloxane/silicone chemistry and side-chain-fluorinated polymers (carbon backbone instead of siloxane) are marketed. The exact substances/mixtures are not known to the association.

A Danish survey of textile proofing spray products (Feilberg et al, 2008), reviewed product information for 26 impregnation (proofing) spray products on the Danish market for consumer products. Sixteen of the spray products were provided in aerosol dispensers, the latter ten in pump sprays (type not further specified). The active substances were indicated for seven of the products, but only at overall type level. The substances were PFAS-based impregnation agents (indicated as fluoroalkylpolymer, fluoropolymer, acrylate fluoropolymer, aliphatic fluorine compound, etc.), silicone-based agents, or melamine.

No data have been submitted during consultation with industry indicating which substances/-mixtures are used in aerosol dispensers, pump or trigger sprays, but data on substances for relevant applications may indicate which substances could be used. Most products marketed for water- and oil-repelling coatings, besides mixtures based on polyfluoroalkylsilane, are based on either silane/siloxane chemistries or side-chain-fluoroalkyl polymers (PFAS-based polymers). The actual products are often copolymers e.g. siloxane/acrylic copolymers.

Examples of impregnating agents based on PFAS-based polymers for similar applications are DuPont's Capstone® ST-100HS, ST-110, ST-300 and ST-500 that can be diluted in water, and Capstone® ST-200 that can be diluted in organic solvents, to create oil- and water-repellent sealers for natural stone (e.g., granite, marble or limestone), porous tile, grout and masonry (Dupont, 2014). The product data do not indicate the application on glass or enamel. The mixtures are based on short chain, C₄₋₆ fluorine chemistry. It is indicated that the products may be applied using a saturated brush, roller, or mop, or a low-pressure garden-type sprayer.

Examples of silane/siloxane-based mixtures for application on stone, concrete and masonry protection "easy-to-clean" applications are some of the products in the SILRES® product range from Wacker Chemie AG (2014). The SILRES® BS 38 masonry water repellent furthermore is indicated to be based on an organic solvent-based mixture of silane, siloxane and side-chain fluorinated polymers (< C₈). It is not clear from the description whether the mixtures contain polyfluoroalkyl trialkoxysilanes. Many products based on silane/siloxane mixtures without the fluorinated polymers are marketed, e.g. SILRES® BS 280 water repellents for impregnating mineral building materials.

For consumers, various polyfluorosilane-based products are provided in pump or trigger sprays. From internet stores it is the impression that trigger sprays account for a larger share of the market than aerosol dispensers. Due to limited information on the content of the actual products, it is difficult to assess to what extent the trigger spray products contain TDFAs or other per- or polyfluorosilanes.

C.5.4 Technical and economic feasibility of products without polyfluoroalkyl trialkoxysilanes

Technical feasibility

Table 10 shows difference in performance between mixtures based on polyfluorosilanes (F-silanes) and other mixtures. The comparison is from an older technical datasheet from Bayer Silicones (2004) who manufactured/formulated some of the alternatives. The mixtures containing polyfluorosilanes, are according to the comparison, outstanding as concern stain resistance on concrete, terracotta and claybrick, but have less water repellence than some of the alternatives and are relative expensive. The differences are reflected in the fact that the mixtures containing polyfluorosilane are mainly marketed for applications where oil and stain resistance (including anti-graffiti) is required. Mixtures based on silicones/siloxanes (without fluor) are efficient in water repellence and are today the mixture of choice for applications where water repellence is the main property required. For oil-repellence, mixtures based on PFAS-technology (with silane or carbon backbone) are the most efficient.

TABLE 10 COMPARISON BETWEEN IMPREGNATING AGENTS BASED ON MIXTURES CONTAINING POLYFLUOROSILANES AND IMPREGNATING AGENTS BASED INTENDED FOR TREATMENT OF MASONRY MATERIALS. (BASED ON GE BAYER SILICONES, 2004)

Impregnating agent	Performance			Costs
	Water repellency	Anti-stain performance	Change of surface appearance	
WO	++	++	+	Reasonable
F-Polymer	+/0	++	-	High
Siloxane	++	-	++	Fair
F-Silane	+/0	++	--	Very high
Organic AS	--	-	--	Fair-high

Legend: ++ = very good, + = good, 0 = fair, - = bad, -- = very bad

WO: Water-based emulsion of an alkylated alkoxy siloxane and a fluorinated polymer from Bayer. Organic AS: non-defined organic anti-stain product.

The same result is reached in a research report on "Durable Water and Soil Repellent Chemistry in the Textile industry" published within the framework of the Roadmap to Zero Discharge of Hazardous Chemicals (ZDHC) concerted action (ZDHC, 2012). According to the report, there are a number of products based on non-PFAS available on the market, which provides durable water repellence to textiles whereas non-fluorinated chemistries for oil and dirt repellence are very limited or non-existing. (ZDHC, 2012).

Compared to mixtures containing poly- or perfluoroalkyls, mixtures containing polyfluoroalkylsilanes make a stronger binding to non-absorbing surfaces. As an example a Swiss building sector company in a comparison between different surface mixtures for concrete, notes that graffiti-protecting mixtures based on polyfluoroalkylsilanes have a service life of >15 years whereas the listed alternative has a service life of 2-3 years. (Wolfseher, 2014).

The R&D expert of an identified formulator presumes that other per- or polyfluorinated silanes such as polyfluorooctyl trichlorosilan theoretically may be used for impregnating formulations. Nonetheless, longer reaction times due to the smaller reactivity of the chlorosilanes have to be expected, making their application less efficient and less feasible.

Substituting polyfluorinated silanes with non-fluorinated alternatives such as waxes and silicones is considerably more demanding, since it requires different production facilities and possibly more additives (e.g. preservatives) would be needed. Furthermore, a decline of the oleophobic performance of the formulation is inevitable.

Economic feasibility

Mixtures based on polyfluoroalkylsilanes are considered more expensive than mixtures not based on polyfluoroalkylsilanes.

On non-absorbing surfaces, mixtures based on polyfluoroalkylsilanes make a stronger binding and the impregnation last for longer time. For the consumer applications, the impact of the shorter service life of the impregnation on the feasibility is difficult to estimate. However, for applications where the properties provided by the polyfluoroalkylsilanes are desired (water repellence, anti-stain performance and surface appearance), the consumer most likely would rather select an alternative application method than products that are not based on polyfluoroalkylsilanes.

C.6 Summary on alternatives

The assessment of alternatives is summarised below in Table 11. From a technical point of view the most feasible alternative for non-absorbing surfaces, are to use alternative application methods (brush, roller or cloth) for the addressed TDFAs. For absorbing surfaces the most feasible alternative are to use mixtures containing polyfluoroalkyl triethoxysilanes with polyfluoroalkyl chain different from octyl or water-based mixtures containing TDFAs in aerosol dispensers, pump or trigger sprays. By use of alternative application methods, the exposure of users is considered to be smaller whereas no data exist to assess whether the use of polyfluoroalkyl triethoxysilanes with polyfluoroalkyl chain different from octyl in aerosol dispensers, pump or trigger sprays would result in less effects compared to the use of the targeted substances in aerosol dispensers pump or trigger sprays. For alternatives with water-based TDFAs it is uncertain whether the alternatives have acceptable technical properties on non-absorbing surfaces and products without polyfluoroalkylsilanes apparently have some technical drawbacks.

The alternative, of not using any impregnating agents at all for the relevant applications, but use more time on cleaning or accept more dirt, have not been assessed.

TABLE 11 EXAMPLES OF ALTERNATIVES TO USING AEROSOL DISPENSERS, PUMP OR TRIGGER SPRAYS WITH MIXTURES CONTAINING TDFAs AND ORGANIC SOLVENTS

Alternative	Availability	Technical feasibility	Economic feasibility (price compared to targeted mixtures)	Human health	Environment
Alternative application methods for the mixtures concerned (brushes, rollers or cloths)	Readily available for some applications. Not available for all absorbing surfaces	Less - it may be more difficult to make an even distribution of the impregnation agents	From lower to approximately the same	Exposure of users is lower	Environment releases from outdoor uses are probably smaller
Aerosol dispensers, pump or trigger sprays containing water-based mixtures with TDFAs	Readily available	Uncertain whether alternatives have the same application spectrum - seems mainly to be used for absorbing surfaces	Approximately the same, but not readily comparable due to different application spectra	Appears to be less toxic to the user	Environmental releases and effects are probably approximately the same
Polyfluoroalkyl triethoxysilanes with polyfluoroalkyl chain length different from octyl without TDFAs as impurities	Readily available for similar applications (uncertainty in relation to impurities)	More or less the same - final coating may be slightly less stable	Approximately the same	No data on differences in toxicity to the user by aerosol, pump or trigger spray application	Environmental releases and effects are probably approximately the same
Products without polyfluoroalkylsilane	Readily available	Silicones/siloxanes do not provide the same oil and dirt repellency PFAS-based impregnation agents do not provide the same adherence to non-absorbing mineral surfaces	Lower, but the coatings may last for shorter time - not readily comparable due to partly different application spectra	No data on differences in toxicity to the user by aerosol, pump or trigger spray application - effects may be the same for some substances, but have not been demonstrated	May be approximately the same, but data are sparse

D. Justification for action on a Union-wide basis

D.1 Considerations related to human health and environmental risks

Aerosolised products containing mixtures of TDFAs and organic solvent have been shown to cause serious lung injury in mice. In addition numerous cases where consumers have contacted poison control centres or admitted to hospital with acute respiratory illness after using proofing/impregnation sprays product confirm that exposure to spray products containing fluorinated constituents and solvents may result in the same effects as observed in mice.

Little information is usually available to the consumers on the hazard of the products and it is therefore difficult for the consumers to be aware of the specific hazards and conditions that may result in a high risk. Although labelled on spray products that they should only be used outdoors, experience shows that consumers have used the products indoors with resulting health effects. For some product types such as impregnation products for tiles it is also not realistic to expect that these products will be used outdoors.

A worst case risk assessment based on realistic worst case scenarios involving a floor sealant shows that the related exposure would impose an unacceptable risk for the consumer.

Environmental risks are not considered significant.

D.2 Considerations related to internal market

The proposed restriction covers products that are marketed and probably used in all Member States. According to the consultation of Member States, no Member States have established national restrictions on the targeted spray products.

The spray products may both be produced in and imported into the EU. The justification for acting on a Union-wide basis originates from preventing Member States from adopting different legislative requirements with the risk of creating unequal market conditions:

- The proposed restriction would remove the potentially distorting effect that national restrictions may have on the free circulation of goods;
- Regulating TDFAs through Union-wide action ensures that the producers and importers of the targeted spray products in different Member States are treated equally. As noted in section G the European Aerosol Federation covers more than 350 companies active in 18 European countries. Furthermore some manufacturers may be relatively small companies and not members of business organisations. Therefore, most probably relevant actors are scattered in various EU countries;
- Acting at Union level would ensure a 'level playing field' among all producers and importers of the targeted spray products.

According to industry, the use of TDFAs for aerosol sprays and pump and trigger sprays for consumers represent a relatively small part of the market for TDFAs.

E. Justification for the proposed restriction being the most appropriate Union-wide measure

This section provides justification for why the proposed restriction is the most appropriate Union-wide measure. It gives an overview of the effectiveness, practicality and ease of monitoring of the proposed restriction. Other risk management options are also evaluated.

E.1 Identification and description of potential risk management options

See section E.1.2 for an outline of the proposed restriction.

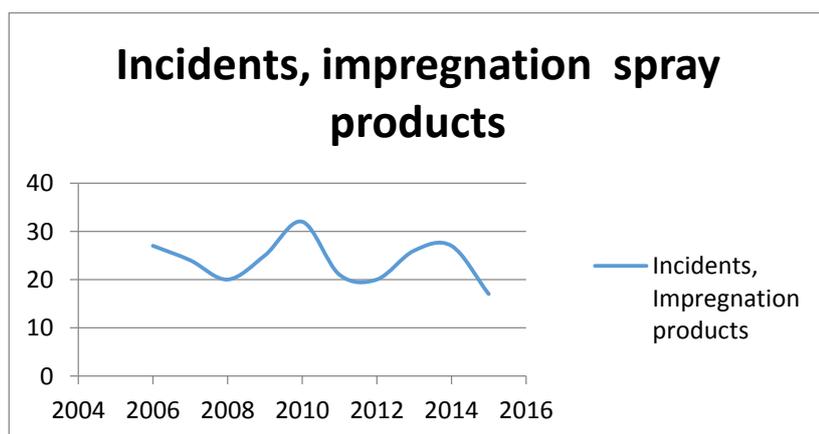
E.1.1 Risk to be addressed – the baseline

As described in section B.5.2.2, incidents of respiratory illness related to exposure to spray products typically occur in outbreaks related to the release of new or reformulated products on the market. Often these products are subsequently withdrawn from the market. Table 5 provides an overview of those incidents in Europe that have been reported in the literature as well as information directly received from poison centers or hospitals. It is likely that there are even more incidents where the exposed consumers suffer milder symptoms and do not report to poison centers, doctors or hospitals. In addition it could be expected that many incidents are not identified as related to the actual exposure.

The identified incidents of pulmonary distress related to consumer use of impregnation sprays containing TDFAs and organic solvents in Europe in the period from 1979 to 2011 presented in Table 5 provides a figure of 272 incidents or on average 8.5 incidents per year. The figure of 272 incidents is considered largely to underestimate the real number as the majority of incidents are not likely to be recorded and as it is not likely that a link between the actual exposure and the effects will be established in all cases.

In the period 2006-2015, the Poison Control Hotline in Denmark annually received 250 calls (range 100 to 360) related to spray products in general. Except for one year, the number has increased over the period. Of these 24 calls (range 17 to 32) were related to impregnation products. Figure 2 shows the number of such calls over the years.

FIGURE 2 CALLS TO DANISH POISON CONTROL HOTLINE REGARDING IMPREGNATION SPRAY PRODUCTS



Extrapolating these numbers of calls to the Poison Control Hotline regarding impregnation spray products from the Danish population to the total EU population¹¹, would correspond to 2200 calls (range 1500 - 2900 calls). Assuming that in line with Table 5 that 20 to 40% is re-

¹¹ EUROSTAT, 2015: Danish population 2014: 5.6 M, EU population 2014: 507.4 M.

lated to exposure of TDFAs in organic solvents, the yearly average number of incidents in EU28 is between 430-860 incidents. According to The Danish Poisoning center, app. 75% of the calls regarding impregnated products are related to consumer products.

In conclusion, the best estimate of reported incidents in Denmark extrapolated to EU28 is 330-660 incidents. It is stressed that the number is based on outbreaks of poisoning and that the chemical content of the products was not reported, and the number of products potentially containing TDFAs is not known. On the other hand, not all incidents are reported.

Little information is available on the occupational use of and exposure to spray products containing the TDFAs in the EU. However, as described in B.8.2.1 only few incidents of occupational exposure to impregnation sprays in aerosol dispensers resulting in respiratory illness are reported (Appendix 1, Table 1 - 2) and three of the occupational incidents reported involved pump spray. Therefore, it is considered that it is only relevant to address risk for consumers.

E.1.2 Options for restrictions

Three options for restriction are assessed (see section E.2)

- **RMO 1:** (the proposed restriction): Ban of mixtures containing TDFAs and organic solvent in spray products (aerosol dispensers, pump and trigger sprays and mixtures marketed for spray application) for consumer use in a concentration of TDFAs equal to or greater than 2 ppb by weight.
- **RMO 2:** Risk-based ban of mixtures containing TDFAs and organic solvent in spray products for consumer use in a concentration of TDFAs equal to or greater than 0.00004 % (0.4 mg/kg, 400 ppb). In order to address that the TDFAs may be present as impurities.
- **RMO 3:** Ban of mixtures containing TDFAs and organic solvent in aerosol dispensers for consumer use in a concentration of TDFAs equal to or greater than 2 ppb by weight.

E.1.3 Other Union-wide risk management options than restriction

The following other Union-wide risk management options have been considered in the process of developing the proposal for a restriction.

Risk Management Options that can be initiated by Member State Competent Authorities under REACH or CLP:

- Harmonised C&L
- Inclusion in the candidate list and eventual inclusion in Annex XIV

Other Risk Management Options at EU level and relevant for this type of risk management:

- Amendment to CLP Annex II part 3
- Establishment of an IOEL for the workers environment under Workers' Legislation
- Product Safety Directive
- Voluntary agreements
- Information "campaigns"
- Labelling

The risk is associated with certain applications of impregnating agents where TDFAs are used in combination with organic solvents. The main risk is not related to TDFAs *per se*, but with the hydrolysates and condensates of TDFAs and organic solvents used under certain conditions by consumers.

Screening of other Risk Management options under REACH/CLP

Harmonised C&L – Introducing a harmonised classification and resulting labelling of spray products may, depending on the classification, either prevent the marketing of the products to consumers or provide consumers with appropriate advice on which risk management measures that should be introduced and adhered to.

Based on the limited information available, the parent substances do not fulfil the criteria in CLP, Article 36(1) for proposing a harmonised classification.

The mixture of TDFAs and organic solvents may fulfil the classification criteria as acute toxic depending on the organic solvent – a mixture of TDFAs and 2-propanol fulfil the criteria for classification with Acute Toxicity, Category 1, while the product NFP 1 fulfils criteria for classification with Acute Toxicity, Category 2. Therefore, producers of the spray products containing TDFAs and organic solvents should classify and label the containers appropriately in accordance with this. However, it seems that in none of the incidents reported, the products were labelled as acute toxic to humans. Nevertheless, as only classification of substances can be harmonised under the CLP Regulation (cf. articles 36-38), it is not relevant to consider this risk management option for the mixture.

Inclusion in the Candidate List with the aim of inclusion in Annex XIV - Based on the limited information about the substances and the lack of registrations, the substances do not fulfil the Article 57 criteria for identification as a Substance of Very High Concern and already for this reason this RMO is not relevant.

