Committee for Risk Assessment (RAC)
Committee for Socio-economic Analysis (SEAC)

Background document

to the Opinion on the Annex XV dossier proposing restrictions on (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

ECHA/RAC/RES-O-0000001412-86-142/F
ECHA/SEAC/ RES-O-0000001412-86-150/F

EC Number	CAS Number
N.A. (group entry)	N.A. (group entry)

15 June 2017

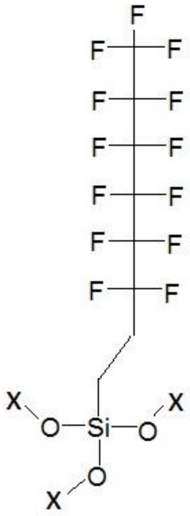
Contents

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). The scope of the restriction does not include export.

Proposed restriction

***Column 1*. Designation of substance**	***Column 2*. Conditions of restriction**
(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: (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 (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 (3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)triisopropoxysilane CAS No. 1240203-07-9	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.

RAC Assessment

The purpose of the proposal is to reduce or prevent consumers' exposure (via inhalation) to mixtures of TDFAs and organic solvents. The scope of the proposal is targeted at all spray products on the market for supply to consumers and the general public whether they are manufactured or imported into the EU.

Mixtures of TDFAs and organic solvents are used to provide water, stain and oil repellent properties to surfaces (particularly non-absorbing). They are sold in different forms of packaging, one that allows application in spray form (aerosol cans, pump or trigger spray) and other type that allows application using a brush or a cloth. The proposal is only targeted at the form sold in packaging that permits spray application i.e. aerosol cans, trigger and pump sprays.

The risk is not related to exposure to TDFAs but to exposure to the hydrolysis and condensation products formed when TDFAs are used with organic solvents. The mechanism behind the observed toxic effects has been studied in mice and is believed to involve inhibition of the pulmonary surfactant in the deeper parts of the lungs (bronchioles) 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 explains 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 bronchioles (particle size < 10 μm).

Toxicity is dependent on these hydrolysates and condensates reaching the deep lung tissue i.e. particle size <10 μm and concentration. The evidence provided by the dossier submitters to support the risk, is based on the testing of a spray containing TDFA & Isopropanol and general information from posioning incidents involving impregnation/proofing sprays.

Evidence supporting a risk from pump sprays is weaker as there are no human cases even with the "Magic nano" pump spray which provides stronger supporting evidence of the presence of TDFA's and organic solvents in impregnating sprays. In addition the studies performed on animals do not provide supporting justification of a risk that is not controlled as the samples from the pump sprays were nebulized which ensured the exposure was in the respirable range. Although no incidences were observed in relation to the Magic Nano pump spray, a potential risk cannot be excluded for pump and trigger sprays as some pump and trigger spray products generate particles below 10 μm.

Voluntary guidance recommends that the ratio of MMAD particles <10 μm should not exceed 0.6%. While some reference has been made to a value of 1% setting a limit of 1% is not appropriate as no robust information is available to support setting a safe concentration limit for particles <10 μm.

The proposal is not restricted to impregnation/proofing sprays but covers all sprays containing organic solvents and TDFA even though no evidence of other uses of such mixtures apart from impregnation/proofing sprays has been provided, the scope has been justified on the basis that if at some time in the future other uses were identified for such spray formulations they would also need to be covered (precautionary approach).

The dossier demonstrates that there have been respiratory incidents from the use of some impregnating/proofing sprays on the market. The dossier also provides evidence of respiratory effects in animal studies following exposure to a nebulized spray mixture of TDFA & Iso-propanol. Using modelling to predict exposure a risk is demonstrated by the dossier submitter under worst case conditions.
While the scope of the proposal is clear RAC have proposed some slight revisions to the propsed text to aid clarity & enforceability.

Substance Identity (or group identity)	Conditions of the restriction
(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: (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 (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 (3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)triisopropoxysilane CAS No. 1240203-07-9	1. Shall not be formulated with organic solvents in the manufacture of spray products which are 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 of the mixture, in spray products containing organic solvents, for supply to the general public. 3. Organic solvents referred to in paragraph 1 and 2 also include organic solvents used as aerosol propellants. 4. For the purpose of this restriction spray products should be interpreted as **any** aerosol cans, pump or trigger ***(impregnation/proofing)*** spray. 5. Paragraph 1 & 2 shall not apply to spray products for use by professionals. Spray products for use by professionals shall be labelled "for professional use only" 6. REACH Annex II Section 2.3 (Other Hazards) shall contain the following information. Mixtures of TDFA's in a concentration equal to or greater than 2ppb and organic solvents intended for professional use shall be labelled "fatal if inhaled". 7. This restriction shall entry into force on the "date"

SEAC assessment

In the original restriction proposal (RMO 1), the Dossier Submitter proposed a TDFAs concentration limit of 2 ppb in mixtures with organic solvents, which in practice is a ban for the use of mixtures in sprays products. SEAC is not aware of other possible uses than for proofing/impregnation sprays. The information available for evaluation by SEAC only addresses the proofing/impregnation spray products. Therefore, SEAC considers that the text of the restriction proposal should only address the use of proofing/impregnation spray.

SEAC has also proposed other changes of the wording of the restriction text in order to improve the practicality and enforceability. SEAC has further suggested some rewording in order to clarify that the restriction only applies to spray products when TDFAs and organic solvents are used together in the mixture. With these considerations and changes SEAC agrees and finds that the proposed restriction would be implementable, enforceable and manageable.

The conditions of the restriction proposed by SEAC are:

Substance Identity	**Conditions of restriction**
(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: (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 (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 (3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)triisopropoxysilane CAS No. 1240203-07-9	1. Shall not be placed on the market in mixtures with organic solvents in proofing/impregnation spray products for supply to the general public in a concentration equal to or greater than 2 ppb by weight. Spray products should in this context be understood as aerosol dispensers, pump and trigger sprays and mixtures marketed for proofing/impregnation spray applications. 2. The products should be labelled with information that the product can only be placed on the market for professional use.

A.2 Summary of the justification

A.2.1 Identified hazard and risk

Mice exposed to aerosolised mixtures containing TDFAs and 2-propanol (non-volatile 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/m^3 group one day after exposure. 3 out of 20 mice died at 18.4 mg/m^3 and 10 out of 10 died at 24.4 mg/m^3.

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 (bronchioles) 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 bronchioles (particle size < 10 μm). 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, and indicates that such a risk also exists for trigger and pump spray. The calculated risk characterisation ratios for aerosol dispensers, trigger- and pump spray drops in the order: aerosol dispensers > trigger spray > pump spray, which indicates the highest risk for application by aerosol dispenser and the lowest for application by pump spray.

Evidence of risk to consumers

725 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 6. 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 725 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 725 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. Therefore the scope is limited to mixtures of 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 6 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 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). Two occupational cases with three trigger spray incidents were reported in Switzerland (2002-2003). In this cases the causative agent belonged to the chemical group of fluoroacrylats. 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 indicates a risk when applied by trigger- or pump spray.

Since very little information is generally available on the chemical identity of the active ingredients of the spray products involved in the identified incidents and since documentation from animal studies is not available for other combinations than TDFAs and organic solvents[1] the scope is limited to mixtures of TDFAs and organic solvents.

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[1] The exception to this is the tile coating product containing a non-fluorinated alkylsilane and organic solvent studied by Duch et al. (2014). The product were reported to cause respiratory and systemic symptoms in 39 persons in Greenland in 2010 when applied under high pressure (139 bar). 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.

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

Several incidents of lung injuries from application of impregnating agents in aerosol dispensers based on mixtures both with and 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 and indicates that a risk exists when applied by pump- or trigger sprays. In order to adequately protect consumers, a restriction should both target imported spray products (aerosol dispensers, pump and trigger sprays and mixtures marketed for spray application) and spray products produced in the EU. The risk seems to be higher for aerosol dispensers than for pump and trigger sprays, but still a risk is indicated for pump and trigger sprays. A Union-wide ban is justified by the fact that risks can arise in all Member States due to free movement of goods across borders and to avoid different legislative requirements in Member States with the risk of creating unequal market conditions.

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 like 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 indicates a risk that is not adequately controlled for these mixtures applied by pump- and trigger 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. 0.00008% (0.8 mg/kg, 800 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 complex and costly as an extra analytical technique has to be added for quantification (e.g. an elemental determination of the total amount of silicon). This also means that it might take a longer time before an adequate analytic standard is developed. 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 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 and the restriction can be enforced. A standardised method would ensure reproducible enforcement. Nørgaard et al. has tested a number of methods for analysing the targeted substances. Based on these test a Danish research laboratory has suggested to use a combination of direct infusion electrospray ionization mass spectrometry (ESI-MS) and atmospheric pressure chemical ionization mass spectrometry (APCI-MS) for the analysis of the parent

substances (TDFAs). The analytical detection limit of this method is according to Nørgaard 2 ppb, see E.2.1.2.1.

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.

Socio-economic assessment

It is estimated that – as a maximum - 20 - 200 kg TDFAs per year (~ 6 800 – 100 000 units) are sold in spray impregnation products to the general public. It has not been possible to identify spray products containing TDFAs in combination with organic solvents currently on the market as available information on the chemical identity of the active ingredients of the spray products is scarce. However, based on 725 incidents reported in the EU, it is estimated that 20 – 40 % of incidents is related to impregnation sprays that might contain mixtures of TDFAs and organic solvents intended for the general public.

725Extrapolating from DK data on consumer incidents with impregnation sprays during 2006-2015 and assuming that 20 - 40 % of these were related to sprays containing mixtures of TDFAs and organic solvents, it is estimated that in average 330-660 incidents each year arise in EU28 due to these spray products. The possible benefit by avoiding these 330-660 incidents is estimated to €160 000 - €460 000 per year.

With regard to cost these are also very uncertain as no information is available on the number of formulas that need to be changed to other substances than TDFAs.

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 polyfluoralkyl chains different from the chain length 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. Based on estimations done with respect to D4/D5, the annualised cost of reformulating is estimated to € 8 000 – 12 000[2] per formulation on the market for which formulation is required. If no coordination of

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[2] It should be noted that this dossier on TDFAs was submitted before the opinion on D4/D5 was agreed. The opinion questions the assumptions on possibilities for coordination and has a medium scenario (Table I.4) , assuming 10 years of coordination and no cost savings due to less minor reformulations of a value 2.5 times higher (€50 - 90M instead of $20-58 M), equivalent to €13,300 -24,000 per formulation on the market.

reformulation activities is possible, the annual reformulation costs would be € 25 000 – 35 000 per formula.

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, and do therefore not constitute substantial additional costs and are considered to be carried out in house.

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.

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 indicates that a risk that is not adequately controlled exists when these mixtures are applied by pump- or trigger spray.

Detailed information on the fluorinated constituents is typically not available as the fluorocarbon monomers alone do not require hazard classification under CLP[3] 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.

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

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[3] 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

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 and the representativeness of the Danish data which has been extrapolated to EU28.
- 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.

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

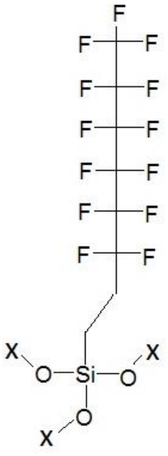
B.1 Identity of the substance(s) and physical and chemical properties

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 condensated 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:



X = alkyl groups or hydrogen

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 alkoxysilanes.

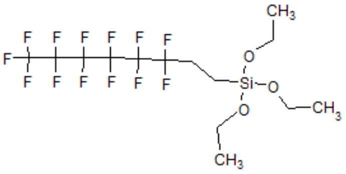
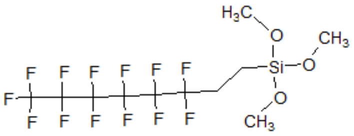
Only two substances meeting the general formula are pre-registered under REACH (see

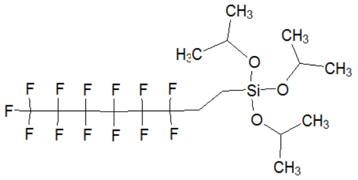
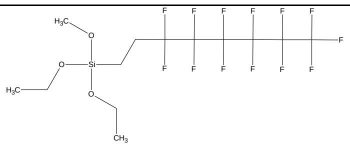
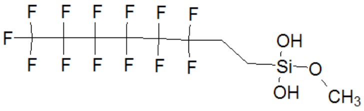
Table 1) (ECHA, 2015a). According to the REACH Reconsile Consortium, polyfluorooctyl trimethoxysilane and polyfluorooctyl triethoxysilane are planned to be registered by its members by 31 May 2018 (Reconsile, year not indicated).

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 triethoxysilane 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.

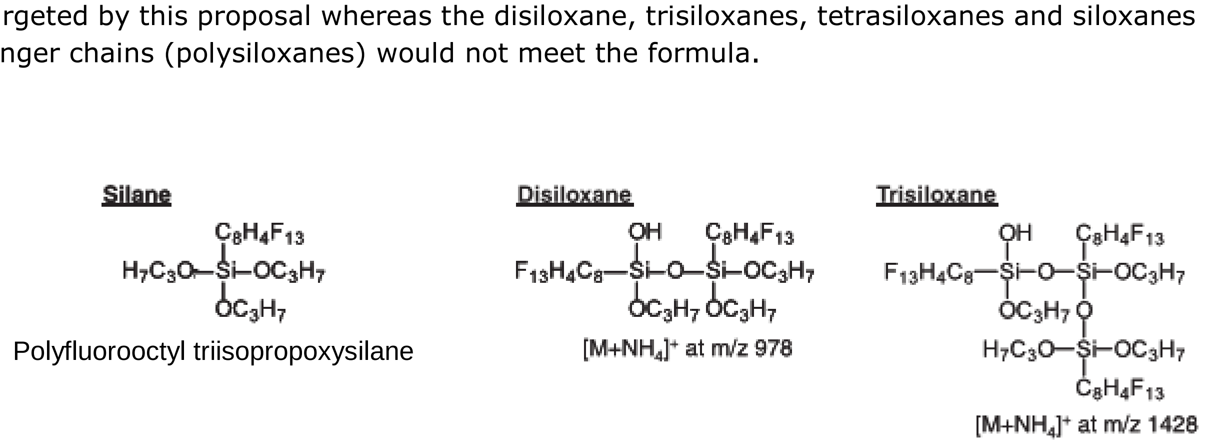
According to the SDS for one of the commercial polyfluorooctyl triethoxysilanes, the product contains approximately 3% tetraethyl silicate (CAS No 78-10-4; EC No 201-083-8).

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. According to a formulator, who have previously formulated impregnations product based on TDFAs, can water is used as a solvent in mixtures containing TDFAs but it requires that a surface modifier is added to the formulation.

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 intended for non-absorbing floors (NFP 1). The product were based on fluorosilanes in 2-propanol. The constituents were identified as polyfluorooctyl triisopropoxysilane and di-, tri- and tetrasiloxane condensated 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 as an intermediate, since the commercial polyfluorooctyl triethoxysilane is dissolved in slightly acidic 2-propanol. If this hypothesis is correct, the alkoxy groups on silicon in the intermediate 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, tetrasiloxanes and siloxanes with longer chains (polysiloxanes) 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 constituants were not quantified by Nørgaard et al. (2010b). The total content of non-volatile 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±0.1%.