Screening of Other Risk Management Options at EU level

Amendment to CLP Annex II part 3 on special rules on packaging – Introducing an amendment to CLP Annex II part 3 stating that “Substances or mixtures classified as Acute Toxic in Category 1 or 2 by inhalation shall not be supplied to the general public in aerosol dispensers, pump and trigger sprays and mixtures marketed for spray application” will remove the most dangerous impregnation products from the market if they are classified correctly. According to CLP, Article 53 it is the Commission that may adjust and adapt the Annexes to CLP. Since it at the same time looks as though none of the incidents reported, the products were labelled as acute toxic to humans introduction of an amendment to CLP is not considered a relevant RMO in the context of this proposal

Establishment of an IOEL - Another legislative measure that theoretically could be an option is the establishment of an IOEL for the workers environment under Workers’ Legislation. However, this measure will not address the risks posed to the consumers, which is the target group for this restriction proposal. Therefore, this is not considered a relevant RMO in the context of this proposal.

Product Safety Directive - This option is rejected as it seems that the knowledge by importers/producers about the risk when combining polyfluoroalkyl silanes with organic solvents in spray products is limited (if existing). Furthermore, regulating through this directive can only be done on a case-by-case basis and will have to be reviewed at regular intervals as was the case for dimethyl fumarate (DMFu). Lastly according to Art. 13 of the Directive, this legal instrument can only be used when the risk cannot be dealt with, in view of the nature of the safety issue posed by the product, in a manner proportionate with the degree of urgency of the case, under other procedures laid down by the specific Union legislation applicable to the products concerned. In this case REACH is the relevant specific Union legislation dealing with regulation of substances and mixtures. For all these reasons the PSD is not considered to be an appropriate measure.

Voluntary agreements - It is considered not possible to achieve a comprehensive and effective result by a voluntary agreement. The targeted problem is an EU wide problem as there

have been several incidents in different Member States. As indicated under the Stakeholder Consultation, the European Aerosol Federation, FEA, does not consider Risk Management Options of the targeted mixtures to be an issue for its members. Many importers and/or producers of the targeted spray products are likely to be small and medium-sized companies which are not members of the national trade associations. The risk that companies, which are not parts of an voluntary agreement, will still place such spray products on the market despite a voluntary agreement among some parties is very high and therefore voluntary agreements (either Union-wide or national) are not an option that would effectively eliminate the risks.

Information campaigns, including labelling - Information campaigns directed to the consumers would have very limited effect, if any, on this problem. Only very few consumers are in a position to choose other products than those recommended by retailers. Experience shows that even if it is stated on the label of the spray products that the product should only be used outdoors, consumers have used the products indoors with resulting health effects. For some product types such as impregnation products for furniture it is also not realistic to expect that these products will be used outdoors in all cases. For those designated for being used in bathrooms it is obviously not possible to use them outdoors.

Since human incidents are reported for impregnation product with content different than mixtures containing TDFAs and organic solvents an Union-wide information campaign directed at formulators, producers and distributors on how to classify and label impregnation spray products correctly according to CLP could be suggested. The effect of such a campaign is considered to be uncertain.

Conclusion

Based on the screening it is concluded that a restriction is the most appropriate option.

E.2 Assessment of risk management options

E.2.1 Restriction option 1

Introducing a ban of mixtures containing TDFAs and organic solvent in spray products (aerosol dispensers, pump and trigger sprays and mixtures marketed for spray application) for consumer use in a concentration of TDFAs equal to or greater than 2 ppb by weight (the proposed restriction).

E.2.1.1 Effectiveness

E.2.1.1.1 Risk reduction capacity

Lung injuries from use of spray products containing TDFAs and organic solvent by consumers will be avoided.

The proposed restriction clearly targets the risks for the consumer documented by risk assessment based on animal experiments and supported by human case histories. A restriction on the use of spray products containing TDFAs and organic solvents would directly remove the risk to consumers related to this application form. A limit value of 2 ppb for placing on the market is introduced as this is the detection limit of the proposed analytical methods (see E.2.1.2.1).

Other sources (substance combinations or application methods) might result in pulmonary injuries. However, no animal studies are available which might link these with the human inci-

dents. For the incidents reported there is not sufficient information available on the product composition in order to prepare a restriction proposal.

Even if the mixtures may not be placed on the market for filling into sprays by the consumer, mixtures marketed for application by cloth, roller or brush may be used by some consumers in various types of spray guns. It is speculated that only few consumers would go through the trouble of buying spraying equipment separately. Consumers doing so will probably be more willing to read the label.

The possible environmental impact of the use of the mixtures is considered to be associated with the possible releases of polyfluoroalkyl substances (fluorotelomers) and the subsequent formation of persistent per- or polyfluorinated substances in the environment. The most likely alternatives will be the use of other application methods of the same mixtures. Used outdoors, the application by spray products may lead to higher releases to the surroundings. The releases of the polyfluoroalkyl substances may take place both during application and by the subsequent weathering of the surfaces. In the perspective of the releases during the entire lifecycle of the impregnating agents, the changes in the environmental risks/impacts due to changed application methods are considered small.

E.2.1.1.2 Costs

For some non-absorbing surfaces, application by brush, roller or cloth is technically feasible (and mixtures are marketed for such application), but for some applications, e.g. on rough absorbing or non-uniform surfaces, application by brush, roller or cloth would be more difficult. However, for consumer use, the difference is considered to be small for the typical use of the mixtures on non-absorbing surfaces such as glass, enamel, ceramics and stone. Products to be applied by cloth, rollers or brushes are available at similar prices¹² as spray products.

For other applications, where the mixtures are used for water and dirt repellence of non-absorbing surfaces, water-based spray products containing TDFAs are available at prices that are comparable to prices for pump and trigger sprays¹³. Impregnating agents based on mixtures without polyfluoroalkyl trialkoxysilanes may not provide the same properties and the impregnation may not bind so strong to the surface (i.e. they last for shorter time) according to industry. Spray products based on mixtures without TDFAs are available at similar prices.

Thus, the alternatives (e.g. use of alternative application techniques) are in general considered not to be more expensive than the restricted mixtures/application techniques. The consumer may use marginally more time for the application and use marginally more of the product by the use of alternative techniques.

Significant costs for the producers are not expected. Producers may have to adjust the production to other substances. If polyfluoroalkyl trialkoxysilanes with a polyfluoroalkyl chain different from octyl are used, the costs are expected to be negligible, as these substances are readily available as drop in alternatives at comparable prices, cf. Table 9

As described under C.4, TDFAs may be present in small percentages in mixtures based on organic solvents and polyfluoroalkyl trialkoxysilanes with polyfluoroalkyl chain different from octyl. If TDFAs are present in an aerosol dispenser in a concentration above 0.00004 % (400 ppb) in a mixture containing organic solvent, this spray product presents a risk of serious injury, which needs to be controlled (see B.9.1.1.2). In these cases, the only substitutes would be water-based mixtures containing TDFAs, mixtures without TDFAs in combination with organic solvents as well as alternative application methods for the mixtures concerned.

¹² For one product the difference in price for a trigger spray product is about 50-100 % higher than a product for other application methods, while for other uses the price for a trigger spray product is about 40% less than a product for other application methods

¹³ According to one producer of a nano film product

In a call for evidence carried out in spring 2015, industry was asked to submit information on costs of substituting polyfluorooctyl trialkoxysilanes in aerosol dispensers. However, no information was submitted and, therefore, it is proposed to repeat this question in the public consultation in order to get a quantitative cost estimate.

On the basis of data available and on indications from e.g. the European Aerosol Federation it is concluded that no significant costs are envisaged. Consequently, the actors should be capable of complying with the proposed restriction by supplying adequate products.

E.2.1.1.3 Proportionality

The proposed restriction is considered to be a proportional risk management option because:

- It has been demonstrated in animals studies that the targeted substances applied as aerosol cause adverse effects of the same type as reported from many incidents of a syndrome of acute lung injury. A risk assessment for spray products containing hydrolysates and condensates of TDFAs and 2-propanol shows a risk that is not adequately controlled for these reaction products applied by aerosol dispenser or trigger and pump sprays.
- For producers, the proposed restriction has limited impact. Manufacturers of the active substances also produce the alternatives. Furthermore, the supply to the general public is limited compared to the supply to professionals.
- Products applying alternative, less dangerous application methods, water-based spray products containing TDFAs or spray products based on mixtures without TDFAs are widely available for consumers at prices comparable to the prices of the targeted products.
- Furthermore, if products for professional uses are available, consumers might in specific cases require professional assistance. The most critical use is considered to be easy-clean-applications for non-absorbing materials. In these cases more cleaning might be needed in case "protection" mixtures can not be applied.
- No other "impacts" are envisaged (reference to F).

E.2.1.2 Practicality, incl. enforceability

The proposed restriction is easy to understand and to communicate down the supply chain and can be enforced.

As explained in the previous sections, replacement of spray products containing TDFAs and organic solvent by alternative application methods or alternative chemistry seems to be economically and technically feasible.

Producers who replace TDFAs with polyfluoroalkyl trialkoxysilanes with a polyfluoroalkyl chain different from octyl, would only need to do minor adjustments as these substances are considered as drop in alternatives. However, as TDFAs may be present in small percentages in mixtures based on organic solvents and polyfluoroalkyl trialkoxysilanes with polyfluoroalkyl chain different from octyl, producers of spray products would need to ensure that the content of TDFAs in these polyfluoroalkyl trialkoxysilanes is below 2 ppb. It should be underlined that there is no indication from industry on to which extent this is a real issue.

The number of manufactures of TDFAs in the EU is relatively small (less than four). Therefore, communication down the supply chain would effectively support the producers of spray products with the relevant information in order to comply with the restriction. As the restriction targets a small subgroup of marketed impregnating agents in spray products, and the substances do not have a harmonised classification, manufacturers outside the EU and importers may not be aware of the restriction. For imported final spray products, in particular import by

small market actors with limited experience in managing chemical products, there could consequently be more need for ensuring compliance. However, there are already several legislative issues that needs to be known by the importer concerning functionality, safety and restricted substances in especially aerosol dispensers.

A transition period of 18 months is proposed as this should be sufficient for producers to reformulate some mixtures and for retailers to deplete their stocks. This is based on the rapid turnover of these kinds of spray products as well as the short production period for aerosol dispensers, pump and trigger sprays. It is also recognised that FEA (European Aerosol Federation) has indicated that a restriction would not be an issue for its members.

E.2.1.2.1 Enforceability

With regard to enforceability it might be difficult to identify spray products containing mixtures with TDFAs and organic solvents. Usually, due to low concentrations, the name of the active substances in the products is not indicated by the suppliers of the product (e.g. on the label or in safety data sheets). For products for professional use, it would be indicated in the SDS if the spray product contains organic solvents.

Enforcement authorities may request information on content of product composition from the suppliers of the consumer products who can request this information from producers and importers. In addition, some compliance tests could be required.

Compliance tests are expected to be undertaken as spot test campaigns targeting spray products for relevant applications on the market. The main instrument for the enforcement is expected to be a request of supply chain information on the composition of the spray products.

Analytic techniques - Laboratory grades of polyfluorooctyl trimethoxysilane and polyfluorooctyl triethoxysilane are available from major suppliers of laboratory chemicals, but standards covering all polyfluorooctyl trialkoxysilanes seem not to be available.

The mixtures in the spray products are highly reactive which complicate an exact quantification of the substances.

No EN-standard is available for analysis of the targeted substances at the moment. A commercial laboratory is currently implementing a method for analysing PFOA and PFOA precursors. The method is known as the Total Oxidisable Precursor Assay (TOP Assay), Houtz (2013). Since TDFAs are considered a PFHxA precursor, this TOP Assay, where precursors are oxidised to its corresponding perfluorinated carboxylic acid (PFCA) and subsequently analysed by LC-MS, can most likely also be used for analysis of the targeted substances. The detection limit of the TOP Assay is 2 ppb.

Nørgaard et al. (2010) have tested various analytical techniques for analysis of the products. The content of organo-functionalized silanes (including TDFAs) and their hydrolysates and condensates makes the products unsuitable for liquid chromatography (LC) due to their intolerance of water and possible reaction with the column material. Transmission-mode desorption electrospray ionization (TM-DESI), low temperature plasma (LTP) ionization and nano-assisted laser desorption ionization (NALDI) were compared with electrospray ionization (ESI) and atmospheric pressure chemical ionization (APCI) for the analysis of two nanofilm products. The LTP spectra were dominated by the silanes, while the corresponding di-, tri- and tetrasiloxanes were common in ESI, APCI and TM-DESI. According to the authors, LTP seems superior in showing the substances in their pristine, unreacted state, which would be of most relevance for compliance testing.

LTP-tests are not available from commercial laboratories. A Danish research laboratory has suggested to use a combination of direct infusion ESI-MS and APCI-MS for the analysis of the

parent substances (TDFAs). The detection limit of this method is expected to be of the same order of magnitude as the TOP Assay, since they are both based on MS.

Costs of analysis - The Danish research laboratory estimates that the costs of each laboratory test would probably be around €1 000 if all substances in the product, meeting the target group formula, should be identified, but not quantified (assuming a batch of at least ten samples is analysed).

If the objective of the analysis is to indicate whether the product contains one or more substances meeting the target group formula (i.e. an identification at group level), but not identifying all substances, the costs may likely be limited to around €300 per test.

No costs of the TOP Assay are available, but it is not expected to be more expensive than combination of direct infusion ESI-MS and APCI-MS.

Conclusion - For enforcement purposes, an indication whether the product contains one or more substances meeting the target formula above the detection limit of 2 ppb would in most cases be sufficient.

E.2.1.3 Monitorability

E.2.1.3.1 Direct and indirect impacts

The efficacy of the restriction can be monitored at two levels:

- Monitoring of the number of incidents of poisoning due to the use of the targeted substances in spray products.
- Monitoring of non compliance.

Monitoring of the number of incidents

The direct impact of the restriction may be monitored by use of national systems for monitoring of poisonings. Comprehensive monitoring systems covering all poisoning incidents seems not to exist for most (if any) Member States. Monitoring of inquiries to poison centres and hot lines exists as exemplified below.

As the active substances of the spray products are usually not indicated on the packaging, the poisoning incidents would most probably be recorded as a poisoning caused by the use of impregnation mixtures in organic solvent-based spray products, but the chemical identification of the active substances would not be recorded. As a consequence it may be possible to monitor if the number of inquiries due to poisoning by impregnating agents (all agents) decrease, but it would not be possible to monitor whether this specifically is due to fewer incidents of poisoning by the targeted substances.

In Denmark, a monitoring system is established by "Giftlinjen" (The poison hotline) which is giving advice to the general public as well as professionals within the health sector. The hotline receives more than 20 000 calls annually regarding acute poisoning cases. The hotline monitors the reasons for the telephone inquiries.

In Germany, the National 'Committee for the Assessment of Poisonings' at the Federal Institute for Risk Assessment (BfR) has in 2013 set up a Working Group that evaluates opportunities for establishing a continuous national monitoring of poisonings in Germany, based on case data of all nine German poisons centres with model from the US National Poison Data System (GIZ Nord, 2014).

In the UK, the National Poisons Information Service (NPIS) monitors the types of poisonings as reported in telephone enquiries to the NPIS (50 000 in 2013/14) and TOXBASE user sessions (600 000 in 2013/14) (NPIS, 2014).

Even though the monitoring is not comprehensive, the impact of the restriction may be monitored by changes in the number of inquiries regarding poisoning incidents. However, as 1) the number of incidents is small, 2) only some of the incidents are due to the targeted substances, and 3) the annual variation is high, the statistical "noise" would be high. Most probably, many years of monitoring would be needed before the direct impact of the restriction could be evaluated on the basis of the monitoring data.

Monitoring on non-compliance

The EU Rapid Alert System for Non-Food Products (RAPEX) can be used to monitor compliance with the restriction at EU level. National control campaigns may be launched as a mean to monitor the compliance, e.g. coordinated by Forum.

E.2.1.3.2 Costs of the monitoring

Monitoring of inquiries regarding poisoning already exists in many Member States and no extra costs are expected.

E.2.1.4 Overall assessment of restriction option 1

Overall, restriction option 1 (the proposed ban) is considered to be an adequate measure for addressing the risks due to the use of TDFAs and organic solvent in spray products for consumers. It is easy to understand that the targeted substances shall not be used in mixtures with organic solvents in spray products for supply to the general public. This message is easy to communicate down the supply chain. The restriction can be enforced as analytical methods exist with a detection limit of 2 ppb.

With a limit value of 2 ppb (based on detection limit instead of a risk based limit), some mixtures with a low, unintentional content of TDFAs may be targeted by the restriction as well, but it is due to the reactive nature of mixtures considered difficult to enforce a restriction with a higher risk-based limit value for the content of TDFAs.

E.2.2 Restriction option 2

Introducing a risk-based ban of mixtures containing TDFAs and organic solvent in spray products for consumer use in a concentration of TDFAs equal to or greater than 0.00004 % (0.4 mg/kg, 400 ppb).

E.2.2.1 Effectiveness

Based on available information from case reports and investigations by Nørgaard et al. (2010a and 2014), the content of TDFAs in commercial products is assumed to be about 0.5 – 2 %.

However, as described in C.4, TDFAs could likely be present at low concentrations in mixtures based on polyfluoroalkyl trialkoxysilanes with polyfluoroalkyl chain different from octyl. The proposed limit value of 0.00004 % (0.4 mg/kg; 400 ppb) is based on the risk calculation for an aerosolised NFP 1-like product in B.9.1.1.2. and an extra assessment factor of 10 for combinations of TDFAs and organic solvent that could be more toxic (like e.g. Rim sealer, see B.5.2.1).