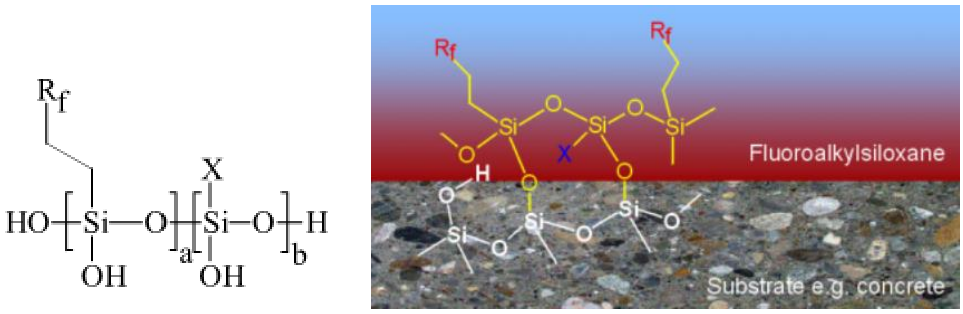
According to a formulator, who have previously formulated impregnations product based on TDFAs, the reason for using volatile organic solvents like ethanol or 2-propanol for non-absorbing substrate surfaces are multiple. The formulator explains that the volatile organic solvents enhance cross linking and make a good wetting of the substrate. Ethanol is able to penetrate into the material (stone, wood) and infiltrate the material. The hydrophobic and oleophobic TDFAs will be going deeper into the material (a few millimetres up to a few centimetres) and will therefore protect the substrate for a longer time even if the material will be changed by abrasion on the surface. TDFAs can be stable in volatile organic solvents (for up to 2 years) but if water is used as a solvent a hydrolysis reaction will take place and the impregnation product will lose all its hydrophobic and oleophobic properties (stability less than one day).

According to Nørgaard (personal communication) controlled amounts of water is added to impregnation products based on TDFAs and organic solvents in order to control the hydrolysis reaction.

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 intended for absorbing substrates. 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. Rf 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.

According to a formulator, who have previously formulated impregnations product based on TDFAs, a surface modifier can be added to water-based formulations containing TDFAs to enhance stability.

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 form octyl.

Five polyfluoroalkyl trialkoxysilanes with polyfluoroalkyl chain different form 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 Reconsile Consortium (Reconsile, 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)-	Heptadecafluoredecyl 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 PHYSICOCHEMICAL 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 mmHg) [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]	<1mmHg (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 triisopropoxysilane.

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 Reconsile 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 Reconsile Consortium members: polyfluorooctyl triethoxysilane (EC No. 257-473-3) and polyfluorooctyl trimethoxysilane (EC No. 288-657-1).

According to the information from the Reconsile 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 distributers 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 Reconsile 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 Fluorcouncil 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. According to an EU manufacture of polyfluorooctyl triethoxysilane, the substance has been marketed globally for more than 15 years (Public Consultation 2016).

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 polyfluoroctyl triethoxysilane into the EU is most likely small compared to the manufacture within the EU. Possible use of polyfluoroctyl 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 distributers 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/m^2 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/cm^2, 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/cm^2 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 CO_2 are used as propellants (FOPH, 2008).

Typical impregnating compounds (active substances) for water-proofing are silicones (i.e. polysiloxanes), 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 cloth[4].

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.

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[4] 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.

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.

<u>In conclusion</u>, 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%[5], the total number of spray products can be estimated to approximately 6 800[6] – 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 fomulators 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.

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.

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[5] 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

[6] 20/0.79*4/(1.5/100): 6751 = rounded 6800

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 sealer", 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 29 impregnation (proofing) spray products on the Danish market for consumer use. 19 of the spray products were provided in aerosol spray cans, the latter ten in pump sprays (not further specified if this covers pump sprays, trigger sprays or both). 3 pump sprays were water-based, for 3 pump sprays there are no information on solvents and the rest of the products (23) contains organic solvents. 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 5) 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 nanopro-ducts 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 ECHAs website may indicate how widespread the use of the substances are (ECHA, 2015b). As indicated in Table 5, 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 National Product databases

A search in the SPIN (2014) database with data from the Nordic Product Registers showed that polyfluorooctyl triethoxysilane was registered in Denmark 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.

For the period 2010-2015 four products containing TDFAs, and which are intended for consumer use, were registered in the Swedish Product Registry, all from the same company. The products contained less than 10% TDFAs. Three of them were based on organic solvents. For 2014 and 2015 the reported quantity for import was zero for all products, showing that there were no TDFAs-products on the Swedish market for consumers in 2014 and 2015. According to the company this is due to a change in business strategy, from wholesaling of impregnation products to actual performing the impregnation activities. Thus, the substitution of the products was not due to health concerns related to TDFAs (Public Consultation 2016).

For other TDFAs, no use in the Nordic Countries is recorded in the SPIN database.

In relation to a call for evidence, in the spring of 2015, the German Federal Institute for Risk Assessment (BfR) carried out an analysis of the German Product Database for products containing TDFAs. 13 products were be identified in the Product Database that contain an ingredient that could be related to the group of TDFAs. Only one ingredient was notified for all 13 products, i.e.: Triethoxy (3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro octyl)silane, CAS-No 51851-37-7. From the answer to the call for evidence no information is available on the: application form, solvents or use eventual by consumers.

In a response to the Public Consultation (2016) Spain have identified 8 impregnation spray products containing TDFAs for occupational use.

In a response to the Public Consultation (2016) Cyprus have replied that no information are available in the Cyprus Chemicals Registry (article 45 CLP) related to such sprays containing TDFAs.

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- or trigger sprays. The producers of the products described by Nørgaard et al. inform that the polyfluorosilane mixtures are delivered in pump- or trigger 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)

None of the TDFAs substances are listed in Annex VI of Regulation (EC) No 1272/2008 (CLP Regulation).

Classification information of organic solvents listed in Annex VI of Regulation (EC) No 1272/2008 identified to be used in combination with TDFAs are shown in Table 4. According to the information from manufacturers of the substances, polyfluorooctyl triethoxysilane can be dissolved in ethanol and various other organic solvents, e.g. n-hexane, xylene, acetone and ethyl acetate. The two spray products NFP 1 and Rim sealer, tested by Nørgaard et al. (2010b), were based on TDFAs in 2-propanol and on TDFAs in a mixture of 2-propanol, 1-methoxy-2-propanol and ethyl acrylate, respectively. Methanol has not been identified as solvent in any commercially available impregnation product based on TDFAs, methanol was however, used as one of the solvents in the studies by Nørgaard et al.

TABLE 4 CLASSIFICATION AND LOGP$_{OW}$ OF ORGANIC SOLVENTS AND PROPELLANTS LISTED IN ANNEX VI OF REGULATION (EC) NO 1272/2008 IDENTIFIED TO BE USED IN COMBINATION WITH TDFAS

EC no.	Substance name	logPow	Hazard Class, Category Codes and Hazard Statement Codes[1]
200-659-6	Methanol	-0.77	Flam. Liq. 2; H225, Acute Tox. 3; H301, Acute Tox. 3; H311, Acute Tox. 3; H331, STOT SE 1; H370
200-578-6	Ethanol	-0.77 to -0.3	Flam. Liq. 2; H225
200-661-7	2-propanol	0.05	Flam. Liq. 2; H225, Eye Irrit. 2; H319, STOT SE 3; H336
203-539-1	1-methoxy-2-propanol	1.0	Flam. Liq. 3; H226, STOT SE 3, H336
205-500-4	Ethyl acetate	0.68 to 0.73	Flam. Liq. 2; H225, Eye Irrit. 2; H319, STOT SE 3; H336
200-662-2	Acetone	-0.24 to -0.23	Flam. Liq. 2; H225, Eye Irrit. 2; H319, STOT SE 3; H336
110-54-3	n-hexane	4.0	Flam. Liq. 2; H225, Skin Irrit. 2; H315, Asp. Tox. 1; H304, STOT SE 3; H336, STOT RE 2; H373, Aquatic Chronic 2; H411, Repr. 2; H361f
215-535-7	Xylene	3.12 to 3.2	Flam. Liq. 3; H226, Acute Tox. 4; H312, Skin Irrit. 2; H315, Acute Tox. 4; H332
Propellants			
204-065-8	Dimethyl ether	0.07	Press. Gas, Flam. Gas 1; H220
200-827-9	Propane	1.09 to 2.8	Press. Gas, Flam. Gas 1; H220
203-448-7	Butane	1.09 to 2.8	Press. Gas, Flam. Gas 1; H220
200-857-2	Isobutane	1.09 to 2.8	Press. Gas, Flam. Gas 1; H220

[1] H220: Extremely flammable gas; H225: Highly flammable liquid and vapour; H301: Toxic if swallowed; H304: May be fatal if swallowed and enters airways; H311: Toxic in contact with skin; H312: Harmful in contact with skin; H315: Causes skin irritation; H319: Causes serious eye irritation; H331: Toxic if inhaled; H332: Harmful if inhaled; H335: May cause respiratory irritation; H336: May cause drowsiness or dizziness; H361f : Suspected of damaging fertility; H370: Causes damage to organs; H373: May cause damage to organs through prolonged or repeated exposure; H411: Toxic to aquatic life with long lasting effects

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 ECHAs 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 5 SELF-CLASSIFICATION OF THE SUBSTANCES ACCORDING TO THE C&L INVENTORY (ECHA, 2015B)

EC No	Substance name	Hazard Class and Category Code(s)	Hazard Statement Code(s) *	Number of Notifiers
257-473-3	polyfluorooctyl triethoxy-silane	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 tri-methoxy-silane	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 environmental issues are related to the possible release of per- or polyfluoroalkyl substances present either as trace content of raw materials and intermediates or release of non-hydrolysed TDFAs during production and use. The release of TDFAs to the environment during use in impregnation spray products is considered small as the substances will rapidly hydrolyse and subsequently condensate. At the same time the market share of spray impregnation products containing TDFAs seems to be small. When cured, the mixtures form a siloxane polymer with polyfluorinated side-chains.

As the self-cleaning effect of the TDFAs impregnated surface weaken over time it may be necessary to repeat the treatment. This indicates that either the polyfluorinated side-chains are released from the polymer or the polymer is abraded and released as small polymer particles.

See more on environmental fate properties in 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 trigger 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 TDFAs[7] and 2-propanol (hydrolysates and condensates of polyfluorooctyl triisopropoxysilane) and hexadecyl trimethoxysilane, respectively. The concentration of non-volatile material (hydrolysates and condensates) in NFP 1 and NFP 2 were estimated to 1.1 ± 0.1% and 1.5 ± 0.1% 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 mixture were diluted with ethanol until 1.2 % solutions were obtained. 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 μm) and that a large fraction of these also can reach the alveolar region of the lung (< 4 μm).

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 3.3–60 mg/m^3 (10^5–10^6 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).

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

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 decrease 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/m^3 group one day after exposure. Several mice in the 24.4 and 42.4 mg/m^3 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/m^3) 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/m^3 (2.3×10^6 fine particles/cm^3) 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/m^3) and the lethal concentrations (18.4 mg/m^3). 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, lymphosites, 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, Nørgaard et al., 2010 shows that when aerosolised the particle size distribution of all the tested mixtures has a large fraction that can end up in the bronchioles or 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 hydrolysation/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 containing a non-volatile mass fraction of 0.33% – 14.8%[8] (hydrolysates and condensates of TDFAs) were included in the study representing products to be applied on 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 µm) and that a large fraction of these also can reach the alveolar region of the lung (< 4 µm). 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.

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[8] Concentrated version of the product Textile & Leather delivered by the producer. The product is not commercially available in this form.

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, Nørgaard et al., 2014 shows that when aerosolised the particle size distribution of both water-based and solvent-based mixtures containing hydrolysed TDFAs generates a large fraction of particles that can end up in the bronchioles or 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 lipopholicity 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 Larsen et al., 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/m^3. This is approximately 6 times below the wet weight LOAEC for NFP 1 that were found to 3380 mg/m^3 (18.4 mg/m^3 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 polyfluoroacrylate 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/m^3 and 114 mg/m^3, respectively. It should be underlined that Footware protector and Wood impregnation has not been investigated as thoroughly as NFP 1.

In conclusion, from Sørli et al. (2015) it seems that a change in organic solvent have made Rim sealer more toxic than NFP 1. At the same time the *in vivo* study showed that a 8:2 polyfluoroacrylate co-polymer 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 post exposure day in all groups exposed to the "Magic Nano Glass & Ceramic Spray". At the lowest dose tested 2 269 mg/m^3 1/10 rats died. The 4-hour standard LC_{50} was calculated to 5 098 mg/m^3. No mortalities were observed with the aerosol spray "Magic Nano Bath Bath & WC" at the highest dose tested 28 100 mg/m^3. One rat exposed to the pump spray at the highest dose tested 81 222 mg/m^3 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 post exposure week. No effects were observed in rats exposed to the aerosol spray "Magic Nano Bath & WC". Analysis on the first post exposure 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[9]) 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 LC_{50} 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".

<u>In conclusion</u>, according to Koch et al., 2009 it is likely that the active substance in the three "Magic Nano" product is a fluorosilane. The length of the polyfluoroalkyl chain is unknown but it is possible that the substance belongs to the group of TDFAs.

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[9] In Koch et al., 2009 it says: "release of the can content (approximately 200 g)". However, according to personal communication with Prof. W. Koch 120 g and 80 was released from the aerosol spray and pump spray, respectively. This is consistent with Pauluhn et al., 2008 were it says: "The test articles were Magic Nano Glass & Ceramic (spray can, content: 150 ml), Magic Nano Bath (spray can, content: 100 ml) and pump spray (content: 100 ml)".

The dry weight LOAEL and LC_{50} 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 C_9-C_{13} (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, in Duch et al., 2014 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/m^3 (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/m^3 (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/m^3 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 (hydrolysates 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/m^3 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 ($SP\text{-}B_{1\text{-}25}$), mimicking the natural SP-B, the impaired film could partly be restored. In contrast, addition of SP-C peptide ($SP\text{-}C_{33}$), 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 $SP\text{-}C_{33}$ 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 examnation. 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 $SP\text{-}B_{1\text{-}25}$ 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 $SP\text{-}B_{1\text{-}25}$ in absence of NFP 1 was located exclusively at the interface, addition of NFP 1 led to distribution of $SP\text{-}B_{1\text{-}25}$ into the organic phase, i.e., $SP\text{-}B_{1\text{-}25}$ is removed from its site of action.

The interaction of SP-$B_{1–25}$ and NFP 1 (hydrolysates and condensates of TDFAs) were studied by mass spectrometry. Complexes of SP-$B_{1–25}$ 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-$B_{1–25}$. A covalent binding of the siloxanes to SP-$B_{1–25}$ 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 by Larsen et al., 2014 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-$B_{1–25}$, 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-B_{1-25} 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-B_{1-25} 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 hydrolysates and condensates of TDFAs to the SP-$B_{1–25}$ 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 showed that the number of free hydroxyl groups (i.e. degree of hydrolysation/condensation) is critical for the toxicity. The interaction of the pulmonary surfactant protein SP-B and NFP 1 (hydrolysates 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 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-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 hydrolysates and condensates of alkylsilane tested in Duch et al. (2014) seems to have the same effects on VT og expiratory flow rate as hydrolysates 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 waterproofing 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). Two occupational cases with three trigger spray incidents were reported in Switzerland (2002-2003). In these cases the causative agent belonged to the chemical group of fluoroacrylats, Vernez et al. (2004). In Table 6 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 6 and Table 1 - 1.