It is not known to which extent RMO 1 would also restrict mixtures with polyfluoroalkyl chain different from TDFAs due to the content of TDFAs as impurities. The impurities in the raw material polyfluorohexyl ethyl iodide, DuPont™ Capstone™ 62-I (see C.4.3) indicate that it is like-

ly that TDFAs could appear as an impurity in mixtures based on polyfluoroalkyl chain different from TDFAs. However, information is very limited, even if this issue was raised directly in the call for evidence in spring 2015.

E.2.2.1.1 Risk reduction capacity

Compared to RMO 1, the risk reduction capacity is the same. However, it is not known whether polyfluoroalkyl trialkoxysilanes with polyfluoroalkyl chain lengths different from octyl may result in similar pulmonary effects as TDFAs. In that case the risk reduction would be higher.

The limit value is rather low and as very few products are expected to contain TDFAs in concentrations between 2 and 400 ppb, it is most likely that the RMO 2 would not reduce the human health risks different to the level achieved by RMO 1.

E.2.2.1.2 Costs

It is not known to which extent mixtures with TDFAs as impurities between 2 and 400 ppb exist.

Assuming they exist, the costs related to compliance would be lower than in RMO 1, as some substances with alkyl chain lengths different from TDFAs containing TDFAs as impurities might still be used in spraying. This would give the consumer the possibility to choose such impregnation products and the producers of spray products containing TDFAs and organic solvents for consumer use would get a more easy drop in alternative.

However, the cost of checking compliance will most likely be higher, as tests are expected to be more expensive available. For industry these costs would not outweigh possible gains due to surplus from marketing some substances with polyfluoroalkyl chain different from TDFAs, as in this case industry would not place these products on the market. For enforcement authorities, testing costs might be more burdensome, implying that less control can be envisaged.

E.2.2.1.3 Proportionality

No information is available to which extent substances with polyfluoroalkyl chain lengths different from TDFAs may result in the same pulmonary effects as seen for TDFAs.

The costs for industry might be lower compared to RMO 1 and the consumers would gain from the functionalities. For the enforcement authorities the same level as enforcements would imply higher costs.

E.2.2.2 Practicality, incl. enforceability

E.2.2.2.1 Implementability, incl. enforceability

Compared to RMO 1, introduction of a risk-based limit value would allow polyfluoroalkyl trialkoxysilanes with polyfluoroalkyl chain length different from octyl in combination with organic solvents to be used in spray products, provided that they are not present as impurities above the 0.00004 % (400 ppb) limit. It is not known to which extent such products actually exist on the market. Furthermore, if the production process of polyfluoroalkyl trialkoxysilanes with polyfluoroalkyl chain length different from octyl results in the presence of TDFAs as impurities, it is not known to which extent it is possible to reduce the presence below the limit value and to make the appropriate tests.

As discussed under RMO 1, section E.2.1.2.1, it is challenging to quantify the concentration of individual components of highly reactive mixtures. The costs of analysis would most probably be significantly higher than the analyses necessary for enforcement of RMO 1.

As the handling of the mixtures would highly influence the results (the formation of condensation products before analysis) it would be necessary to develop a standard to be used for the analysis. If the TOP Assay method (as described in E.2.1.2.1) is used, it might have to be adapted to these reactive mixtures.

The extra costs and the possible time needed for development or adaptation of a standardised analytical method are considered disproportionate to the advantages of not targeting some mixtures with a polyfluoroalkyl chain different from octyl.

E.2.2.3 Monitorability

The monitorability is considered to be similar to RMO 1. The direct impact of the restriction may be monitored by use of national systems for monitoring of poisonings. The EU Rapid Alert System for Non-Food Products (RAPEX) can be used to monitor compliance with the restriction at EU level, and no extra costs are expected.

Quantification of the substances within the spray products is complicated as even just an identification of all substances within the mixture without quantification is quite expensive. No cost estimate is available.

E.2.2.4 Overall assessment of restriction option 2

The advantage of RMO 2 would be not to target some mixtures where TDFAs are present at low concentrations (below 400 ppb). To which extent this would actually be an issue is not known. At the same time it is not known whether polyfluoroalkyl trialkoxysilanes with polyfluoroalkyl chain lengths different from octyl will result in similar pulmonary effects as TDFAs. As it is challenging to make quantitative analysis of substances in highly reactive mixtures, a standard describing the sampling and analytical procedures should be developed. The costs of monitoring would probably be significantly higher. Consequently, overall it is considered that RMO 1 would be a more proportional management option than RMO 2.

E.2.3 Restriction option 3

Introducing a ban of mixtures containing TDFAs and organic solvent in aerosol dispensers for consumer use in a concentration of TDFAs equal to or greater than 2 ppb by weight.

E.2.3.1 Effectiveness

E.2.3.1.1 Risk reduction capacity

The risk reduction capacity is expected to be lower compared to the risk reduction capacity of RMO 1. Most of the reported incidents in Appendix 1 are for aerosol dispensers and only five are for pump spray (of these three are occupational). This is in line with the risk assessments that have shown that an aerosolised mixture of TDFAs and 2-propanol presents a high risk. However, risk assessments have also shown that the same mixture applied by pump spray also presents a risk.

E.2.3.1.2 Costs

Replacement of aerosol dispensers containing TDFAs and organic solvents by alternative application methods or alternative chemistry is economically and technically feasible and alternatives are widely used today.

The restriction would impact much fewer market actors than RMO 1 (also including pump and trigger sprays) as the market for impregnation products where the TDFAs are applied by trig-

ger/pump sprays seems to be much larger than the market for aerosol dispensers with TDFAs. In terms of cost per unit mixture, aerosol dispenser application is a relative expensive method. For the consumer using small quantities of the mixtures for minor applications, this may be outweighed by the convenience of the method and the fact that the sealed package protects the product and extends its service life.

In relation to the properties, the use of aerosol dispensers may result in a thinner and more uniform coating, but for consumer applications this is considered to be of marginal importance. This is also indicated by the fact that the targeted substances are mainly sold for other application methods (pump/trigger spray, brush etc.).

E.2.3.1.3 Proportionality

Available data indicate that the adverse effects for consumers of the TDFAs are depending on the application method and the adverse effects have been demonstrated in animal studies for spray applications comparable with the application with aerosol dispensers. Risk assessments have shown that an aerosolised mixture of TDFAs and 2-propanol presents a higher risk than the same mixture applied by pump spray. Consequently, a ban of only aerosol dispensers for consumer use containing TDFAs and organic solvent will remove the products with the highest risk of causing lung injury from the market, implying a higher average cost-effectiveness than RMO 1.

E.2.3.2 Practicality, incl. enforceability

Compared to RMO 1, a ban only on aerosol dispensers would be even easier to implement, as in many cases other spray applications methods can be used.

For enforcement, less resources should be allocated compared to RMO 1, as fewer products would need to be controlled to ensure compliance.

E.2.3.3 Monitorability

The monitorability is similar to the monitorability of RMO 1.

E.2.3.4 Overall assessment of restriction option 3

RMO 3 would result a lower level of consumer protection than RMO 1 as aerosol dispensers is a subgroup of the impregnation spray products containing TDFAs for consumer use. Aerosolised mixtures of TDFAs and 2-propanol present a higher risk than the same mixtures applied by pump spray and are therefore the most important products to be regulated. However, risk assessments have also shown that the same mixture applied by pump spray also presents a risk. This risk is not handled if only aerosol dispensers containing TDFAs and organic mixtures are banned.

E.3 Comparison of the risk management options

The following can be concluded:

- RMO 1 is considered to be the most proportionate option for restriction. The potential negative practical and economic impact on consumers is very small and the restriction would have a positive effect in reducing the number of incidents. It is easy to understand and to communicate down the supply chain and it can be enforced. The RMO may unintentionally target polyfluoroalkyl alkoxysilanes with alkyl chain length different from octyl where TDFAs is present in concentrations below 0.00004% (400 ppb) and thereby not expected to represent an unacceptable risk. However, as alternative application methods are readily available, the loss in consumer benefits due to unintentional targeting is considered marginal.

- RMO 2 excludes the unintentionally targeted polyfluoroalkyl alkoxy silanes from the restriction. As mentioned above it is considered less proportionate than RMO 1 as the enforcement of the restriction will be more costly since it requires quantification. It may take quite a long time before an adequate analytic standard is developed and adopted. At the same time, it is not known whether polyfluoroalkyl trialkoxy silanes with polyfluoroalkyl chain lengths different from octyl will result in similar lung effects as TDFAs.
- RMO 3 is considered to be less proportionate than RMO 1 as risks related to hand pump and trigger sprays are not addressed, and as other application methods seem to be available at comparable prices.
- Except for the enforceability of RMO 2, there are no major differences with regard to enforceability and monitorability between the 3 RMOs.

E.4 Main assumptions used and decisions made during analysis

In the assessment, it is assumed that the effects observed in the many case reports of humans exposed to proofing/impregnation sprays are similar to the demonstrated effects of mixtures with TDFAs and organic solvents observed in animal studies. The strongest relationship between animal studies and human incidents seems to be for "Magic Nano" products that were responsible for 154 incidents in Germany in 2006. The products were tested in rats by Pauluhn et al. (2008). Koch et al. (2009) finds it likely that the causative agents in these products were a fluorosilane in mixture with organic solvents. In the assessment, this fluorosilane is assumed to belong to the group of TDFAs even though the chain length of the polyfluoroalkyl chain is not known.

If future studies demonstrate strong relationship between effects seen in human incidents and animal studies of other mixtures applied as impregnating agents in spray products, it may be considered to propose a new restriction.

It has been very difficult to obtain specific information on spray products with organic solvent based TDFAs actually marketed.

Manufacturers of TDFAs indicate that a small part of the manufactured volume is probably applied in aerosol spray products. However, no precise information is available.

For aerosol products The Danish Aerosol Industry Association (AIB) indicates that TDFAs are probably used by some producers of aerosol dispensers. The European Aerosol organisation FEA has indicated that a restriction would not be an issue for its members¹⁴. Some of the former providers of aerosol dispensers with TDFAs indicate that the use of TDFAs has recently ceased.

E.5 The proposed restriction(s) and summary of the justifications

The proposed restriction is:

- Ban of use of mixtures containing TDFAs and organic solvent in spray products for supply to the general public.
- Ban of placing on the market mixtures containing TDFAs and organic solvent in spray products for supply to the general public in a concentration of TDFAs equal to or greater than 2 ppb by weight.

The proposed restriction informs formulators/producers, that they should not add TDFAs to their mixtures if it contains organic solvents and is intended for spray products for use by the general public. The 2 ppb limit ensures that an eventual placing on the market of spray

¹⁴ The statement from FEA was linked to aerosol dispensers.

products containing TDFAs and organic solvents can be enforced (2 ppb is the LOD for the proposed test method).

The justifications for the proposed restrictions are summarised below:

Identified hazard and risk - Mice exposed to aerosolised hydrolysates and condensates of TDFAs and organic solvents at certain concentration levels have been shown to develop serious lung injury following short term exposures.

Besides the content of TDFAs, the toxicity of the products depends on the solvents, particle size distribution and particle concentration (application method). The mechanism behind the observed effects is believed to involve inhibition of the lung surfactant.

A risk assessment for hydrolysates and condensates of TDFAs and organic solvents shows a risk that is not adequately controlled for these reaction products applied by aerosol dispenser or pump spray. The risk for trigger sprays is expected to be similar to the risk seen for pump sprays.

Evidence of consumer exposure - In the EU, 713 incidents reported during the past four decades have demonstrated a relationship between short-term exposure to various impregnation sprays and development of respiratory illness, which have required hospitalisation. Incidents have often occurred as outbreaks, which have been linked to use of specific consumer spray products on the market. In several cases, the identified sprays have subsequently been withdrawn from the market shortly after their introduction.

Fluorinated polymers are contained in most of the spray products involved in the identified incidents (see Table 5). However, very little information is generally available on the chemical identity of the polymeric active ingredients, as they usually occur in low concentrations (< 2 %) and do not result in any classification of the products. No active ingredients with a structure similar to TDFAs have been positively identified in the products investigated in relation to the incidents. Of products known to have caused human incidents "Magic Nano Glass & Ceramic" and "Magic Nano Bath & WC", that were responsible for 154 incidents in Germany in 2006, is the products with the highest probability of being "spray product(s) containing mixtures of TDFAs and organic solvents for the general public".

Different types of impregnation sprays have been linked to the identified incidents. They include products for both absorbing surfaces (textile and leather) and non-absorbing surfaces (tile and ceramics). Information is not always available regarding the solvent system, and some products may also be water-based, with some content of organic solvent (e.g. alcohols). Outbreaks have in some cases been linked to a change in the solvent used in the mixture, e.g. when alternatives to 1,1,1-trichloroethane were introduced due to regulatory restrictions on the use of the solvent, indicating that not only the active ingredients were responsible for the effects.

Justification that action is required on a Union-wide basis - In order to adequately protect consumers, a restriction should both target imported and aerosol dispensers produced in the EU. A Union-wide ban is justified by the fact that risks arise in all MS where such products are used, since incidents with consumers have been seen throughout the EU and to ensure equal market conditions.

Justification that the proposed restriction is the most appropriate Union-wide measure - Several incidents of lung injuries from application of impregnating agents in aerosol dispensers based on mixtures without TDFAs have been reported. Animal experiments have demonstrated similar effects from the application of aerosolised mixtures with TDFAs and solvents. However, a risk assessment for hydrolysates and condensates of TDFAs and 2-propanol shows that a risk exists for these reaction products applied by aerosol dispensers or pump sprays. Other risk management options have been evaluated but none were considered to pro-

vide the necessary protection of consumers or they were considered as less proportionate due to less targeting.

Effectiveness in reducing the identified risks - The restriction is considered effective in reducing the risks related to use of spray products containing TDFAs and organic solvents for which documentation of risks exist. The potential risk from the use of other impregnating agents in spray products will not be addressed as well as possible risks for professionals.

Proportionality to the risks - As alternative application methods or water-based spray products containing TDFAs are readily available, negative effects on consumers, manufacturers of TDFAs, formulators of TDFAs-based impregnation agents and suppliers of TDFAs-based impregnation agents are marginal. Considering the potential health effects of the application of the targeted mixtures in spray products, a restriction is considered proportionate.

Practicality, including enforceability - The implementation of the restriction is considered practical and feasible as alternative application methods or water-based spray products containing TDFAs are readily available. As chemical analysis of substances in highly reactive mixtures are challenging, it is proposed that the restriction should not apply a risk-based limit value in order to ease the enforceability of the restriction.

F. Socio-economic assessment of the proposed restriction

F.1 Human health and environmental impacts

F.1.1 Human health impacts

Human health impacts of spray products containing TDFAs and organic solvents are described in section B.5.2.2 The main health impacts are linked to a syndrome of acute lung injury ranging from a mild, non-specific chemical pneumonitis to severe incidents with symptoms such as strong cough, dyspnea and severe lung edema.

F.1.1.1 Valuation of human health impact

In section E.1.1 the yearly average number of EU28 consumer incidents related to spray products containing TDFAs and organic solvents is estimated to 330-660 incidents.

On the basis of information from several sources (Jacobsen et al. (1999), Swiss case in Appendix 1, Table 1 - 2 and Appendix 1, Table 1 - 3) approximately 30% (range 23%-40%) of the reported incidences are considered to be severe. Pulmonary effects resulting from exposure may involve a period of illness and even hospitalisation in serious cases. The remaining about 70% is assumed to be equally distributed between mild and moderate pulmonary effects. Moderate effects imply consultation by GPs or emergency centres.

Hence the incidents are distributed as follows:

TABLE 12 ESTIMATED YEARLY NUMBER OF EU28 CONSUMER INCIDENTS DUE TO SPRAY PRODUCTS CONTAINING TDFAS AND ORGANIC SOLVENTS

	Minimum estimate (20% of incidents due to TDFAs in organic solvents)	Maximum estimate (40% of incidents due to TDFAs in organic solvents)
Severe incidents	100	200
Moderate incidents	115	230
Mild incidents	115	230
Total	330	660

With regard to the severe incidents, there is no detailed information about the duration of the hospitalisation period, but according to an expert estimate (Jacobsen et al., 1999) the majority has been hospitalised for a few days and in the more severe incidents up to two weeks. In addition, some had symptoms after hospitalisation preventing them from normal activities a further few days. Long term effects have not been identified.

The valuation of the health impacts includes the following cost elements:

- Health sector costs (hospitals);
- Medication costs (for the affected individuals);
- Production losses (costs of lost working days);
- Welfare costs.

The hospitalisation costs will vary depending on the severity of the exposures and the general costs for hospital treatment across Member States. As no detailed recording of the specific treatment is available, the hospitalisation costs are assessed here as an order of magnitude estimate per incident.

The assessment of the hospitalisation costs is based on two different approaches and associated data sources. One approach is to use internationally presented costs of one hospital day taken from WHO 2011¹⁵. They present a very rough estimate of the costs per hospital bed per day where the cost of drugs and diagnostic tests are not included. An EU28 average is estimated to be around 300 EUR per day plus drugs and diagnostic tests. Another source could be data related to the type of diagnostics relevant for this type of incident. The Danish Ministry of Health applies standard rates by diagnosis. The 2014 rate for one incident of "Observation of respiratory disease"¹⁶ is estimated to 1800 EUR per treatment. The Danish price/cost level as measures by purchasing power parities is 140% of EU28 average. Adjusting this hospitalisation costs gives then an estimate of 1300 EUR per treatment. It is assumed that these two estimate provide an lower and upper value for the hospitalisation costs.

The costs associated with absence from work are estimated assuming that the absence means a loss economic production value which is approximated by the salary of those absent. The estimate is based on average EU salaries¹⁷ and adjusted to current price level. It is assumed to be 180 € per day.