In a response to a call for evidence, carried out in the spring of 2015, the Norwegian Poison Information Centre answered that they didn’t have any reporting of respiratory illness from spray cans used for proofing purposes that contain TDFAs in an organic solvent. To the same call for evidence the German Federal Institute for Risk Assessment (BfR) submitted a list of 19 case stories with impregnation sprays . The case stories are presented in Appendix 1, Table 1 - 3. BfR further informed that they had identified 13 products in the German Product Database containing an ingredient that could be related to the group of TDFAs (cf. B.2.2.2.5). Unfortunately, the exact chemical identity of the causative agent was not identified in the human case stories (identified as: fluorocarbon resin, silane, fluoro-acrylat-copolymer etc.) and it has therefore not been possible to assess if the human incidents could be linked to any of the TDFAs containing products in the German Product Database. However, it should be noted that the cases with BfR case ID 1529706 and 3463706 in Appendix 1, Table 1 - 3 seems too belong to the “Magic Nano” case.
No information on product names, solvents and number of incidents are available for the case stories submitted by BfR. Therefore they are not included in Table 6.

In a follow up to the “Call for Evidence” carried out by ECHA all poison centers in the EU were 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. This information are included in Table 6. Spain had information on 13 phone calls related to incidents related to polyfluorinated silanes or fluorinated compounds and organic solvents (aromatic or isoparafinic hydrocarbons). Of the 13 incidents 5 were due to inhalation. These 5 incidents are included in Table 6. From the information available it has not been possible to asess if the causative agent of the human incidents in Spain and Sweden can be linked to the spray products containing TDFAs and organic solvent that are or has been available on the Spanish and Swedish markets (cf. B.2.2.2.5 on information from information from National product databases). The information available on active substances from labels and safety data sheets to the poison centers is not detailed enough to make this link.

Lithuania, Slovenia and Cyprus has responded to the Public Consultation (2016) that their National Poison Control Centers do not have any cases of poisoning incidents related to TDFAs substances in spray product. Industry (manufacture of polyfluorooctyl triethoxysilane) informed that they have got no hints or information of cases with pulmonary effects with TDFAs.
Sweden added that according to a Swedish survey on PFASs from 2015 a lack of available information is substantial for the whole PFAS-group.
During Public Consultation Ireland submitted information of 16 case stories with 21 human incidents elated to proofing/impregnation product from 2006 to 2016. Of these 21 incidents 12 (4

consumers and 8 occupational) were due to inhalation. These 12 incidents are included in Table 6.

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 is therefore possible that the active substances in the "Magic Nano" products belongs to the group of TDFAs.

For most cases in Table 6, 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. fluoracrylats or alkylsilanes). In Table 6 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 725 incidents with impregnation sprays in the EU are available. These incidents are the incidents in Table 6 minus cases from Switzerland and Greenland. It is estimated that 20 – 40 % of these 725 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 6 OVERVIEW OF REPORTED INCIDENTS OF PULMONARY DISTRESS RELATED TO IMPREGNATION SPRAYS IN EUROPE

Country/ year	**Product name**	**Container type and product use**	**Active ingredients**	**Solvent**	**Individuals affected**	**Source**	**Likely TDFAs**[1]
Germany, 2006	Magic Nano Glass & Ceramic Magic Nano Bath & WC	Aerosol dispensers Surface sealants, bathroom	(fluoro)silanes	Dimethyl ether, ethanol	154	BfR 2010 Pauluhn et al., 2008 Koch et al. 2009 Appendix1 Table 1-2	++
Netherlands, 2011	No information	Aerosol dispensers Rain-proofing spray for shoes	Fluorocarbon polymer	No information	1	Epping et al. 2011 Appendix 1 Table 1-2	+
Germany, 2006	Nano HiTech	Aerosol dispensers Use: No information	No information	No information	16	FOPH 2008	+
Ireland 2006-2016	3-4 different products,	3 Aerosol dispensers and 1 unknown		No information	4	Info from the Irish	+

Country/ year	**Product name**	**Container type and product use**	**Active ingredients**	**Solvent**	**Individuals affected**	**Source**	**Likely TDFAs** [1]
	names not available	Use: 2 Footwear products, 1 fabric protector and 1 wood sealer	No information	Propanol & hydrocarbons Alcohol, isopropanol, petroleum Mineral spirits		Poison Information Centre	
Sweden, 2001-2015	6 different products, names not available	3 products: Aerosol dispenses 3 procucts: Application form not specified Use: Not specified	Fluorocarbon resin Fluorinated polymer Fluorinated polymer Fluorinated polymer Fluorocarbons Fluorinated polymer	n-heptane, butyl acetate, 2-propanol and isopropylacetate n-heptane, 2-propanol and ethylacetate 2-propanol and metylisobutylketon isoparaffins Tripropyleneglykol Petroelum destilates and aceton	98	Info from the Swedish Poison Information Centre	+
Germany, 1979-83	Different products, names not available	Spray products Leather impregnation	Fluorocarbon polymer	No information	224	FOPH 2008	÷
Netherlands, 2002-2003	Different products, names not available	Spray products Impregnation sprays	Fluorocarbon resin	n-heptane, mixture of solvents	99	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	÷
France, 2003	No information	Spray product Leather and textile waterproofing spray	No information	No information	1 (fatal)	FOPH 2008	÷

Country/ year	Product name	Container type and product use	Active ingredients	Solvent	Individuals affected	Source	Likely TDFAs[1]
Scotland, 2005	Rucoguard EPF 1610	Spray gun connected to an air compressor Textiles	Fluorocarbon polymer (cationic fluorocarbon polymer made by telomerisation)	Isopropanol	4	Wallace et al. 2005 Appendix 1 Table 1-2	÷
Netherlands, 2013-2015	HG protector for untreated wooden furniture HG water, oil, fat & dirt proof for leather HG water, oil, fat & dirt proof for textile Scapino trend spray No information for the other 22 products	Spray products (types not specified) Wooden furniture, leather, textile, unknown	Fluorocarbon polymer	No information	26	Info from National Poisons Information Center	÷
Denmark, 1991-2007	Different products, names not available	Spray products (type not specified) Furniture, clothes, shoes, ceramic surfaces, carpets, tents, riding equipment, car seats , sealing foundation for paint, unknown	Fluorinated compound (most products) Fluoroacrylates (dodecylacrylate) and cyclosiloxanes (16 incidents) Silicones (some products with silicones alone)	No information	84	Lyngenbo et al. 2008 Appendix 1 Table 1-2 Info from Danish Poison Information Center	÷
Spain, 2004-2015	No information	Spray products Uses specified as industrial, cleaning and other	Fluorinated silanes or fluorinated compounds	Aromatic or isoparafinic hydrocarbons	5	Info from National Poisons Information Center	÷
Ireland 2006-2016	3 different products, names not available	No information on application Occupational uses: fabric protector, concrete sealant and a product for	No information Silanes/siloxanes	No information	8	Info from the Irish Poison Information Centre	÷

Country/ year	Product name	Container type and product use	Active ingredients	Solvent	Individuals affected	Source	Likely TDFAs [1]
		absorbing porous surfaces	Fluoropolymer				
Switzerland, 2002-2003	RapiAquaStop (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 incidents)	Fluorinated acrylate polymer	Isoparaffinic hydrocarbons	180	Vernez et al. 2006 Vernez et al. 2004 Appendix 1 Table 1-2	÷[2]
Greenland, 2010	Stain Repellant Super®	High pressure airless spray gun (135 bar) Surface coating product used for ceramic tiles	Non-fluorinated alkylsiloxanes	Hydrogenated naphtha C_9-C_{13}. (50–100%)	40 (of these 39 were evacuated to larger hospital and clinically evaluated)	Duch et al. 2014 Appendix 1 Table 1-2	÷[2]
Total number of incidents in EU					725 (100%)		
Know or most likely TDFAs in organic solvents for consumer use					154 (21%)		
Possible TDFAs in organic solvents for consumer use					118 (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] Not part of EU

In Table 6 "+++" is for spray products that are known to be product(s) containing mixtures of TDFAs and organic solvents for the general public. It has not been possible to link human incidents with products containing TDFAs with a 100% certainty. According to Koch et al. (2009) it is likely that the 3 "Magic Nano" products contained a fluorosilane. Since polyfluorooctyl triethoxysilane and polyfluorooctyl trimethoxysilane, which belongs to the group of TDFAs is commercially available and know to be used in impregnation product like "Magic Nano", it is assumed that the 3 Magic Nano product contained TDFAs. "Magic Nano" is therefore rated as "++" (Most likely to be spray product(s) containing mixtures of TDFAs and organic solvents for the general public) in Table 6.