The last cost element is welfare loss due to the individuals discomfort of the poisoning incident. There are no specific studies on the individual's willingness to pay (WTP) for avoiding this type of incident. The reference study of COWI (2004) includes a discussion of using the benefit transfer approach, and on this basis the study suggests applying a WTP to avoid a symptom day as value indicator. The value for WTP applied in the COWI (2004) study was approximately 15 € per symptom day. A recent review of estimates of the welfare costs of restricted activity days presents values in the order of 50 EUR for welfare loss associated with minor restricted activity days. The estimates are for restricted activity in relation to air pollution and therefore related to effects of respiratory health effects. This level is used here¹⁸.

The per day unit costs for hospitalisation, work absence and welfare are presented below.

TABLE 13 UNIT COSTS ASSUMPTION FOR VALUATION OF HEALTH EFFECTS

Source: see notes

Cost item	EUR per day
Hospitalisation	300 – 650 ¹⁾
Loss production	180
Individual welfare loss	50

¹⁾ Assuming 2 days per treatment

Based on these unit costs and the medical expert assessment of the average number of days per exposed person, it is possible to estimate the costs associated with each case of exposure. The average number of days an exposed person is affected are included in the below table.

¹⁵ WHO-CHOICE unit cost estimates for service delivery – see: http://www.who.int/choice/country/country_specific/en/

¹⁶ Covers all expenses related to hospital sector distributed on specific diseases. Stationære DRG takster 2015 <http://www.ssi.dk/~media/Indhold/DK%20-%20dansk/Sundhedsdata%20og%20it/NSF/Sundhedsokonomi-%20og%20finansiering/Sundhedokonomi/Takster/Takster%202015/Stationære%20DRGtakster%202015.ashx> – DRG:0445: 13838/7.5

Harmonised indices of consumer prices (HICP):

http://appsso.eurostat.ec.europa.eu/nui/show.do?dataset=prc_hicp_aind&lang=en

PPP: http://epp.eurostat.ec.europa.eu/portal/page/portal/purchasing_power_parities/introduction

¹⁷ Eurostat Labour Costs Survey 2008 and Harmonised indices of consumer prices (HICP). EU27 labour costs at 21.84 EUR per hour in 2008 and price index of 10% increase from 2008 to 2013. Assumed 7.5 hours per day.

¹⁸ [RICARDO-AEA 2014](#) "Update of the Handbook on External Costs of Transport"

TABLE 14 ASSUMPTION FOR VALUATION OF HEALTH EFFECTS

Cost item	Number of days per average incident
Hospitalisation	2
Loss production	4
Individual welfare loss	4

Source: Own estimates

Combining the unit costs and the number of days, the costs per severe incident can be compiled.

TABLE 15 ASSUMPTION FOR VALUATION OF HEALTH EFFECTS, SEVERE INCIDENTS

Cost item	Number of days per average incident	Unit costs EUR/day	Total costs EUR
Hospitalisation	2	300-650	600-1 300
Loss production	4	180	720
Individual welfare loss	4	50	200
Total costs			1 520-2 220

Source: Own estimates

The respiratory symptoms of the moderate severe intoxication incidents from spray products containing TDFAs and organic solvents can be compared to those seen from inorganic ammonium salts. Therefore the cost for the moderate severe incidents are similar to those Cost-of-illness estimates derived in the French Annex XV dossier proposing restrictions on inorganic ammonium salts (ECHA. 2015d) estimated to be €49.

For the mild incidents the costs have been assumed to 10€.

The benefits of the proposed restriction will be a reduced number of incidents of respiratory illness. The total annual health benefits in the EU can be seen in Table 16.

TABLE 16 ANNUAL HEALTH BENEFITS IN EU28

	Number of EU28 consumer incidents due to spray products containing TDFAs and organic solvents	Cost per incident, €	Cost EU28, if 20% of incidents are due to TDFAs in organic solvents), €	Cost EU28, if 40% of incidents are due to TDFAs in organic solvents, €
Severe incidents	100-200	1 520-2 220	152 000	444 000
Moderate incidents	115-230	49	6 000	11 000
Mild incidents	115-230	10	1 000	2 000
Total	330-660		159 000	457 000

Thereby as a very rough estimate, the total annual health benefits in the EU of the restriction can be estimated to €160 000 - €460 000.

F.1.2 Environmental impacts

The environmental impact of the proposed restriction is considered to be small as the substances concerned most likely are replaced with other application methods of the same substances or replace by substances with a similar environmental profile. Alternative mixtures based on polyfluoroalkyl trialkoxysilanes with shorter polyfluoroalkyl chains (C4) may possibly

be considered preferable from an environmental view, but the data on environmental effects of the short-chained alternatives are limited.

F.2 Economic impact

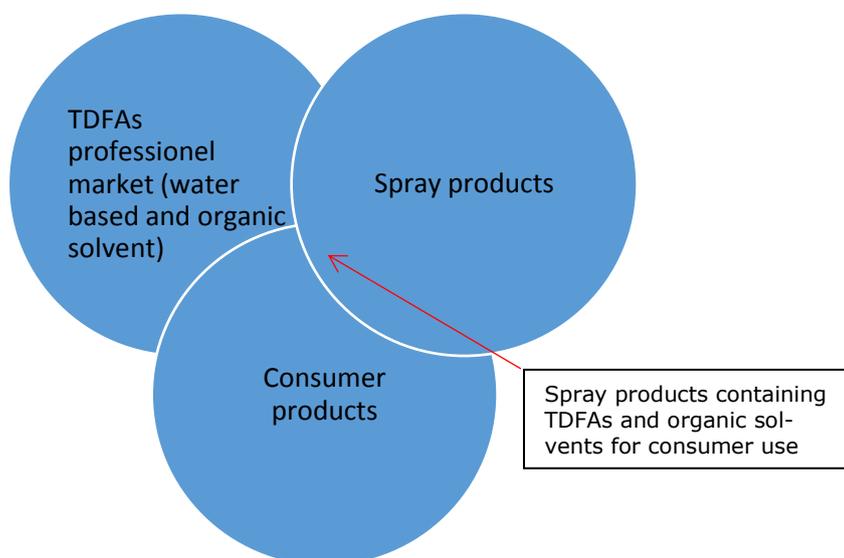
F.2.1 Compliance costs

Overall the compliance costs of the actors in the supply chain is considered to be small.

An overview of spray products covered by the proposed restriction is shown in Figure 3. As mentioned in B.2.2, it is estimated that app. 20-200 kg TDFAs (approximately 6 800 – 100 000 units) are sold in spray products in combination with solvents and sold to the general public. This would also constitute the volume for the coming years (baseline) as the market is considered to be rather stable.

Assuming a consumer price at €16-24 per can (exclusive VAT) and retailers cost of 50 %, the turnover of such products for producers of spray cans are estimated to 8-12 €, these can represent an annual turnover between €54 000 and €1 200 000.

FIGURE 3 OVERVIEW OF THE PRODUCTS COVERED BY THE PROPOSED RESTRICTION.



For producers replacing the spray products by the same mixtures in products to be applied by other application methods some savings will be achieved as packaging in cans to be applied by e.g. brush or roll will be a more simple process. However, it is considered that the price of the final products probably also will be lower, due to lack of functionalities and convenience offered by the easy-to-use methods.

As indicated in C.4.4, alternatives to TDFAs seem to be available at the same price levels. According to the available information, changing the substance with a shorter polyfluoroalkyl chain has not influenced the price of the final spray product.

No specific information on reformulation costs for mixtures of TDFAs and organic solvents to be used in spray products for consumers is available.

Where TDFAs are substituted by polyfluoroalkyl trialkoxysilanes with polyfluoroalkyl chains different from the chain of TDFAs, reformulation should be quite simple as drop-in alternatives exist.

Substitution of TDFAs by other substances than polyfluoroalkyl trialkoxysilanes might be more complicated.

In the UK proposal for a restriction of D4 and D5 in wash-off personal care products (ECHA. 2015c), reformulation costs were estimated based on US interview data from 2012 on reformulation of Cosmetics. The costs were calculated on the basis of costs for the different elements: idea generation, product development, purchasing, legal, marketing, and quality control, product testing, safety studies, shelf-life studies, packaging development, market testing, production or manufacturing adjustments, changing the process, running a plant trial, conducted starting up and verification were estimated for changes in minor and major ingredients. For Cosmetics, the reformulation costs for substitution of major ingredients were estimated to \$271,480 which in the D4/D5 proposal was transferred to €350 000 (2012 prices) for one formula. Reformulation of spray products containing TDFAs and organic solvents is considered to be much less demanding, as the products are not applied on the skin and the requirements for consumers are considered to be much more related to functionality than to taste, consumer acceptance etc. For instance 25 % of the costs related to reformulation of cosmetic was market testing. Furthermore 15 % of the costs were related to process development even if that is considered to be quite simple. Therefore, as a rough estimate, the reformulation costs is assumed to be app. 30 % of the reformulation costs for Cosmetic, i.e. app. €120 000. However, this estimate seems to be too high, especially if one polyfluoroalkyl alkoxy silane is substituted by another polyfluoroalkyl alkoxy silane as a drop in replacement.

With regard to testing for water and oil repellency properties, such tests are usually performed on a regular basis as part of the quality assurance of the formulators using standard tests for oil and water repellency (e.g. AATCC TM 118 Oil Repellency, AATCC TM 130 Soil Release, AATCC TM 193 Aqueous Liquid Repellency). Repellency tests with new formulations do therefore not constitute substantial additional costs and are considered to be carried out in house.

In the D4/D5 dossier the costs were annualised using the assumptions given in Table 17.

TABLE 17 ASSUMPTIONS ON ANNUALISED COSTS FOR D4/D5

Assumptions/Input Data	Value
Total Number of product formulations	3 600
Cost of 'major' baseline reformulation (€2012)	€350 000
Cost of 'minor' baseline reformulation (€2012)	€52 000
Compliance period	2 years – 5 years
Discount rate	4%
Annual average 'minor' reformulation rate	15%
Annual average 'major' reformulation rate	5%

The annual reformulation costs were for that proposal estimated as to € 20 M – 58 M, equivalent to €5 500 - 16 100 per formula.

Assuming that the cost of reformulation of TDFAs in organic solvents the annualised cost are 30% thereof, the annual costs of reformulation per formula would be € 1 700 – 4 800.

In the D4/D5 estimations it is assumed, however, that the reformulation of Cosmetics with regard to D4/D5 can be combined with other reformulation activities assuming that the average life time of cosmetics is 10 years. If no coordination of reformulation activities is possible the annual reformulation costs would be 25 000 – 35 000 per formula¹⁹. Assuming as above that the costs of reformulation of TDFAs in organic solvents the annualised cost are 30% thereof, the annual costs of reformulation per formula would be € 8 000 – 12 000.

¹⁹ In the D4/D5 dossier, this is called "Annualised gross costs (20y)"

The main problem is, however, that no information is available on the number of formulas that need to be changed to other substances than polyfluoroalkyl trialkoxysilanes, in the case where a manufacturer does not already have placed alternative impregnation products on the market.

The relative low quantity of the estimated use (6 800 – 100 000 units) and turnover of up to €1.2 Million covering all uses, make it reasonable to believe that reformulation will only take place where the reformulation costs are low as indicated by the formulator cited above, or where reformulation is part of broader company strategy covering more products than consumer sprays.

For users the most obvious alternative is spray products containing TDFAs in water-based mixtures or impregnation products that are not based on TDFAs. These alternatives seem to be available at same or lower prices.

However, in some cases the consumers would face lower functionality of the products as polyfluoroalkylsilans make a stronger binding to non-absorbing surfaces and have a service life than e.g. siloxanes. In these cases mixtures with organic solvents and polyfluoroalkylsilans with shorter or longer polyfluoroalkyl chain lengths might be used. However, also alternative application methods (brush, roller or cloth) may be used. For suppliers this would mean that they would have to offer the product in normal cans or bottles instead of as spray products. In conclusion, the compliance costs in general would be quite limited.

F.2.2 Cost for ensuring compliance

The most obvious alternative is use of alternative application methods which would not require any monitoring of compliance.

The exact composition of the per- or polyfluorinated substances in the spray products does typically not appear from the Safety Data Sheets. Importers, gross-dealers and retailers would need to request such information from the producers of the aerosol dispensers, but the costs of such compliance documentation is considered to be very small.

The actors may, however, decide to perform additional compliance checks in order to verify that the spray products are in compliance. The extent of such additional compliance work is very difficult to assess. As the supply chain is used to exchange information on hazardous substances in the products, it could be assumed that downstream users and dealers rely on information from manufactures, and the need for verification by laboratory test would probably be relatively small (as compared to supply chains with limited exchange of information on hazardous substances).

The importers are likely to require documentation that the imported products comply with the restriction. The costs for documenting compliance for imported products are expected to be borne by the foreign producers. For the importer, the administrative costs to collect and verify the documentation are considered insignificant.

Where enforcement authorities test the composition of spray this would require costs for carrying out these tests. As described in E.2.1.2 these costs would be approximately €300 per tested mixture for the presence of substances at group level.

F.3 Social impacts

F.3.1 Potential for loss of employment

The loss of employment is considered to be marginal. The most obvious alternatives are other application methods (e.g. brush, cloth or roller), use of mixtures based on polyfluoroalkyl trialkoxysilanes with other polyfluoroalkyl chain length than TDFAs (if these does not contain TDFAs as impurities). In the first case, the restriction may result in a small distributional effect due to

a change from companies specialised in the manufacture of spray products to companies producing other impregnation products. In the latter case due to the very low volumes, it is estimated that the restriction will have very limited effect on employment in the EU for the manufacturers of the substances, even if the substances with other polyfluoroalkyl chain than TDFAs are imported.

F.3.2 Changes in price for end users

Alternatives are not considered to be more expensive for the user.

F.4 Wider economic impacts

F.4.1 Loss of export revenue

The restriction will not influence the export of the substances on their own or in mixtures apart from mixtures in spray products in case the loss of European market makes the production of these products unprofitable.

The products that would be affected by the restriction, seem mainly to be produced by small companies with their own brands (or the spray products are produced as contract work for small companies) acting on a local or regional market. This is e.g. indicated by the fact that the restriction is not considered an issue for producers of spray products organised in the trade associations. The export to countries outside the EU, and the loss of revenue as consequence of a restriction, is therefore estimated to be marginal.

F.5 Distributional impacts

The restriction may result in a small distributional effect due to a change from companies specialised in the production of spray products to companies filling the mixtures on trigger sprays.

F.6 Main assumptions used and decisions made during analysis

Limited information is available on the actual content of the spray products which have caused the observed effects. In the socioeconomic assessment it is assumed that the incidents described under baseline in E.1.1 can be attributed to spray products with organic solvent-based TDFAs. Using data from the Danish Poison Center from 2006 - 2015 provides an estimate of 330 - 660 incidents at EU level on an annual basis.

Specific information on aerosol dispensers containing TDFAs and organic solvents actually marketed in the EU today is limited. It is assumed that the main alternatives will be the same substances applied in trigger sprays or by other application methods. The effect on the different market actors is assumed to be small. As limited information on the actual producers and suppliers of the targeted aerosol dispensers is available, the distributional effects are difficult to estimate, but it is assumed that they will be marginal. For some applications, the use of alternative application methods may be more time consuming for the consumers, but the costs of this is assumed to be marginal.

F.7 Uncertainties

The major uncertainties of importance for the socioeconomic assessment are:

- The number of the reported poisoning incidents for which the targeted mixtures have been responsible.
- The annual number of poisoning incidents and the trend in incidents caused by the targeted mixtures in spray products. It is uncertain to what extent the market has already changed as a reaction to the reported poisoning incidents and the research regarding the effects of the substances.

- The total number of spray products with targeted mixtures sold annually within the EU.
- To what extent active substances and mixtures for impregnation products that are not based on TDFAs, are manufactured within the EU or imported into the EU, respectively.
- To what extent the proposed action would target aerosolised spray products based on polyfluoroalkyl trialkoxysilanes with polyfluoroalkyl chain length different from TDFAs due to trace levels of TDFAs in the mixtures.
- The threshold of 2 ppb is derived from the so-called TOP Assay that is expected to be used for enforcement of the PFOA and PFOA precursor restriction. This method has not been tested for fluorinated silanes, silanols and siloxanes yet.

F.8 Summary of the socio-economic impacts

The impact of the proposed restriction on health is estimated to 330 - 660 incidents prevented annually, which based on avoided costs related to respiratory diseases is monetized to €160 000 - €460 000 per year.

20 - 200 kg TDFAs (approximately 6 800 – 100 000 units) are sold in spray products in combination with solvents and sold to the general public.

Alternatives to TDFAs in combination with organic solvents seem to be available at the same price levels.

Where substitution to other substances than polyfluoroalkyl trialkoxysilanes of TDFAs in organic solvents is considered, the annualised cost of reformulation per formula is € 8 000 – 12 000.

Table 18 summarises the main economic impacts on different actors in the supply chain for in spray products articles.

The first column indicates possible additional production and compliance costs. The second column presents the distribution of the costs based on the expected pass-through of the costs.

TABLE 18

SUMMARY OF ECONOMIC IMPACT ON DIFFERENT ACTORS

Actor	Direct cost impacts	Distribution of costs - impacts on sales etc.
Manufacturers of TDFAs	No significant impacts, only a minor fraction might be affected. The main manufacturers also offer alternatives	No significant impacts
Formulators of mixtures based on TDFAs	No significant impacts. In most cases they are offered mixtures that are nearly ready to use.	No significant impacts
Manufacturers/importers of other polyfluoroalkyl trialkoxysilanes than TDFAs and formulators/importers of mixtures based on these substances	No significant impacts. In general the same as the manufacturers of TDFAs	No significant impacts
Manufacturers/importers of chemistries without polyfluoroalkyl trialkoxysilane and formulators/importers of mixtures without polyfluoroalkyl trialkoxysilane	No significant impacts.	No significant impacts
Companies producing spray products with TDFAs (either as contract work or own label)	No significant impacts. In most cases they are offered mixtures that are nearly ready to use.	No significant impacts
Suppliers of spray products with TDFAs and organic solvents	No significant impacts	No significant impacts
Consumers using spray products with TDFAs and organic solvents	No significant impacts. Substitution to mixtures with shorter-chain substance have not influenced the price of the final spray product. For some niche applications some loss of functionality	No significant impacts

G. Stakeholder consultation

Information about uses of the polyfluorooctyl trialkoxysilanes, tonnages used, the availability and technical and economic aspects of alternatives, practical handling of the products etc. has been collected.

Stakeholders including manufacturers of TDFAs, formulators of mixtures based on TDFAs, formulators/importers of mixtures based on these substances and companies producing spray products with TDFAs and suppliers of in spray products with TDFAs, were contacted by letter and afterwards by telephone or email, see below for further details.

Furthermore, a "Call for Evidence"²⁰ was carried out by ECHA in March/April 2015. The stakeholders were invited to provide information on uses and quantities of polyfluorooctyl trialkoxysilanes in aerosol dispensers as well as the availability, technical and economic feasibility of alternatives. 2 Member States, 1 EEA country and 1 from industry responded. By including pump and trigger sprays in the final proposal this has a broader scope. **It is recommended to highlight this in the public consultation in order to get further information on the impacts of restricting these products.**

As the polyfluorooctyl trialkoxysilanes are not produced in high volumes they are not registered, so important information on the substances is to a great extent lacking.

G.1 Industry

European or global industry associations/federations FEA (Fédération Européenne des Aérosols or **European Aerosol Federation**) represents the business associations in 18 European countries which include more than 350 companies active in the aerosol industry. These range from small and medium-sized enterprises (i.e. SMEs) to multinationals. The associations represent both the active ingredients in the aerosol dispensers, aerosol fillers and manufacturers of containers and other parts. The organisation answered that the proposal would not be a major issue for the members and were not able to provide specific information for the dossier.

CES - Silicones Europe is representing all major producers of silicones in Europe (six member companies). CES provide information on silicones from a health, safety and environmental perspective. CES is a sector group of the European Chemical Industry Council (**Cefic**). CES facilitated the further contact to the **Reconcile REACH Consortium** where the manufacturers of silanes and siloxanes have joined efforts for the REACH registration of the substances. The Consortium is administrated by ReachCentrum under Cefic. The Reconcile REACH Consortium facilitated contact to manufacturers of the relevant substances in the EU, and the further contact were with those companies. A meeting was held in the premises of the Danish EPA with one of the main manufacturers of the substances.

The **FluoroCouncil** is a global organization representing the world's leading fluoro-technology companies (six member companies), with a primary focus on fluorinated polymers and fluorotelomer-based performance products. The FluoroCouncil answered that the proposal was not within the scope of the FluoroCouncil and the organisation did not hold specific information on the substances concerned.

The European Apparel and Textile Confederation, **Euratex**, and the German Association of producers of textile, paper, leather and fur auxiliaries and chemicals, **TEGEWA**, were contacted, but could not provide any specific information.

In order to better understand the supply chain, the **Chemical Business Association (CBA)** was contacted. CBA is the voice of the UK chemical supply chain. The organisation did not answer the request.

²⁰ http://echa.europa.eu/documents/10162/13641/bd_call_for_evidence_pfas_en.pdf

One manufacturer of TDFAs replied in the Call for Evidence.

Danish industry organisations

Relevant national trade organisations in Denmark was contacted as part of the consultation process.

Danish Aerosol Industry Association (AIB). **(In Danish: Aerosolindustriens Branche forening)** has been contacted. The organisation has on the basis of contacts with its members and similar organisations in other Member States provided some information on the use of the substances in aerosol dispensers.

Other Danish industry organisations, The **Confederation of Danish Industry (DI)**, the **Plastics Federation, Danish Fashion** and **Textile and the Danish Textile Organisation** have been contacted, but did not hold specific information on the use of the mixtures.

Individual companies

The main producers and importers of the polyfluorinated trialkoxysilanes for the relevant applications are expected to be organised in the FEA and CES (or organised in the national associations organised in FEA) and have been contacted via these organisations. However, considering the answer from FEA, some producers of the aerosol dispensers may be relatively small companies and not be members of business organisations.

Suppliers of the products (different "nano products") investigated for their effects e.g. by Nørgaard et al. were contacted. Via these suppliers, the manufacturers of TDFAs and the producers of the investigated products was contacted and various information was received and used in the preparation for this dossier, especially in section B.1.2, B.2.1.1, B.2.1.3, B.2.2.1, B.2.2.2, C.2.1, C.2.4, C.3.4, C.4.1, D.2 and E.2.1.1.2.

In order to identify other suppliers/manufacturers of aerosol dispensers with the TDFAs, internet searched for SDS's or other indications of the presence of the substances in products were performed. A few companies were identified in this way and contacted by e-mail.

G.2 European Poison Centres, research and health institutions

The main part of the research is the effects of the use of the mixtures concerned has been conducted by the Danish National Research Centre for the Working Environment. The sections on human health effects have been prepared in close consultation with the Centre.

In addition information has been received from the Poison Control Hotline at Bispebjerg Hospital in Denmark on the annual number of calls related to consumer exposure to spray products in general.

In a follow up to the "Call for Evidence" carried out by ECHA all poison centers in the EU was contacted by e-mail in order to get more information on human incidents with impregnation spray products. Five poison centers replied. Finland and Estonia did not have any incidents involving impregnation spray products. Whereas Sweden had information on 98 incidents from 2000 to 2015 and The Netherlands had information on 26 incidents from 2013 to 2015. These information are included in Table 5. Spain had information on 13 phone calls related to incidents related to polyfluorinated silanes or fluorinated compounds and organic solvents (aromatic or isoparaffinic hydrocarbons). Of the 13 incidents 5 were due to inhalation. These 5 incidents are included in Table 5.

G.3 Member State consultation

In addition to the stakeholder consultation addressing the market actors, the Danish EPA circulated a discussion paper on risk management options and a request for information to Member

States. 2 Member States, 1 EEA country replied in the Call for Evidence. The comments received have been used in the preparation for this dossier, in section B.5.2 and D.2.

H. Other information

No other information.

Abbreviations and acronyms

10:2 FTOH	10:2 Fluorotelomer alcohol
6:2 FTOH	6:2 Fluorotelomer alcohol
8:2 FTOH	8:2 Fluorotelomer alcohol
AF	Assessment Factor
AIB	Danish Aerosol Industry Association (AIB).
APCI	Atmospheric pressure chemical ionization
ARDS	Acute respiratory distress syndrome
BAL	Bronchoalveolar lavage
BALB/cA	An albino, laboratory-bred strain of the house mouse
BALF	Bronchoalveolar lavage fluid
BfR	German Federal Institute for Risk Assessment
C&L	Classification & Labelling
CAS	Chemicals Abstract Service
CBA	Chemical Business Association
CLP	Classification, labelling and packaging (Regulation (EC) No 1272/2008)
CVD	Chemical Vapour Deposition
DMEL	Derived Minimal Effect Levels
DMFu	Dimethylfumarate
DNEL	Derived No Effect Level
EC	European Community
ECETOC	European Centre for Ecotoxicology and Toxicology of Chemicals
ESI	Electrospray ionization
ESIMS	Electrospray ionization mass spectrometry
ETC	Easy-to-clean
EU	European Union
EUR	€
FEA	Fédération Européenne des Aérosols
FTOH	Fluorotelomer alcohol
GLP	Good laboratory practice
HVLP	High Volume Low Pressure
IOEL	Indicative Occupational Exposure Limit
LC	Liquid chromatography
LC ₅₀	LC ₅₀ is the dose required to kill half the members of a tested population after a specified test duration.
LDH	Lactic dehydrogenase
LOAEC	Lowest Observed Adverse Effect Concentration
LTP	Low temperature plasma
NALDI	Nano-assisted laser desorption ionization
NCP	New Chemicals Program
NFP	Nano film product
NOAEL	No Observable Adverse Effect Level
OECD	Organisation for Economic Co-operation and Development
PBT	Persistent, bioaccumulative and toxic
PDMS	Polydimethylsiloxanes
PFAS	Per- and polyfluoroalkyl substances
PFHpA	Perfluoroheptanoic acid
PFHxA	Perfluorohexanoic acid
PFNA	Perfluorononanoic acid
PFPA	Perfluoropentanoic acid
PFOA	Perfluorohexanoic acid

PFOS	Perfluorooctane sulfonic acid
POTs	1H,1H,2H,2H-Perfluorooctyl trialkoxysilanes
RAPEX	Rapid Alert System for Non-Food Products
RCR	Risk characterization ratio
REACH	Registration, Evaluation, Authorisation and Restriction of Chemical Substances (Regulation EC 1907/2006)
RMO	Risk management option
RV	Recreational van
SDS	Safety Data Sheet
SVHC	Substance of very high concern
TDFAs	(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanetriol tri-O-(alkyl) derivatives
TM-DESI	Transmission-mode desorption electrospray ionization
TP	Time of pause
UK	United Kingdom
US EPA	United States Environmental Protection Agency
USA	United States of America
VOC	Volatile organic compound
vPvB	Very persistent and very bioaccumulative
VT	The volume of inspired or expired air in a single breath during regular breathing
WTP	Willingness to pay
ZDHC	Zero Discharge of Hazardous Chemicals

Definition of terms used

Different terms are used in the literature and technical data sheets for application methods and for description of the mode of action of the methods. The term "aerosol" is e.g. used in at least four different meanings. In order to avoid confusion, the following terms are used throughout the proposal.

Aerosol	Is in this proposal used for airborne fine solid particles or liquid droplets. In other contexts, the term may be used for 1) a suspension of fine solid particles or liquid droplets in a gas (here designated "aerosol mist") 2) a mixture enclosed under pressure and released as a fine spray by means of a propellant gas, or 3) the dispenser or package used to change the ingredient inside the container into an aerosol by the use of a propellant gas (here designated "aerosol spray can"). The European Aerosol Federation use the term "aerosol" for both the suspension and the dispenser/package.
Aerosol dispenser	Any non-reusable container made of metal, glass or plastic and containing a gas compressed, liquefied or dissolved under pressure, with or without a liquid, paste or powder, and fitted with a release device allowing the contents to be ejected as solid or liquid particles in suspension in a gas, as a foam, paste or powder or in a liquid state.
Aerosol spray can	The dispenser or package used to change the ingredient inside the container into an aerosol by the use of a propellant gas. The aerosol spray can is made up of four components: the container, the valve, the actuator and the cap.
Aerosol mist	A suspension of fine solid particles or liquid droplets (aerosols) in a gas.
Aerosolised	The process of converting the mixture inside the aerosol spray cans or other dispersers into an aerosol mist.

HVLP guns	High Volume Low Pressure guns - type of spray gun used by professionals and consumers. The HVLP gun is similar to a conventional spray gun using a compressor to supply the air, but the spray gun itself requires a lower pressure (LP). A higher volume (HV) of air is used to aerosolize and propel the paint at lower air pressure. The HVLP gun has a container where the user fill in the mixture from a can.
Impregnating agent	The mixture inside the dispensers is where relevant in the context designated "impregnating agent". In the technical literature the agents may alternatively be designated "water and dirt repellents", "easy to clean coatings", "surface protection products" "surface protection agents" or "corrosion inhibitors". The terms may also be used to designate the final polymer film.
Pump spray	Pump which contains mixtures to be sprayed. Most common are dispensers where the pressure is generated by a vertical press a button at the top of the dispenser by the hand.
Spray application	Used collectively for all applications where the mixture
Spray products	Used collectively for marketed aerosol dispensers, trigger sprays and pump sprays
Trigger spray	A type of dispenser where the pressure is generated by a horizontal press on a trigger by a hand.

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Appendix 1 – Human incidents

TABLE 1 - 1 OVERVIEW OF REPORTED INCIDENTS OF PULMONARY DISTRESS RELATED TO IMPREGNATION SPRAYS IN NON-EUROPEAN COUNTRIES

Country/year	Product name	Container type and product use	Active ingredients	Solvent	Individuals affected	Source
USA, 1992	Different products, names not available	Spray products Leather, suede and fabric impregnation	Fluoroaliphatic compounds	Isobutane, ethyl acetate, n-heptane	157	FOPH 2008
Canada, 1992-1993	Oiled Nubuck Leather protector	237 mL pump spray Leather	FS-4565 2% (stoddard solvent, heptane, fluoropolymer resin, and a copolymer), silicon (1%), and polymerized C10 alkanes (1%)	Soltrol-10 isooctane 95% (trimethylpentane (70%) and C7 and C8 isoparaffins (30%)) Isooctane	2 incidents described 14 additional calls to the Poison Center	Laliberté et al. 1995 Appendix 1 Table 1-2
USA, 1993	Different products, names not available	Spray products Leather, suede and fabric impregnation	Fluoroaliphatic compounds	Isobutane, ethyl acetate, n-heptane	39	FOPH 2008
Japan, 1992-1996	Different products, names not available	Spray products Waterproofing sprays	No information	No information	84	FOPH 2008
Japan, 2002-2003	No information	Spray product Waterproofing spray	No information	No information	1	FOPH 2008
UK, 2003	No information	Spray product Waterproofing spray	Fluorocarbon compounds	No information (Solvent change to low-odour solvent mix)	1 (fatal)	FOPH 2008
USA, 2005-2006	1) Jobsite Heavy Duty Bootmate 2) Rocky Boot Weather and Stain Protector	Aerosol spray cans Boot sealants	Fluorinated polymer (0.33%) Silicone (0.33%)	Heptane (45%) Petroleum distillates (20-30%)	172 (reported) 150 (investigated) 19 animals (pets)	CDC 2006 Appendix 1 Table 1-2
USA, 2005	Stand'n Seal "SprayOn" Grout Sealer (Stand'n Seal)	Aerosol spray can Tile and grout sealant	Fluorinated polymerresin	C8-C9 petroleum hydrocarbon solvents	30 (admitted to hospital)	Daubert et al. 2009 Appendix 1 Table 1-2

TABLE 1 - 2 CASE STORIES FOR THOSE INCIDENTS PRESENTED IN TABLE 5 AND APPENDIX 1 TABLE 1-1 WERE MORE DATA ARE AVAILABLE IN THE LITERATURE

1992-1993, Canada: Exposure to leather protector sprays (2 incidents)

1992-1993	Canada		
Product name	1) Oiled Nubuck Leather Protector (Vanguard Chemical Corporation) (2 incidents)		
Product description	1) 237 mL pump spray		
Product ingredients	Active substances	Solvents	Other substances
	FS-4565 2% (stoddard solvent, heptane, fluorinated polymer resin, and a copolymer), silicon (1%), and polymerized C10 alkanes (1%).	Soltrol-10 isooctane 95% (trimethylpentane (70%) and C7 and C8 isoparaffins (30%)) Isooctane	No information
Application (intended)	Pump spray		
Application (actual)	Pump spray		
Treated area/object	One pair of shoes.		
Exposure concentration	No information		
Exposure period	No information		
Exposure conditions	Spraying was carried out in a large apartment with windows and doors closed.		
Number of exposed	One person spraying, one bystander (several feet away)		
Number of affected	Both the sprayer and the bystander		
Symptoms and effects	<p><u>Patient 1:</u> 15 minutes after spraying acute respiratory symptoms of dyspnea, a dry cough, and anterior chest pain developed. The patient felt dizzy and chilly; his temperature at that time was 38.5°C. The patient appeared to be in moderate respiratory distress without evidence of cyanosis. Vital signs were blood pressure, 120/70 mm Hg; pulse, 108; respirations, 28; and temperature, 37°C. Head and neck examination was normal. Cardiac examination showed tachycardia without murmurs. Lung auscultation showed good air entry with diffuse bilateral wheezing. The chest radiograph was normal. Portable spirometry was performed before treatment and showed a mild obstructive syndrome.</p> <p><u>Patient 2:</u> A few minutes later the bystander developed similar respiratory symptoms. Physical examination revealed moderate respiratory distress with tachypnea, diaphoresis, and mild cyanosis. Vital signs were blood pressure, 140/80 mm Hg; pulse, 120; respirations, 32; and temperature, 37.8°C. Oxygen saturation was not recorded, but the cyanosis corrected rapidly after administration of 100% oxygen. Cardiac examination showed tachycardia without murmurs. Lung auscultation showed good air entry with diffuse, bilateral wheezing. A chest radiograph showed diffuse bilateral interstitial infiltrates consistent with pulmonary edema.</p>		
Treatment	Oxygen, supplemental oxygen, 5 mg nebulized salbutamol in normal saline solution, and 40 mg of prednisone/methylprednisolone orally. Patient 1 discharges after 8 hours, Patient 2 discharged after 24 hours.		
Other information	<p>14 additional calls to Quebec Poison Control Center from individuals complaining of acute respiratory symptoms associated with the use of Oiled Nubuck Leather Protector were reported over a 5-week period. In seven incidents, a medical evaluation was performed and pulmonary edema was documented in one case. These patients received supportive care with supplemental oxygen; some received nebulized salbutamol and IV corticosteroids. All were discharged within 24 hours.</p> <p>The authors also refer to 29 similar incidents reported in December 1992 associated with the use of another aerosolised leather shoe conditioner, Wilson's Leather Protector, based on fluorinated polymer resin and isooctane.</p>		

1992-1993	Canada
	In addition 3 incidents of acute respiratory illness from November 1993 were reported. The incidents were related to the use of an aerosolised leather-shoe conditioner similar to Oiled Nubuck Leather Protector and included 2-2-4 trimethylpentane, isooctane, and FS-4565.. The patients developed severe cough, shortness of breath, and tachypnea. Two had interstitial infiltrates on chest radiography. All treated patients responded well to bronchodilator therapy. Clinical findings suggested either a chemical or hypersensitivity pneumonitis
Source	Labiberté M., Sanfaçon G, Blais R. 1995. Acute pulmonary toxicity linked to use of a leather protector. <i>Ann Emerg Med.</i> 1995 Jun;25(6):841-4.