"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/m^3. The 4-hour standard LC$_{50}$ was calculated to 5098 mg/m^3 (10 mg/m^3 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/m^3, 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/m^3. 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 waterproofing impregnation agents has been linked to acute lung injury. It is estimated that 20 – 40 % of the 725 incidents reported in the EU were likely to be 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/m^3 group one day after exposure. 3 out of 20 mice died at 18.4 mg/m^3 and 10 out of 10 died at 24.4 mg/m^3. A similar picture was observed for the aerosol spray product "Magic Nano Glass & Ceramics" when tested in Wistar rats where the 4-hour LC_{50} was calculated 10 mg/m^3 (dry weight). No toxicologically significant changes occurred in rats exposed to the aerosol spray "Magic Nano Bath & WC".

Cardinal symptoms of the 154 incidents reported for the aerosol sprays "Magic Nano Glass & Ceramics" and "Magic Nano Bath & WC" were strong cough, dyspnea, and in 13 severe cases also severe lung edema.

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/m^3, 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 andpolyfluorooctyl 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 polyfluororooctyl 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 polyfluoralkyl 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 form the authors on the number of animals dead or in a moribund state within 24 hours (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 mg/m^3. By using Harber's law, the 4 hour LC$_{50}$ is estimated to 5 mg/m^3. 1 hour NOAEC and LOAEC is estimated to16.1 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 LC_{50}. 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 LC_{50} 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. By using Harber's law the 1 hour LC_{50} in rats of "Magic Nano Glass & Ceramic" can be estimated to 40 mg/m³. 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 LC_{50} 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), there are two ways for deriving an acute inhalatory DNEL:

- by applying a large assessment factor (AF) for severity of effect to the LC_{50}-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.
- by using NOAEC and default AF on mice according to Table R.8-6: Inhalation (no allometric scaling) 2.5 (remaining interspecies) x 10 (intraspecies differences, general population

In addition an AF of 3 are used because of the very steep concentration-response curve in both cases.

The derived 1 hour no-effect concentration (DNEL) for TDFAs and 2-propanol (hydrolysates and condensates of polyfluorooctyl triisopropoxysilane) can therefore be calculated by using 1 hour LC_{50}-value along with a total assessment factor of 300 or by using the NOAEC along with a total assessment factor of 75:

$$DNEL(acute) = \frac{20\,mg/m^3}{300} = 0.068\,mg/m^3$$

and

$$DNEL(acute) = \frac{16.1\,mg/m^3}{75} = 0.21\,mg/m^3$$

In the same way the product specific acute 1 hour DNELs for "Magic Nano Glass & Ceramic" can be calculated to 0.13 mg/m³ and 0.24 mg/m³ (by using LOAEL, as no NOAEC exists for "Magic Nano Glass & Ceramic").Both of derived DNELs will be used for risk characterisation in section B.9

RAC ASSESSMENT

RAC agreed that the dossier has provided evidence of acute inhalation toxicity from impregnation/proofing aerosol product use. The main evidence to support the restriction proposal comes from data from a previous outbreak in 2006, consisting of 154 cases of intoxication that were caused by two aerosol spray products (Magic Nano Glass & Ceramic and Magic Nano Bath & WC); these products are no longer on the market. There is no data on the ingredients of these two products or the concentrations of TDFAs in the mixtures used but analytical investigations at the time of the incidents were able to identify fluorosilanes and organic solvents in these products.

The clinical symptoms in 154 persons observed following the use of the two Magic Nano aerosol sprays were strong cough and dyspnoea, in 13 cases also severe lung edema was diagnosed (Table 6 of the BD, Pauluhn, 2008, BfR, 2010). A detailed description of the clinical symptoms was reported for 10 out of the 154 incidents (Groneberg, 2010). For six of them information was available that treatment by a physician or at hospital were needed. Taking the information from Groneberg (2010) on strong cough, strong dyspnoe or persistent dyspnoe for more than 24 h as indicators for severe effects, seven out of the 10 incidents could be considered (as proposed by RAC) as severe cases.

RAC found it difficult to assess how much the cases with less defined components contribute to the evidence for the mixtures of TDFAs and organic solvents that is proposed for restriction.

Animal studies have shown that TDFAs alone were not able to induce lung injury and mortalities, the fatal effect became obvious only in combination with organic solvents. RAC concluded that mixtures of TDFAs in combination with organic solvents with a particle MMAD <10 µm are necessary to cause acute lung injury.

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 materials. In an animal study (Nørgaard et al. (2010a), which tested the effects of TDFA's and 2-propanol on mice, a significant concentration-dependent decrease of the tidal volume (VT) was seen following short term exposure, which was still significantly suppressed in the 18.4 mg/m³ group one day after exposure. Three out of 20 mice died at 18.4 mg/m3 and 10 out of 10 died at 24.4 mg/m3. Histological examinations revealed atelectasis (collapsed alveoli), haemorrhage, and emphysema or lung over-distension (emphysema) because of maldistribution of ventilation.

Higher toxicity (measured as the time until a 25% reduction in the VT was reached) were seen for 2-propanol in comparison to other solvents with shorter chain length and lower lipophilicity (2-propanol>methanol> ethanol) (Nørgaard et al. (2014). In vitro tests demonstrated that the lipophilicity of the solvent determined the toxicity of TDFA's on the surfactant function.

RAC agreed with the proposed hypothesis regarding the toxicity of mixtures of TDFA and organic solvents is in the deeper parts of the lung, the organic solvent (depending on its lipophilicity) facilitates contact between the hydrolysates and condensates of TDFAs and the SP-B proteins in the lung thus inhibiting the pulmonary surfactant through depletion of the pulmonary surfactant protein, SP-B. This hypothesis of the solvent facilitating contact between the hydrolysates, condensates and the SP-B protein is also the hypothesis used to explain why no effects on the lungs are seen for spray products that contain no solvent but only hydrolysed TDFAs and water. Therefore, toxicity of the product is dependent on the presence of TDFA's with organic solvents reaching the deeper parts of the lungs.

At present no specific (TDFA-related) information on pump and trigger sprays is available. Taking the recent information from commercially available impregnation pump and trigger sprays into account that identified particle sizes < 11 µm or in the nanometer sizes in pump and trigger sprays (Kawakami et al. 2015, Losert et al., 2015), the generation of respirable particles < 10 µm can not be excluded. The percentage of <10 µm particles is likely to be lower than from aerosol for the same product. The potential risk for trigger and pump spray applications were quantified based on the limited information on the generation of particles <10 µm from trigger and pump spray products.

DNEL calculation

RAC found that the available human data shows that the lung injury manifested shortly after application of the spray product, however, the data does not allow identification of a no-effect concentration and no information on the application duration can be derived from the case reports.