2002-2003, Switzerland: Exposure to waterproofing sprays (180 incidents)

2002-2003	Switzerland		
Product name	Three products: RapiAquaStop (Werner & Mertz GmbH, Mainz, Germany) was the most frequently involved spray (46% of incidents). The two other sprays reported were K2R (K2R Produkte GmbH, Gottmadingen, Germany) and RapiIntemp (Werner & Mertz) in 27% and 12% of the incidents, respectively. Three occupational exposure occurred with Patina-Fala (PATINA-FALA Beizmittel GmbH, Haar, Germany), a liquid stain-repellent mixture, when coated with a manual trigger spray.		
Product description	Three commercial spray cans intended for domestic or light occupational waterproofing.		
Product ingredients	Active substances	Solvents	Other substances
	Fluorinated acrylate polymer	Isoparaffinic hydrocarbons	No information
Application (intended)	Aerosol spray cans Patina-Fala: Paintbrush		
Application (actual)	Aerosol spray cans Patina-Fala: Trigger spray		
Treated area/object	Different water proofing sprays. No details. Patian-Fala: Tiled surface		
Exposure concentration	Concentration estimations were obtained using a two-zone model. For the aerosol application the maximal concentrations assessed ranged from 0.003 mg/m ³ to 35.98 mg/m ³ (mean value 4.21 mg/m ³) whereas the estimated doses range from 0.2 · 10 ¹ mg to 11.27 mg (mean value 0.657 mg). The two distributions are of approximate lognormal shapes. In a general sense, both assessed doses and concentrations exhibit wide ranges of values. The array of values is particularly large for the estimated dose, where seven orders of magnitude separate the upper and lower limits. This scattering mostly results from the variety of spraying and residence times reported in a questionnaires.		
Exposure period	The spraying times ranged from a few seconds to 90 min, whereas the residence time (time spent in the same room after the spraying activity) ranged from 0 to 12 hours. Eighty percent of the exposure times were shorter than 20 min and 80% of the residence times were shorter than 25 min.		
Exposure conditions	Fourteen percent occurred in open air and 32% in a partially open area, such as a terrace or a balcony. Indoor environments were reported in 54% of the incidents. Ventilation (either natural or forced) was present in most of them (92%). No ventilation (no open door, no open window) was reported in only 8% of the indoor incidents. The average volume of the rooms in which spraying took place was 49 m ³ (ranged between a minimum of 5.7 m ³ and a maximum of 250 m ³ , in the case of a garage). Eighty percent of the exposures took place in rooms of less than 75 m ³ .		
Number of exposed	It is not known how many in total have been exposed to the products. The same waterproofing agent appeared to be involved in a simultaneous outbreak reported in the Netherlands and in a fatal case reported from France. A fatal case occurred also in the UK at about the same period and under similar conditions.		
Number of affected	About 180 incidents were reported by the Swiss Toxicological Information Centre between October 2002 and March 2003, whereas fewer than 10 incidents per year had been record-		

2002-2003	Switzerland
	ed previously.
Symptoms and effects	Nearly all exposed individuals reported respiratory symptoms, such as cough or dyspnea (98% of incidents); 22% had digestive troubles, such as nausea, vomiting, or abdominal pain; 37% experienced general symptoms like fever, shivers, or myalgias; 40% had neurological troubles, such as giddiness, headache or loss of consciousness. Eye or throat burning was reported in 20% of incidents. For 23% of the exposed individuals, the symptoms were serious enough to require emergency hospital admission. Another 39% received ambulatory medical care, either from their regular physician or a hospital facility. The remaining 38% merely called the toxicological information center; they were not examined clinically.
Treatment	No information
Other information	In summary, the authors conclude that new outbreaks of waterproofing spray toxicity may occur if a particular combination of fluororesin and triggering factors (solvents, nebulization system) appears in a marketed product. The potential toxicity of such a product is likely to remain undetected in the premarketing phase if new preventive strategies are not applied.
Source	Vernez, D., Bruzzi, R., Kupferschmidt, H., Batz, A.D. Pierre Droz, ¹ and Lazor R. 2006 Acute Respiratory Syndrome After Inhalation of Waterproofing Sprays: A Posteriori Exposure-Response Assessment in 102 Incidents. <i>Journal of Occupational and Environmental Hygiene</i> May (5):250-261 Vernez, D., Droz, P-O., Lazor-Blanchet, C and Jaques, S. 2004 Characterizing Emission and Breathing-Zone Concentrations Following Exposure Cases to Fluororesin-Based Waterproofing Spray Mists. <i>Journal of Occupational and Environmental Hygiene</i> , 1 582-592

2005 (reporting), Scotland: Exposure to a waterproofing spray

2005 (reporting year)	Scotland		
Product name	Rucoguard EPF 1610		
Product description	Water proofing agent (mixture) for textiles (horse rugs)		
Product ingredients	Active substances	Solvents	Other substances
	Fluorocarbon polymer (cationic fluorocarbon polymer made by telomerisation)	Isopropanol	No information
Application (intended)	-		
Application (actual)	Spraying was undertaken in an 8×8×10 foot booth using a spray gun connected to an air compressor.		
Treated area/object	The water proofing agent was applied to horse rugs following laundering.		
Exposure concentration	No information.		
Exposure period	No specific information.		
Exposure conditions	The booth had a single extractor fan in the ceiling and the walls and floor were lined with residue of the fluorocarbon polymer plus horsehair. The door was frequently left open, allowing fumes to escape into the adjacent factory environment where rugs were washed and packaged. A filter mask, precise specification unclear, was available.		
Number of exposed	14 people employed. No information on how many were working in the spray booth, but possibly all 14 when the spray booth door was left open.		

2005 (reporting year)	Scotland
Number of affected	<p>Four workers in the horse rug cleaning company were referred to a chest clinic with cough and dyspnoea over a 15 month period.</p> <ol style="list-style-type: none"> 1. A 23 year old man who dismantled the air compressor inside the booth without respiratory protection during his first week of work. Compressed air escaped and disturbed the fluorocarbon residue on walls and floor, producing a fume and dust cloud. 2. An 18 year old man who regularly undertook fluorocarbon spraying 3. A 37 year old man who regularly undertook fluorocarbon spraying 4. A 35 year old female packaging the processed rugs nearby the spraying process.
Symptoms and effects	<ol style="list-style-type: none"> 1. Developed breathlessness and "throat tightness" within 30 minutes. At hospital he had frequent cough, tachypnoea (33 breaths per minute), was cyanosed, and unable to speak sentences. There was no fever, angioedema, or stridor, he had no wheezes or lung crackles, and cardiac examination was normal. 24 hours after onset of treatment his hypoxia and chest x ray abnormalities had nearly resolved. He developed a peripheral blood neutrophilia but remained afebrile. His unproductive cough and breathlessness persisted at 48 hours and pulmonary function tests showed a restrictive defect with reduced gas transfer. He was discharged after three days with a one week course of 50 mg prednisolone daily. Three weeks later he had returned to work but complained of exertional dyspnoea after half a mile, and an unproductive cough when exposed to car fumes. His dyspnoea and cough, however, worsened and he was readmitted to hospital the following month. He was tachypnoeic (24 breaths/minute) at rest but examination was otherwise normal. Transbronchial biopsies showed mildly inflamed pulmonary parenchyma, interstitial thickening, foci of organising exudate, and striking proliferation of type 2 alveolar lining cells in keeping with toxic alveolar injury. He was discharged taking 30 mg once daily prednisolone for four weeks. One month later spirometry showed marked improvement. He failed to attend further appointments. 2. The 18 year old had had mild symptoms for a year, which first occurred four months after starting work. These worsened over several months, although improved during holidays, and he left the job soon after the accident to the index case above. When he attended the clinic four months later his symptoms had greatly improved. He had no lung crackles, CXR was normal, but lung function tests showed a mild restrictive defect and moderate DLCO reduction (45% predicted). He did not attend for lung HRCT or outpatient review then but did so one year later. At this time he had no symptoms, lung volumes were virtually normal, but DLCO was 54% predicted. HRCT showed focal ground glass densities with a centrilobular distribution. Transbronchial biopsies showed patchy fibrosis. Two years after stopping fluorocarbon exposure his gas transfer had not improved further. 3. The 37 year old, had a history of allergic rhinitis. He worked for up to 11 hours daily six days per week with no holidays, using a filter helmet with separate air supply as respiratory protection. He presented with weight loss of 12 kg in addition to cough and dyspnoea, which had started four months after commencing work. He had no lung crackles or evidence of digital clubbing. Lung HRCT showed predominantly upper lobe ground glass shadowing. Transbronchial biopsy specimens were of identical appearance to those described in the index case. He stopped work and his symptoms and lung function improved substantially with treatment. Repeat HRCT was normal four months later. One year after presentation he still had impaired lung function. Peripheral blood showed specific IgE to horse allergen. 4. The 35 year old female developed cough and dyspnoea which did not respond to inhaled corticosteroids. She stopped work and at presentation to the clinic two months later, her symptoms had improved but she had a restrictive defect (FEV1 67%; FVC 68%; TLC 66%; RV 66%; DLCO 45%). Three months later her lung volumes were nearly normal but gas transfer remained low (52%). She did not attend for follow up.
Treatment	<ol style="list-style-type: none"> 1. Received 200 mg intravenous hydrocortisone twice daily for 24 hours for suspected pneumonitis, and 50 mg intravenous furosemide in case of pulmonary oedema, before changing to 50 mg once daily oral prednisolone. 2. No information. 3. Prednisolone 30 mg daily, tapering over several months. 4. Inhaled corticosteroids.
Other information	The authors from the chest clinic consider it likely that the respiratory disease in these patients is due to inhalation of fluorocarbon alone or in conjunction with horsehair. There is

2005 (reporting year)	Scotland
	evidence of persistently impaired lung function despite cessation of exposure
Source	Wallace, G.M.F., Brown, P.H. 2005. Horse rug lung: toxic pneumonitis due to fluorocarbon inhalation. Short report. Occup Environ Med 2005;62:414-416.

2005-2006, Michigan, Indiana, Utah, Pennsylvania, Ohio, and Kentucky, US: Respiratory illness associated with shoe or boot sealant products

2005-2006	US: 172 human and 19 animal (pet cats and dogs) incidents of respiratory illness reported to 6 regional poison control centers in five states from February 2005 to February 2006. 150 incidents from 2005 investigated.		
Product name	Jobsite Heavy Duty Bootmate (126 incidents) (Recalled from stores January 3, 2006) Rocky Boot Weather and Stain Protector (7 incidents) (Recalled from stores January 3, 2006)		
Product description	Shoe and boot leather protection products		
Product ingredients	Active substances	Solvents	Other substances
	Fluorinated polymer (0.33%) Silicone (0.33%)	Heptane (45%) Petroleum distillates (20-30%)	Isobutane (25-30%) Propane (5-10%)
Application (intended)	Aerosol spray cans. Spray application (not specified whether the products were recommended to be used outdoors).		
Application (actual)	Spray application.		
Treated area/object	Shoes/boots and clothing items.		
Exposure concentration	No information.		
Exposure period	No specific information.		
Exposure conditions	The product was sprayed indoors in 131/150 incidents and outdoors in 19/150 incidents. 5 occupational exposures (4 while spraying clothing items and 1 while demonstrating a product to a customer).		
Number of exposed	150 incidents reported to the poison control centers.		
Number of affected	144 patients were symptomatic.		
Symptoms and effects	Symptoms: Cough (78%) and dyspnea (60%). Chest radiographs were positive for infiltration in 13 of 47 patients with this finding. Chemical pneumonitis reported for 8 patients. uration of illness ranges from 0.25 – 360 hours (median 175 hours) in 116 patients where duration was evaluated.		
Treatment	Supplemental oxygen (51%), bronchodilator therapy (31%), and corticosteroids (10%). 80/144 were evaluated at hospitals. 15/144 had a hospital stay of up to 5 days.		
Other information	22 incidents were reported to the poison control centers after the product recall. Among the callers asked, all had purchased the products before the recall date. Among the 19 pets symptoms also included cough (16%), dyspnea (68%) and vomiting (16%) Two cats died from respiratory failure.		
Source	Centers for Disease Control and Prevention (CDC). Morbidity and Mortality Weekly Report. Brief Report: Respiratory Illness Associated with Boot Sealant Products – Five States, 2005-		

2005-2006	US: 172 human and 19 animal (pet cats and dogs) incidents of respiratory illness reported to 6 regional poison control centers in five states from February 2005 to February 2006. 150 incidents from 2005 investigated.
	2006. 2006. http://www.cdc.gov/mmwr/preview/mmwrhtml/mm5517a5.htm

2005, Michigan, Kentucky, Utah, Maine, Arizona, and Nebraska, US: Retrospective case review of exposure to a water proofing grout sealer

2005	US: 30 incidents of pulmonary toxicity from 6 regional poison control centers from June 1, 2005 to December 1, 2005		
Product name	Tile Perfect Stand'n Seal "SprayOn" Grout Sealer (Stand'n Seal) (Recalled in august 2005)		
Product description	Sealant for tile and grout.		
Product ingredients	Active substances	Solvents	Other substances
	Fluorinated polymer resin	C8-C9 petroleum hydrocarbon solvents	N-butyl acetate, isobutane and propane
Application (intended)	Aerosol spray. Used commercially and private.		
Application (actual)	Aerosol spray application		
Treated area/object	Grout (no further information)		
Exposure concentration	No information.		
Exposure period	The vast majority of patients used the product at home (80%).		
Exposure conditions	All patients in this study group used the product in a small, enclosed space with inadequate ventilation and little or no personal protective equipment (PPE).		
Number of exposed	No information.		
Number of affected	88 reported incidents of adverse reactions to Stand'n Seal, with 28 confirmed reports of pulmonary toxicity requiring medical attention.		
Symptoms and effects	<p>Nearly two-thirds of patients complained of either shortness of breath or cough. Almost half of the patients presented with a pulse oximetry reading of <90% on room air. A significant portion (60%) of patients who presented within an hour of symptom onset had a positive chest radiograph. It is not clear if early findings on chest radiograph represent the actual fluorinated polymer compound, early lung injury, or a combination of both.</p> <p>Detailed characteristics of exposed patients available.</p> <p>Only 3 patients had laboratory studies available for evaluation. All 3 had white blood cell counts >19,000 cells/mm³ with 1 patient developing a leukocyte count of 32,000 cells/mm³ at the time of admission. Nearly half of the patients required hospital admission due to the severity of their illness. Patients presenting within 3 hours of exposure were more likely to require hospital admission than those presenting >10 hours after exposure (59% vs. 43%). Long-term outcome was not assessed in this study.</p>		
Treatment	Supplemental oxygen, bronchodilator therapy, oral steroids, and antibiotics. 37% were discharged on the same day, 53% required hospital admission, 10% unknown.		
Other information	The authors conclude as follows: Although a temporal association exists between the use of Stand'n Seal and the development of pulmonary symptoms, the retrospective design prevents an evidence-based determination of causation		
Source	Daubert, G.P., Spiller, H.A., Crouch B.I., Seifert, S.A., Simone, K.E., Smolinske, S.C.2009. Journal Of Medical Toxicology Volume 5, Number 3, September 2009.		

2006, Germany: Exposure to sealing sprays for glass and ceramics and for hygienic facilities "The Magic Nano case"

2006	Germany		
Product name	Magic Nano Glass & Ceramic and Magic Nano Bath & WC		
Product description	Aerosol spray		
Product ingredients	Active substances	Solvents	Other substances
	Silane according to distributor. Likely to be a fluorosilane according to Koch et al. 2009	Dimethyl ether and ethanol	Corrosion inhibitor
Application (intended)	Aerosol spray		
Application (actual)	Aerosol spray		
Treated area/object	No information. Indented to be used for glass and ceramics and for hygienic facilities		
Exposure concentration	Release of approximately 200 g of the aerosol spray "Magic Nano Glass & Ceramic" in a model room with a volume of 60 m ³ resulted in a exposure concentration of non-volatile components (corrosion inhibitor and hydrolysates and condensates of (fluoro)silane) in the inhalable fraction (< 100 µm) of 41.5 mg/m ³ . Of these approximately 11.5 mg/m ³ were able to reach the bronchioles and/or alveoli (< 10 µm). Under the same test conditions the exposure concentration of non-volatile components (corrosion inhibitor and hydrolysates and condensates of (fluoro)silane) of the aerosol spray "Magic Nano Bath & WC" were 9 mg/m ³ in the inhalable fraction of which approximately 5 mg/m ³ were able to reach the bronchioles and/or alveoli.		
Exposure period	No information		
Exposure conditions	No information		
Number of exposed	No information		
Number of affected	154		
Symptoms and effects	<p>From the 27.3.2006 to 30.3.2006 The German Poison Information Centre-Nord (GIZ) registered more than 10 different incidents Groneberg 2010. No prior knowledge of medical history available.</p> <ul style="list-style-type: none"> • <u>Magic Nano Bath & WC:</u> <ul style="list-style-type: none"> - Person 1: Severe shortness of breath, cough, chills. Persistent cough 6 weeks after exposure. - Person 2: Cough and shortness of breath. Cough persisting for 6 days - Person 3: Inhalation stitches and cough within hours. Spontaneous improvement within the following night. • <u>Magic Nano Glass & Ceramic:</u> Respiratory symptoms such as, severe dyspnoea, cough and pain by inhalation. Other symptoms reported: Fever, chills, weakness, chest pain, nausea and headache. Some patients treated with Glucocorticoidspray. <ul style="list-style-type: none"> - Person 4: Severe shortness of breath. - Person 5: Violent cough and shortness of breath. Cough persisted even after 48 hours. - Person 6: Fever, stabbing pain by inhalation, cough. Improved after 24 hours, after 4 days still nausea and weakness. - Person 7: Dyspnoea and cough. Treatment with glucocorticoid. After 7 days even easier cough. - Person 8: Shortness of breath, headache, nausea, difficult breathlessness when lying down. - Person 9: Choking after a moment of use. After 3 day treatment respiratory problems still persisted. - Person 10: Sleep disturbances, chest pain, severe cough and headache. Cough ameliorated after 5 days, wheezing persisted. <p>Of the total of 154 persons affected there were 13 severe cases of pulmonary edema according to Pauluhn et al. 2008.</p>		
Treatment	Some patients treated with glucocorticoid spray		

2006	Germany
Other information	The product was pulled from the market in 3 days because of the respiratory epidemic in users. Investigations into the composition of the product were considerably complicated by the fact that the distributor had no knowledge of the composition of his products, and the suppliers refused to provide information – they argued to keep trade secrets on three components of their preparations Hahn (2007)
Source	Groneberg, D. 2010. Gesundheitliche Effekte von Nanopartikeln – aktueller Erkenntnisstand. <i>Tagungsbericht VIII. Potsdamer BK-Tage</i> . 4-5. June, page13-19. Hahn, A., Spielmann H. 2008. Assessment of early acute lung injury in rats exposed to aerosols of consumer products: attempt to disentangle the "Magic Nano" conundrum. <i>Inhal Toxicol</i> . 2008 Nov;20(14):1245-62. Koch, W., Schwartz, K., Koch, H., Langer, P. 2009. Inhalationstoxizität von Nanosprays: Physikalischchemische Untersuchungen. Fraunhofer Institut ITEM

1991-2007, Denmark: Retrospective review of 84 incidents reported in the Danish Poisons Centres databases

2005	DK: 84 incidents of respiratory effects following exposure to proofing sprays from 1991 to 2007		
Product name	No specific product names are listed. Brand names were known in 64 incidents.		
Product description	Incidents are related to proofing of the following products: Furniture (54), clothes (9), shoes (4), ceramic surfaces (4) carpet (2), tent (2), riding equipment (1), car seat (1), sealing foundation for paint (1), unknown (6). Some information available on product composition for half of the products. This information is however not included in the present source.		
Product ingredients	Active substances	Solvents	Other substances
	Fluorinated compound (most products) Fluoroacrylates (dodecylacrylate) and cyclosiloxanes (16 incidents) Silicones (some products with silicones alone)	No information	No information
Application (intended)	Consumer spray products. No further information on type of spray application.		
Application (actual)	Private use (83), occupational use (1)		
Treated area/object	Furniture, shoes, textiles, ceramics/tiles, other.		
Exposure concentration	Number of cans used ranged from 0.33 to 5.5 (75 – 2200 mL). (information from 27% of incidents). Exposure was considered small in 10 incidents, moderate in 50 incidents, and insufficient information was available in the remaining 24 incidents.		
Exposure period	Time of spraying ranged from 2 to 120 minutes.		
Exposure conditions	All incidents except one related to private use, 53 reported indoor use, 4 outdoor use. Information on 47 incidents. Ventilation present in 15 incidents, no ventilation reported in 17 incidents.		
Number of exposed	In addition to the 84 exposed, information on exposure of bystanders included: 2 pets, 4 children below 10 years, and 1 adult (accidental exposure).		
Number of affected	Respiratory effects present in most patients (92%).		
Symptoms and effects	Clinical data on 84 incidents accidentally exposed to proofing sprays:		
	Parameter	Number of incidents	Percent (%)

2005	DK: 84 incidents of respiratory effects following exposure to proofing sprays from 1991 to 2007																																				
	<table border="0"> <tr> <td>Airway effects only (N=84)</td> <td>27</td> <td>32</td> </tr> <tr> <td>Airways + general (N=84)</td> <td>50</td> <td>60</td> </tr> <tr> <td>General effects only (N=84)</td> <td>3</td> <td>4</td> </tr> <tr> <td>No symptoms (N=84)</td> <td>3</td> <td>4</td> </tr> <tr> <td>Latency till effects (N=49)</td> <td>31</td> <td>63</td> </tr> <tr> <td>Reduced oxygenation (N=47)</td> <td>19</td> <td>40</td> </tr> <tr> <td>Pulmonary infiltrates (N=30)</td> <td>13</td> <td>43.4</td> </tr> </table> <p>Moderate/ severe effects (58%), mild effects (37%), no poisoning (4%). The majority of patients had general symptoms including fever, general malaise, gastrointestinal upset and symptoms from the central nervous system. Symptoms started typically minutes up to one hour after cessation of exposure.</p>	Airway effects only (N=84)	27	32	Airways + general (N=84)	50	60	General effects only (N=84)	3	4	No symptoms (N=84)	3	4	Latency till effects (N=49)	31	63	Reduced oxygenation (N=47)	19	40	Pulmonary infiltrates (N=30)	13	43.4															
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Treatment	No information available via this source.																																				
Other information	<p>Distribution of incidents in the period from 1991 to 2007:</p> <table border="1"> <caption>Data for Distribution of incidents (1991-2007)</caption> <thead> <tr> <th>Year</th> <th>Number of incidents</th> </tr> </thead> <tbody> <tr><td>1991</td><td>2</td></tr> <tr><td>1992</td><td>2</td></tr> <tr><td>1993</td><td>4</td></tr> <tr><td>1994</td><td>6</td></tr> <tr><td>1995</td><td>4</td></tr> <tr><td>1996</td><td>2</td></tr> <tr><td>1997</td><td>3</td></tr> <tr><td>1998</td><td>3</td></tr> <tr><td>1999</td><td>1</td></tr> <tr><td>2000</td><td>0</td></tr> <tr><td>2001</td><td>0</td></tr> <tr><td>2002</td><td>0</td></tr> <tr><td>2003</td><td>3</td></tr> <tr><td>2004</td><td>18</td></tr> <tr><td>2005</td><td>25</td></tr> <tr><td>2006</td><td>14</td></tr> <tr><td>2007</td><td>0</td></tr> </tbody> </table>	Year	Number of incidents	1991	2	1992	2	1993	4	1994	6	1995	4	1996	2	1997	3	1998	3	1999	1	2000	0	2001	0	2002	0	2003	3	2004	18	2005	25	2006	14	2007	0
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Source	Lyngenbo, O., Bang, J., Jacobsen, P. 2008. Lung injuries from proofing sprays. Annex 1 in "Survey and Health Assessment of Possible Health Hazardous Compounds in Proofing Sprays", Danish EPA, 2008.																																				

2010, Maniitsoq, Greenland: Exposure to a tile coating product

2010	Maniitsoq, Greenland		
Product name	Stain Repellant Super®		
Product description	Surface coating product used for ceramic tiles.		
Product ingredients	Active substances	Solvents	Other substances
	Non-fluorinated alkylsiloxanes No fluorinated substances detected (MS and WD-XRF)	Hydrogenated naphtha C ₉ -C ₁₃ . (50-100%) (MSDS and MS)	No information
Application (intended)	Brush, a roll, a floor mop, or a low pressure airless spray gun with maximum pressure less than 1 bar.		
Application (actual)	Workers decided to carry out the work using a high pressure airless spray gun with a working pressure up to 135 bar and a nozzle diameter of 279.4 µm..		
Treated area/object	In a supermarket under renovation 50 m ² of the 300 m ² tile floor was sprayed with 30 L (22.8 kg) of the tile coating product, Stain Repellant Super®		

2010	Maniitsoq, Greenland
Exposure concentration	The ground area of the building was 900 m ² with a ceiling height of 4 m. Total volume 7200 m ³ .
Exposure period	39 exposed persons were present for 10-150 minutes during and/or after the spraying event in the building: 2 men were operating the spray gun and three men worked close to the two persons spraying. They were all present during the spray operation. After the spray event, 25 persons were exposed for 30-150 minutes at ground level or at the above floor close to ground level apertures. 9 persons were exposed less than 30 minutes on the first floor.
Exposure conditions	None of the 39 exposed were wearing eye or respiratory protection, and the mechanical ventilation system of the building was turned off. Upon spray application, a large fraction of the product will immediately be adsorbed to surfaces, but the concentration of aerosolised mixture is assumed to be high, especially near the spraying site. SRS aerosols were visible for hours and spread to the first floor containing the supermarket through open spaces, comprising approximately 10% of the floor separation, and further translocated to the office area at the same floor. The day after the episode, surfaces in most of the building were visibly contaminated by the product.
Number of exposed	43 persons contacted the hospital. No information about the total number of exposed.
Number of affected	40 persons (18 workers) considered significantly clinically affected. 39 evacuated by plane to the larger national hospital (1 declined).
Symptoms and effects	The symptoms developed within few hours and included coughing, tachypnoea, chest pain, general malaise and fever. The physical examination revealed perihilar lung infiltrates on chest radiograph and reduced blood oxygen saturation. All 39 patients had an onset of respiratory symptoms within the first hour from exposure and within 1–12 h they complained of coughing (39/39), shortness of breath (29/39), chest pain (8/39), general malaise (19/39) and headache (18/39). Many patients had tachycardia (15/39) and tachypnoea (17/33) and two-third of the patients had a temperature rise above 38°C. None of the patients had upper respiratory tract manifestations or eye irritation. Within the first 12 h after the spraying event the body temperature normalized on all patients. None of the patients had any worsening of symptoms after 12 h and there were seen no delayed effects in the following days. The acute symptoms resolved gradually within 1–3 days and no delayed symptoms were observed. By means of mass spectrometry and X-ray spectroscopy, it was shown that the product contained non-fluorinated alkylsiloxanes. Two months after the exposure, the patients were interviewed using a structured questionnaire, and all the patients had a standardized clinical follow-up including a pulmonary function test, a plain radiograph of the chest, and an exercise test on a stationary bicycle with a blood oxygen saturation measurement. The patients who had had an abnormal plain chest radiograph two months earlier and all patients that reported symptoms at the follow-up had a plain radiograph of the chest taken at the follow-up examination.
Treatment	Patients were administered supportive therapy, including supplemental oxygen and inhaled glucocorticoid.
Other information	"Among these patients only a partial association between the level of exposure and the degree of respiratory symptoms was observed, which could be because of a high inter-individual difference in sensitivity and time-dependent changes in the chemical composition of the aerosol."
Source	Duch, P., Nørgaard, A.W., Hansen J.S., Sørli, J.B., Jacobsen, P., Lynggaard F., Levin, M., Nielsen, G.D., Wolkoff, P., Ebbehøj, N.E., Larsen, S.T. (2014). Pulmonary toxicity following exposure to a tile coating product containing alkylsiloxanes. A clinical and toxicological evaluation. <i>Clinical Toxicology</i> (2014), Early Online: 1–8.

2011, Netherlands: Exposure to rain proofing spray

2011	Netherlands		
Product name	Product name not provided.		
Product description	Rain-proofing spray		
Product ingredients	Active substances	Solvents	Other substances
	Fluorocarbon polymer	Not specified for the product	Not specified for the product
Application (intended)	Aerosol spray		
Application (actual)	Aerosol spray		
Treated area/object	Impregnation of shoes		
Exposure concentration	No information		
Exposure period	No information		
Exposure conditions	Impregnation of shoes were carried out indoors in a room of about 20 m ² , with the windows closed. She had not noticed any irritation while using the spray. Moreover, she had used the same spray previously under similar conditions without any accompanying complaint.		
Number of exposed	One 36 year old women.		
Number of affected	Case involves one person.		
Symptoms and effects	<p>The patient presented herself with an acute onset of dyspnoea, a dry cough and a high grade fever with a temperature of 39.5°C. These complaints were accompanied by generalized muscle ache and headache. Within an hour she felt nauseated and started vomiting.</p> <p>On physical examination the patient was frankly dyspnoeic, with a respiratory rate of 22 breaths per minute and a peripheral oxygen saturation of 89% while breathing room air. She had a tympanic temperature of 38.5°C. Auscultation of the lungs revealed normal breathing sounds without rhales or crackles appreciated. The remainder of the physical examination was unremarkable. She was not able to complete sentences without taking a breath.</p> <p>Laboratory investigation showed an elevated white blood cell count (13 600/μl), with a marked neutrophilia (12 600/μl). Other laboratory results, including peripheral eosinophil count and C-reactive protein, were normal. The routine chest-X-ray showed bilateral, diffuse, interstitial opacifications.</p> <p>Moreover, the results showed bronchoalveolar lavage with cellular differentiation in the acute phase of a toxic alveolitis due to a water repellent spray.</p>		
Treatment	<p>The patient was treated supportively with supplemental oxygen and anti-emetics. Corticosteroids and bronchodilators initiated as an outpatient were discontinued.</p> <p>The patient made a full recovery, after 4 days of in-hospital observation. The chest X-ray normalized. Lung function testing, including airflows, total lung capacity, and diffusion capacity (DLCO), performed in an out-patient service 2 weeks after discharge was within normal limits for all values.</p>		
Other information	The authors conclude that inhalation exposure to waterproofing sprays containing fluorocarbon polymers is a well known cause of an acute toxic pneumonitis, but the mechanism of injury remains obscure. Several hypotheses have been suggested. One accretive theory is that the polymer may exert its "waterproofing effect" on the alveolar surface, thereby modifying the alveolar surface tension and disrupting surfactant, thus causing alveolar collapse and impairment in gas exchange.		
Source	Epping, G., Baarlen, J.P., Valk, P.D.L.P.M. v.d. 2011. Toxic Alveolitis after Inhalation of a Water Repellent. International Journal of Occupational Medicine and Environmental Health 2011;24(4):409 – 413.		

TABLE 1 - 3 HUMAN POISONING CASES REPORTED TO BFR ON IMPREGNATING SPRAY (1990-01 TO 2015-04)

BfR Case ID	Product Intended Use Category	Water-Proofing Ingredient	Severity of health impairment (PSS)	Symptoms Reported	Causality
1940/07	impregnating spray for textiles	fluorocarbon resin	severe	cough, tachypnea, pulmonary spastic, rale, pulmonary oedema	probably
2151/07	impregnating spray for textiles	fluorocarbon resin	severe	laboured breathing, rale, pulmonary oedema, tachycardia, chills, sleepiness	probably
3083/13	impregnating spray	not known	severe	cough, pulmonary oedema, pneumonia, dyspnea, respiratory insufficiency acute, hypoxia, absence of voice	probably
1529/06	impregnating spray for textiles	Silane	minor	cough, dyspnea, laboured breathing, bronchitis	probably
3463/06	impregnating spray for textiles	Silane	Minor	cough, bronchitis	probably
3630/07	impregnating spray for fabrics	fluorocarbon resin	moderate	cough, alveolitis, fever	probably
0002/10	impregnating spray for fabrics	fluorocarbon resin	moderate	laboured breathing, cough, pulmonary oedema, reduced general condition	probably
0003/10	impregnating spray for fabrics	fluorocarbon resin	severe	laboured breathing, cough, pulmonary oedema, reduced general condition	probably
0174/90	impregnating spray	not known	severe	pulmonary oedema	possible
0900/97	impregnating spray	not known	severe (lethal outcome)	acute respiratory insufficiency, pneumonia, circulatory collapse, death	possible
3569/05	impregnating spray for textiles	fluoropolymer	moderate	cough, airway obstruction, dyspnea	possible
8015/01	impregnating spray for fabrics	not known	Minor		
4242/03	impregnating spray for textiles	not known	moderate	dyspnea	probably
5393/03	impregnating spray for fabrics	impregnating resin	Minor	cough, headache, nausea	probably
2973/02	impregnating spray for fabrics	impregnating resin	moderate	dyspnea, pneumonia, pulmonary oedema, tachycardia	possible
4764/02	impregnating spray for fabrics	impregnating resin	Minor	cough, dyspnea, thoracic pain	probably
4201/03	impregnating spray for fabrics	impregnating resin	moderate	cough, laboured breathing	probably
3532/01	impregnating spray for fabrics	fluoro-acrylat-copolymer	moderate	laboured breathing, cough, pulmonary oedema	probably
2249/07	impregnating spray for fabrics	fluoro-acrylat-copolymer	Minor	respiratory distress	probably

Appendix 2 – Exposure modelling

2.1 Extrapolation of measured exposure concentrations

Inlet flow rates of the high-pressure spray, particle concentration and particle mass sampled on filter in Table 2-1 is taken from Table 1 in Nørgaard et al. (2010a). Total amount of NFP 1 sprayed is given by:

$$Total_NFP1 = \frac{(Inlet\ flow) \times (density)}{Airflow}$$

The density of NFP 1 is 0.78 g/ml and the air exchange (airflow) in the mice exposure chamber were 29.6 L/min in Nørgaard et al.(2010a). The mass percentage of total NFP 1 sprayed that are sampled on the filter are calculated.

TABLE 2 - 1 PARTICLE CONCENTRATION DATA FOR EXPOSURE OF MICE WITH NFP 1

Inlet flow rate	Particle conc.	Total amount NFP 1 sprayed	Particle mass filter	Particle mass filter / Total NFP 1 sprayed
ml/min	n/cm ³	g/m ³	mg/m ³	%
0.01	1.4E+5	0.26	0.5	0.19
0.05	6.8E+5	1.32	3.3	0.25
0.075	1.0E+6	1.98	5.9	0.30
0.1	1.5E+6	2.64	8.5	0.32
0.2	2.5E+6	5.27	15.7	0.30
0.21	2.1E+6	5.53	16.1	0.29
0.23	2.3E+6	6.06	18.4	0.30
0.3	2.5E+6	7.91	24.4	0.31
0.5	4.6E+6	13.18	42.4	0.32
			Mean value	0.29

In the worst case scenario where 40 g/m² NFP 1 is used in the standard room with a floor of 7 m² and a volume of 17.4 m³ the total amount of NFP 1 sprayed pr. m³ equates to 16.1 g/m³.