RAC agreed to use animal data as a starting point. In a weight of evidence approach two different approaches to derive a DNEL were considered which resulted in a range of DNELs. In contrast to the initial proposal of the Dossier Submitter (using the large assessment factor approach) RAC found the 1 hour LC50-value more appropriate (in comparison to the expected application by consumers) than the extrapolation to a 4-hour value. In line with approach (as refined by the Dossier Submitter in the section above) two approaches – the LC50-value in combination with a large assessment factor and the NOAEL as a starting point - are taken forward. The two DNELs are used for risk calculation: 0.068 mg/m³ and 0.21 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 the substances are to a large extent related to the possible release of persistent per- and polyfluoroalkyl substances (PFAS) during the entire lifecycle of the mixtures. When cured, the mixtures form a siloxane polymer with polyfluorinated side-chains. The side-chains resemble 6:2 fluorotelomers (with a perfluorinated part of 6 carbon atoms and two carbon atoms without fluorine).

Data on the content of non-polymer 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 perfluorohexyl 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).

Studies of textiles treated with impregnating agents based on side-chain-fluorinated polymers have demonstrated low levels of PFAS in the final products (e.g. Knepper et al., 2014; SFT, 2006; Herze et al., 2009). 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 found in textiles 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 perfluorinated part of 8:2 FTOH is very stable, the 8:2 FTOH is degraded to the persistent perfluorohexanoic 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 and perfluoroheptanoic acid (PFHpA), perfluorohexanoic acid (PFHxA) and perfluoropentanoic acid (PFNA) in the environment.

No data are available, but most likely PFAS released from surfaces treated with impregnating agents based on shorter-chained fluorosilane chemistry will tend to be shorter-chained. The parent TDFAs will most likely predominantly degraded/transformed to PFHxA.

The data on the fate and effects of shorter-chained PFAS in the environment is more limited than the data on the C_8 PFAS such as PFOA, PFOS and 8:2 FTOH.

PFOS, PFOA and other long-chain perfluorinated carboxylic (PFCAs) and sulfonic acids (PFSAa) and their salts, and the longer 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). PFOA has been identified as a substance of very high concern (SVHC) because in meets the criteria of being a PBT substance (ECHA, 2013).

The short-chain PFCAs and PFSAs are as persistent in the environment as the long-chain homologues, but do not seem bioaccumulate to the same extent as the long-chain homologues, as they are excreted more rapidly from the organisms studied. However, short-chain PFCAs and PFSAs have been seen to accumulate in crops like e.g. maize, Krippner et al., 2015. Based on available information short chain PFCAs and PFSAs appear to have low ecotoxicity (Kjølholt et al., 2015). No information on ecotoxicity of TDFAs has been identified.

Based on QSAR estimations Gomis et al. (2014) predicted the environmental fate of polyfluoroctyl trimethoxysilane. The characteristic travel distance (CTD) of polyfluoroctyl trimethoxysilane was found to 2119 km (slightly longer than the estimated CTD for PFOS, PFOA and 8:2 FTOH) and the overall persistence were found to 131 days (longer than 8:2 FTOH but less than PFOS and PFOA). Half-life in air, water and soil for polyfluoroctyl trimethoxysilane were estimated to 102 hours, 17280 hours and 17280, respectively, and the substance can likely be considered as very persistent according to the REACH guideline. The authors also found that polyfluoroctyl trimethoxysilane are likely to be bioaccumulative as they estimated $\log K_{ow}$ to be above 4.5 (Gomis et al., 2014).

Over time, the self-cleaning effect of the TDFAs impregnated surface weakens and it may be necessary to repeat the treatment. This indicates that either the polyfluorinated side-chains are released from the polymer or the polymer is abraded and released as small polymer particles.

Due to lack of information on the presence of non-polymer PFAS in the mixtures and final surfaces and the fate of the per- or polyfluorinated side-chains of the polymers, it is not possible to assess to what 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 the 4 hour LC_{50} ≤ 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

Release of TDFAs during manufacturing and use cannot be excluded. The release of TDFAs during use in impregnation spray products is, however, considered small due to rapid hydrolysation and condensation. No data are available from manufacturers regarding the environmental release during 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.

As measured exposure data with TDFAs are limited the possible exposure of consumers is estimated using two different exposure models. The two exposure models are used on four scenarios with a NFP 1 like product:

1) Large area with high amount of product used pr. area: Impregnation of 3.4 m^2 floor/wall tiles in a bathroom of 10 m^3 with aerosol, pump and trigger spray. Use of 40 g/m^2 is assumed.

2) Large area with low amount of product used pr. area: Impregnation of 3.4 m² floor/wall tiles in a bathroom of 10 m³ with aerosol, pump and trigger spray. Use of 10 g/m^2 is assumed.

3) Small area with high amount of product used pr. area: Impregnation of 0.3 m² (0.6 m x 0.48 m) mirror in a bathroom of 10 m³ with aerosol, pump and trigger spray. Use of 40 g/m^2 is assumed.

4) Small area with small amount of product used pr. area: Impregnation of 0.3 m² (0.6 m x 0.48 m) mirror in a bathroom of 10 m³ with aerosol, pump and trigger spray. Use of 10 g/m^2 is assumed.

For calculations, two exposure models, with substantial different approaches, are used: The "well-mixed room" ConsExpo 4.1 model and the more advanced "turbulent diffusion" SprayExpo model. Reasonable worst case (RWC) scenarios are estimated. The four scenarios are based on different critical assumptions regarding input parameters such as duration of exposure, mass generation rate, airborne fraction, initial droplet/particle size distribution etc.

For the estimates, it is assumed that the same version of the NPF 1-like formulation is used in both a pump spray, a trigger spray and an aerosol dispenser. Both ConsExpo and SprayExpo uses mass generation rates instead of applied amount. A mass generation rate of 0.55 g product/sec is used for the aerosol dispenser and trigger spray when use of 40 g product per m^2 is assumed. When use of 10 g product per m^2 is assumed a mass generation rate of 0.3 g product/sec is used for the aerosol dispenser and trigger spray. For the pump spray 0.2 g product/sec is used when use of 40 g product per m^2 is assumed and 0.1 g product/sec is used when use of 10 g product per m^2 is assumed. This change in mass generation rate when going from 40 to 10 g product per m^2 is introduced to have realistic duration of application (spray duration) as the mass generation rate are used to calculate the duration of application, based on the surface area of the object being sprayed. To make sure that the duration of application is realistic it has to be compared to the actual physical process of spraying 1 m^2 that takes approximately 25 sec.

The mass generation rates used for aerosol dispenser and trigger spray are in the lower end of the table values of mass generation rates available in Delmaar et al., 2009 and Feilberg et al., 2008 (cf. Table 2-3 in Appendix 2). The mass generation rates used for trigger spray, though, corresponds reasonably well with the mass generation rates of 0.2 g/s measured for the trigger spray NFP 1, Nørgaard (personal communication). For pump sprays only one table value is available - 0.1 g/s for perfume products, Delmaar et al., 2009. Feilberg et al., 2008 gives mass generation rates for 'hand pump sprays', but it is not known if this covers pump sprays, trigger sprays or both. These uncertainties in choosing the mass generation rates for the calculations have an impact on the validity of the resulting estimates. The choices are, though, seen as relative conservative.

SprayExpo contains a droplet impaction module for calculating the overspray during spraying onto a surface. ConsExpo 4.1 does not compute the share of droplets that are not deposited on the wall. It is possible, though, to define an 'airborne fraction' in ConsExpo, to allow for the share that is deposited on the wall to be neglected for the airborne concentration, Koch et al., 2012. For both aerosol dispenser, pump- and trigger spray the 'new' definition for the airborne fraction according to Delmaar et al., 2009, is used (cf. Appendix 2 section 2.2.1)

The most critical input parameter is most likely the initial droplet/particle size distribution. As no initial droplet/particle size distribution data is available for NFP 1 from the Nørgaard studies (cf. Appendix 2 section 2.2.1), the initial droplet/particle size distribution for the ConsExpo 4.1 and SprayExpo are based on other sources.