As can be seen from the table the mass concentration of the hydrolysates and condensates of TDFAs and 2-propanol sampled on the filter equates to a mean value of 0.29 % of the total NFP 1 infused in the exposure chamber. This means that the concentration of hydrolysates and condensates in the gas phase reaches around 46.2 mg/m³. This result is used in section B. 8.3.2.2.

2.2 Detailed information on exposure estimation

2.2.1 Exposure estimation with ConsExpo

An adult with a body weight of 60 kg is used in the calculations. No compound specific data is entered (this is not required in the model). The inhalation model "exposure to spray" is selected, with "spraying" chosen as release mode. The different input parameters entered in the model, as well as the mathematical explanation of the exposure model (the model algorithm) are shown below.

Model algorithm:

To predict aerosol particle concentrations in air, the model takes as input the non-volatile mass that is being sprayed, the initial particle size distribution, room dimensions and room ventilation (Delmaar and Bremmer, 2009).

$$\frac{A_{air}}{V_{room}} = C_{air}(t) = f_{airborne < 20\mu m} \times \frac{M_{tot}}{V_{room}} \sum_{\delta} P(\delta) \times \Delta\delta \times e^{-(V_s(\delta) / h + q)t},$$

where

M_{δ}	:	total mass of aerosols with diameter δ
t	:	time
$f_{airborne < 20\mu m}$:	fraction of respirable (i.e. with diameter smaller than 20 μm) aerosols that becomes airborne.
M_{tot}	:	total mass sprayed
$P(\delta)$:	probability density function for aerosol of diameter δ
δ	:	aerosol diameter
A_{air}	:	airborne mass
C_{air}	:	room air concentration
S_{room}	:	room surface area
v_s	:	Stokes's settling velocity
V_{room}	:	room volume
h	:	room height
q	:	ventilation rate (number of air changes per unit time)

General exposure parameters

General input parameters for the exposure calculations are given in Table 2 - 1.

TABLE 2 - 1 GENERAL INPUT PARAMETERS USED FOR EXPOSURE CALCULATION

Parameter	Explanation	Input value	Reference
Use frequency	The number of times per unit of time (i.e. per year) that the product is used	a) 3 events/year b) 1 event/year c) 8 events/year	RWC Assumption Engelund and Sørensen, 2005
Spray duration	The amount of time between start and finish of the spraying.	a 1) Pump: 13 min Aerosol spray can: 40 sec a 2) Pump: 23 min Aerosol spray can: 70 sec b) Pump: 20 min Aerosol spray can: 62 sec c) Pump: 2.5 min Aerosol spray can: 7.5 sec	RWC Assumption Engelund and Sørensen, 2005
Exposure duration	The amount of time spent in the room where the spraying takes place	a) 30 min b) 1 hour c) 5 min	RWC Assumption Engelund and Sørensen, 2005
Room volume	The volume of the room where the spraying takes place	a1) 10 m ³ a2) 17.4 m ³ b) 58 m ³ c1) 15 m ³ c2) 10 m ³	ECHA, 2012b and Nørgaard, 2010 ECHA, 2012b ECHA, 2012b
Room height	The height of the room where the spraying takes place	a) 2.5 m b) 2.5 m c) 2.5 m	Assumption, based on data on default values for surface area and room volumes for the chosen room types, Bremmer et al, 2006.
Ventilation rate	The number of total air changes in the room per time	a) 0.2 h ⁻¹ b) 0.2 h ⁻¹ c) 0.2 h ⁻¹	ECHA, 2012b

Product specific input parameters

In ConsExpo the inhalation model "exposure to spray" is chosen. This model is used in case a non-volatile compound is released as an aerosol from a spray can or a trigger spray. Chemical analysis using electrospray ionization mass spectrometry (ESIMS) showed that NFP 1 contained hydrolysates and condensates of polyfluorooctyl triisopropoxysilane. Total concentration of non-volatile were found to 1.1±0.1 %, Nørgaard et al. (2009).

No exact data on average particle diameter and width is available for the aerosols generated from NFP 1. However, this input parameter is according to the algorithm used for estimating the air concentration only used to determine the fraction of airborne particles with a particle size < 20 µm and the settling velocity (V_s):

$$\frac{A_{air}}{V_{room}} = C_{air}(t) = f_{airborne < 20\mu m} \times \frac{M_{tot}}{V_{room}} \sum_{\delta} P(\delta) \times \Delta\delta \times e^{-(V_s(\delta) / h+q)t}$$

The particle number size distribution was roughly the same in both animal experiment (Nørgaard et al. 2010a) and in spray chamber experiments with NFP 1 (Nørgaard et al. 2009

and Nørgaard 2010d). However, the number of particles generated by the pump spray in the spray chamber experiments are significantly lower than the number of particles generated the high-pressure nebulization in the animal experiment. It is therefore assumed that 100 % of the released particles are < 20µm, both for the pump spray and for the aerosol spray can. This is entered in the model in that way, that the average (incl. width) and maximum particle diameter is both set at < 20 µm. The chosen particle diameter also affects the settling velocity of the particle, as larger particles have larger settling velocities and are thus faster removed from the air. Again, as a worst case, a small particle size (in the nm) range is therefore chosen.

The resulting exposure estimates should therefore be interpreted carefully, and the results can only be seen as indicative of the expected exposure values.

The product specific parameters inserted in the model are given in Table 2-2.

TABLE 2-2 PRODUCT SPECIFIC INPUT PARAMETERS USED FOR EXPOSURE CALCULATION

Parameter	Explanation	Input value	Reference
Mass generation rate	The amount of compound that will be released from the spray container during the spraying per unit of time	Pump spray: 0.2 g product/pump Aerosol spray can: 4 g product/sec	Nørgaard 2015 (pers. comm.)
Airborne fraction	The fraction of the non-volatile material that becomes airborne after spraying as droplets. The airborne fraction will depend on the way in which the product is being used, i.e. in treating a surface (paint, wood preservative) or as an airspace (spraying against flies), and on the droplet size distribution that has been specified	Pump spray: 0.1 Aerosol spray can: 0.25	Nørgaard 2015 (pers. comm.)
Weight fraction non-volatile	The total fraction of non-volatile compounds in the product. Note that in addition to the compound (which is supposed to be non-volatile) other components with low volatility may be present.	1.1 % (0.011)	Nørgaard et al. 2010
Weight fraction compound	The fraction of compound of interest in the product	1.1 % (0.011)	Nørgaard et al. 2010
Density non-volatile	Mass density of the total of non-volatile compounds	1.329 g/cm ³	Density of perfluorooctyl triisopropoxysilane is used in this case. LookChem n.d.
Initial particle distribution*	The normalized mass distribution of the particles (droplets) immediately after they are ejected. The user has a choice of two parametric distribution functions: normal or lognormal. For both distributions an average particle diameter (mean resp. median) and a width (standard deviation resp. coefficient of variation) has to be specified. In addition the maximal droplet diameter that is produced by the spray has to be given. This maximal droplet diameter should be taken not too high (preferably < 50 µ), since only inhalable droplets are to be considered.	Average particle diameter: 0.1 µm SD: 0.5 Max. droplet value: 2 µm.	Worst case assumptions
The inhalation cut-off diameter	The diameter below which the spray droplet can be inhaled and reach the lower areas of the lungs (the alveolar region).	15 µm	Default value ConsExpo

The resulting exposure estimates from running the ConsExpo model with the input parameters given in Table 2-1 and 2-2 can be seen in Table 2-3 (identical to Table 6 in B.8.3.2).

TABLE 2-3 EXPOSURE ESTIMATES FOR NFP 1 FROM CONSEXPO (IDENTICAL TO TABLE 6)

		Mean event concentration (mg/m ³)
Spraying of 4 m ² in a 10 m ³ bathroom	Pump spray	13
	Aerosol dispenser	41
Spraying of 7 m ² in a 17.4 m ³ bathroom	Pump spray	11
	Aerosol dispenser	42
Impregnation of a 6.2 m ² sofa in a 58 m ³ living room	Pump spray	3.5
	Aerosol dispenser	11
Impregnation of a pair of shoes/boots in a 15 m ³ kitchen	Pump spray	1.6
	Aerosol dispenser	5.4
Impregnation of a pair of shoes/boots in a 10 m ³ bathroom	Pump spray	2.5
	Aerosol dispenser	8.1

The estimation of the consumer exposure to hydrolysates and condensates of polyfluorooctyl triisopropoxysilane from using the product NFP 1 is based on a number of assumptions, which are all subject to different uncertainties, and this reflects the validity of the resulting estimates. The assumptions are specific to the product NFP 1 and based on the expert knowledge of A. Nørgaard.

The assumptions regarding room size and room ventilation rates are based on default values from ECHA guidance document on consumer exposure estimation (ECHA, 2012b), RIVM general fact sheet (Bremmer et al, 2006) and data from Nørgaard et al. (2010b). In ECETOC TRA default room volumes and ventilation are used.

Mean generation rate: this parameter influences both the total amount of product applied and the exposure time entered in the model. For the aerosol dispenser, a mass generation rate of 4 g/sec is used²¹. Using the estimate of 40 g product/m², this corresponds to a spray duration of 10 sec/m². For the pump impregnation spray, and spray duration of 200 sec/m² is calculated using the mass generation rate of 0.2 g/sec²². For the aerosol spray can scenarios, this is probably an underestimation of the actual spraying duration, as it probably takes more than 7.5 sec for a consumer to spray a pair of boots, while in the pump spray scenarios, this spray duration may be a little overestimated.

Initial droplet (particle) distribution: This is the normalized mass distribution of the particles (droplets) immediately after they are ejected. No exact data on average particle diameter and width are available for the aerosols generated from NFP 1. This input parameter is according to the algorithm used for estimating the air concentration, only used to determine the fraction of airborne particles with a particle size < 20 µm and the settling velocity (V_s). According to data from Nørgaard et al. (2009), both nanoparticles and µm-sized particles were generated during spraying of NFP 1, with particle sizes up to 2 µm. As these are far below the cut-off of 20 µm used in the calculations, it was assumed that 100 % of the released particles are < 20 µm, both for the pump spray and for the aerosol spray can. Some aerosols, especially in the pump spray scenarios are likely to be larger than 20 µm, so this scenario represents a worst case

²¹ The applied mass generation rate differ from the default values from the ConsExpo Spray model for spray cans, which is between 0.8 and 2.2 g/sec, depending on the product category. No default value for impregnation sprays are available.

²² The applied mass generation rate for pump sprays is close to the default value in ConsExpo, which is 0.1 g/sec.

scenario. The chosen particle diameter also affects the settling velocity of the particle, as larger particles have larger settling velocities and are thus faster removed from the air. For illustration, the difference in the resulting exposure estimate between an average particle size of $2 \pm 0.5 \mu\text{m}$ and $0.1 \pm 0.5 \mu\text{m}$ calculated in ConsExpo is 100 mg (assuming a maximum particle size of $10 \mu\text{m}$ in both cases, and all other parameters being similar).

Airborne fraction: In this case the fraction of active compound (hydrolysates and condensates of polyfluorooctyl triisopropoxysilane) that will be airborne is assumed to be 10 % from the pump spray and 25 % for the aerosol spray can (based on information from Nørgaard, 2015 (personal communication)). A conservative, worst case scenario could be that 100% is released from the aerosol spray can and 50 % from the pump spray, but this would result in an overestimation of the exposure. In general, the airborne fraction will be higher in the case of smaller objects to be sprayed (such as shoes) and smaller in the case of e.g. a floor where most of the product will stay on the treated surface.

The resulting exposure estimates should therefore be interpreted very carefully, and the results can only be seen as indicative of the expected exposure values.

Refinement of input parameters and resulting exposure estimates

Refinement of ventilation rate is conducted for all scenarios in order to investigate how this affects the resulting exposure estimates. The ventilation rate is set at 0.1 and 1 h^{-1} , respectively. All other parameters are as Table 2-1 and 2-2.

The resulting exposure estimates are shown Table 2-4 below. Original value (using 0.2 h^{-1}) shown in italics, new values shown in bold.

TABLE 2-4 EXPOSURE ESTIMATES FOR NFP 1 FROM CONSEXPO WITH DIFFERENT VENTILATION RATES

		Mean event concentration (mg/m ³)		
		<i>0.2</i>	0.1	1
	Ventilation rate (h ⁻¹)			
Spraying of 4 m ² in a 10 m ³ bathroom	Pump spray	<i>13</i>	13	11
	Aerosol spray can	<i>41</i>	42	35
Spraying of 7 m ² in a 17.4 m ³ bathroom	Pump spray	<i>11</i>	11	9.3
	Aerosol spray can	<i>42</i>	43	35
Impregnation of a 6.2 m ² sofa in a 58 m ³ living room	Pump spray	<i>3.5</i>	3.6	2.6
	Aerosol spray can	<i>11</i>	11	7.4
Impregnation of a pair of shoes/boots in a 15 m ³ kitchen	Pump spray	<i>1.6</i>	1.6	1.6
	Aerosol spray can	<i>5.4</i>	5.4	5.2
Impregnation of a pair of shoes/boots in a 10 m ³ bathroom	Pump spray	<i>2.5</i>	2.5	2.4
	Aerosol spray can	<i>8.1</i>	8.1	7.8

It can be seen that the ventilation rate does not affect the mean event concentration to a very large extent.

A refinement of scenario a) is conducted in order to investigate how changing the exposure duration from 30 min to 15 min affects the resulting exposure estimates. The changed input parameters are shown in Table 2-5.

TABLE 2-5 INPUT PARAMETERS USED FOR EXPOSURE CALCULATION WITH CHANGED EXPOSURE DURATION

Parameter	Input value
Use frequency	a) 3 events/year
Spray duration	a 1) Pump spray: 13 min, Aerosol spray can: 40 sec a 2) Pump spray: 23 min, Aerosol spray can: 70 sec
Exposure duration	a) 15 min
Room volume	a1) 10 m ³ a2) 17.4 m ³
Room height	a) 2.5 m
Ventilation rate	a) 0.2 h ⁻¹

The resulting exposure estimates are shown in Table 2-6 below. The original values (using 30 min as exposure duration) shown in italics, new values shown in bold.

TABLE 2-6 EXPOSURE ESTIMATES FOR NFP 1 FROM CONSEXPO WITH CHANGED EXPOSURE DURATION

	Exposure duration (min)	Spraying of 4 m ² in a 10 m ³ bathroom		Spraying of 7 m ² in a 17.4 m ³ bathroom	
		Pump spray	Aerosol dispenser	Pump spray	Aerosol dispenser
Mean event concentration (mg/m ³)	<i>30</i>	<i>13</i>	<i>41</i>	<i>11</i>	<i>42</i>
	15	9.5	42	5.7	42

The mean event concentrations for the aerosol dispenser is not affected by reducing the exposure duration, but for the pump spray the a1) scenario the exposure concentration is lowered by 3.5 mg/m³ by changing the time spent in the room after spray duration from 17 min to 2 min. For the a2) scenario, the mean event concentration is halved. However, this is due to the fact that it is possible to set up a calculation where the spray duration exceeds exposure the duration. This means that the time to spray the total amount (280 g NFP 1) will be too low.

2.2.2 Exposure estimation with ECETOC TRA

For comparison, exposure estimation was also carried out in ECETOC TRA.

It is not possible to apply user-specified room volumes and ventilation rates in ECETOC TRA, so in this model, the scenarios are only differentiated in terms of applied amounts and exposure times.

The input parameters is given in Table 2-7.

TABLE 2-7 INPUT PARAMETERS USED FOR EXPOSURE CALCULATION WITH ECETOC TRA

Parameter	Input value
Descriptor (i.e. PC)	Aerosol spray can within PC 9a – coating, paints, thinners and re-movers
Subcategory (name)	NPF-1 coating
Exposure (child/adult)	Adult (60 kg (default))
Product ingredient by weight fraction	0.011
Frequency of use (events/day)	1
Amount of product used per application (g)	a) 280****
40g/m ² is used for scenario a and b. For scenario c, the amount used for impregnation of one pair of shoes is set to be 27.8 g, based on data from Engelund and Sørensen (2005).	b) 248
	c) 27.8
Fraction released to air	1*
Exposure time (h)***	a) pump spray: 23 min
	a) aerosol spray can: 1.2 min
	b) pump spray: 20 min
	b) aerosol spray can: 1 min
	c) pump spray: 2.5 min
	c) aerosol spray can: 0.125 min
Place of use	Indoor**
Room size (m ³)	20*****
Inhalation rate (m ³ /h)	1.37*****

* 100% release to air is assumed for sprays per default in the model

** The air changes per hour are based on the selection of "indoor" or "outdoor". Defaults applied by the tool are 0.6 (indoor) and 2.5 (outdoor).

*** Spray duration is used in this case

**** Scenario a2 is chosen

***** Default values used in the algorithm

Results of the ECETOC TRA calculations are shown in Table 2-8.

TABLE 2-8 EXPOSURE ESTIMATES FOR NFP 1 FROM ECETOC TRA

	Spraying of 7 m ² in a 20 m ³ bathroom		Impregnation of a 6.2 m ² sofa in a 20 m ³ living room		Impregnation of a pair of shoes/boots in a 20 m ³ kitchen	
	Pump spray	Aerosol dispenser	Pump spray	Aerosol dispenser	Pump spray	Aerosol dispenser
Exposure (mean event concentration) (mg/m ³)	125	152	114	135	14.9	15.3

The algorithm for calculating inhalation exposure in ECETOC TRA is rather simple and the only way that the use of a spray is taken into account is in the assumption that 100% of the substance is released to the air. The difference in above estimations between pump and aerosol spray can is only due to differences in exposure times entered in the model. Thus, these results represent very conservative exposure estimates, with highly overestimated values as compared to ConsExpo.