For aerosol dispenser the RWC initial droplet/particle size distribution (mass median diameter (MMD) 25 µm and geometric standard deviation (GSD) 1.8) is the aerosol spray default value in SprayExpo. This value is chosen as it is comparable to the value given for water-repellent products in ConsExpo, Delmaar et al., 2009.

To get more information on the initial droplet/particle size distributions of pump and trigger sprays the author of Kawakami et al., 2015 has been contacted. The author provided the actual spray data for 13 trigger sprays and 3 pump sprays. The product B3 (cf. Appendix 2 section 2.2.) with a droplet/particle size distribution estimated to MMD of 65 µm and a GSD of approximately 2.2 is chosen for the RWC calculations as this represents the group of products with the ratio of particles with diameter <9 µm exceeding 0.6%.

The data showed that it is difficult to distinguish the initial droplet/particle size distributions of the 3 pump sprays from the trigger sprays. Therefore the RWC droplet/particle size distribution used for trigger sprays is also used for pump sprays. It should, though, be noted that the statistical justification for this choice is limited with only three pump spray products.

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 applied by a trigger spray on to a target plate and measuring the particles 20 cm behind the trigger spray (Nørgaard et al. 2009 and Nørgaard 2010d). However, the number of particles generated by the trigger spray in the spray chamber experiments is significantly lower than the number of particles generated the high-pressure nebulization in the animal experiment.

There is a substantial difference in how the two models handle the droplet/particle distribution. SprayExpo takes shrinking of particles due to evaporation of the solvents into account whereas ConsExpo 4.1 does not.

The two models, ConsExpo 4.1 and SprayExpo were compared to each other and to experimental exposure values in Eickmann et al. (2007) and Koch et al. (2012). Eickmann et al. (2007) found that the simplifications in ConsExpo 4.1 don't allow for a comparison between measurements and model calculations for particle distributions with a diameter clearly greater than 50 µm. In order to compare ConsExpo 4.1 and SprayExpo Koch et al. (2012) took shrinking of particles due to evaporation of the solvents into account in the ConsExpo 4.1 calculations (cf. Appendix 2 section 2.2.3). This made mean event concentrations estimated by ConsExpo 4.1 comparable to mean event concentrations estimated by SprayExpo. Therefore ConsExpo 4.1 mean event concentrations both with and without evaporation of solvents take into account is shown in Table 7.

Trigger spray
The number of particles generated by the trigger spray for NFP 1 after spraying on to a target plate was approximately 4×10^2 particles/cm^3 per g applied product. For the coating of surfaces, 10 to 40 g/m^2 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/m^2 NFP 1 in the standard room and using trigger spray as application form, the concentration of TDFAs and 2-propanol (hydrolysates and condensates) reaches around 1.4 mg/m^3 (≈ 6x10^3 particles/cm^3) 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). On the other hand instantaneous distribution of the spray in the room this indicates may underestimate exposure if a worker is constantly very close to the source of a substance.

No particle concentration measurements are available for NFP 1 in 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 x 10^5 – 4.6 x 10^6 particles/cm^3) than observed in spray chamber experiments with trigger 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/m^3 – 42.4 mg/m^3 (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/m^2 NFP 1 is used in the standard room and using high-pressure spray (aerosol dispenser) as application form on a surface, the concentration of hydrolysates and condensates reaches around 46.2 mg/m^3 (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 on a surface 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/m^3. Of these approximately 11.5 mg/m^3 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/m^3) 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 7 shows the exposure estimates of particles able to reach the bronchioles and/or alveoli (< 10 µm) made on the basis of above-mentioned assumptions and the input parameters shown in Appendix 2. Table 7 is identical to Table 2-10 in Appendix 2 section 2.2.3.

TABLE 7 EXPOSURE ESTIMATES FOR A NFP 1 LIKE PRODUCT ESTIMATED WITH SPRAYEXPO AND CONSEXPO 4.1 WITH AND WITHOUT EVAPORATION OF THE SOLVENTS TAKEN IN TO ACCOUNT.

		Mean event concentration [mg/m³]		
Scenarios	**Spray type**	**ConsExpo 4.1**	**ConsExpo 4.1 with evaporation**	**SprayExpo**
1) Impregnation of 3.4 m² tiles in a 10 m³ bathroom (use approximately 40 g/m²)	Aerosol	1.9	89.6	97.1
	Trigger	0.0043	20.7	39.2
	Pump	0.0016	7.5	14
2) Impregnation of 3.4 m² tiles in a 10 m³ bathroom (use approximately 10 g/m²)	Aerosol	0.56	25.7	27.3
	Trigger	0.0013	6.1	11.1
	Pump	0.00043	2.0	3.8
3) Spraying of a 0.3 m² mirror in a 10 m³ bathroom (use approximately 40 g/m²)	Aerosol	0.20	9.3	7.5
	Trigger	0.00046	2.2	2.9
	Pump	0.00017	0.79	1.0
4) Spraying of a 0.3 m² mirror in a 10 m³ bathroom (use approximately 10 g/m²)	Aerosol	0.056	2.5	2.5
	Trigger	0.00013	0.6	1.0
	Pump	0.000043	0.2	0.35

As can be seen from Table 7 the mean event concentrations for trigger sprays is approximately three times higher than for pump spray even though the same initial droplet/particle distribution is used for the calculations. This is due to the fact the mass generation rates used for trigger spray is approximately three times higher than the mass generation rates used for pump spray. This also means a lower amount of the product is used when a pump spray is used for application.

From Table 7 it is seen that the mean event concentrations from SprayExpo are much higher than the once estimated using ConsExpo 4.1 when evaporation of the solvents is not taken in to account. This was also seen in Eickmann et al. (2007) who found that the values calculated by ConsExpo 4.1 are way below the experimental data in every case. The differences increase from the respirable through the thoracic to the inhalable fraction and also grow as the MMD increases. According to Eickmann et al. (2007) the large deviations in the calculations from the actual measurements point to the fact that the model simplifications in ConsExpo 4.1 (solvent evaporation not taken into account) do not allow for a comparison between measurements and model calculations for particle distributions with a diameter clearly greater than 50 µm. For SprayExpo Eickmann et al. (2007) found that 63 % of the calculated values do not deviate from the measurement result by more than a factor of 2. All the calculated values were in the correct order of magnitude.

Differences in the calculated mean event concentrations between ConsExpo 4.1 and SprayExpo were also seen in Koch et al., 2012. However, the differences in the mean event concentrations in Table 7 is considerably higher than in Koch et al., 2012 were the maximum difference were 19 times for wall spraying with particles with a small MMD in a larger room. Personal communication with one of the authors of Koch et al. (2012) revealed that in order to compare the two models droplet/particle distribution were re-calculated[10] after evaporation of the solvent for ConsExpo 4.1. As seen from Table 7 when evaporation of the solvents is taken into account the mean event concentrations are comparable to the ones estimated by SprayExpo for all the four 10 m^3 scenarios.

No measured data exist that can be used for direct comparison of an NFP 1 like spray product in a 10 m^3 bathroom. However, results from Vernez et al. (2004) and Nørgaard et al. (2010d) indicates that for a trigger spray the mean event concentration of particles in the < 10 µm fraction should be expected to be above 1 mg/m^3. Vernez et al. (2004) predicted the mean overspray concentration in the < 10 µm fraction to be 40 mg/m^3 and 45 mg/m^3 for two different proofing/impregnation formulations using the same type of trigger spray in a 12 m^3 (cf. C.2.1). Nørgaard (2010d) extrapolated measured NPF 1 data to the treating of 7 m^2 in a 17.4 m^3 room using 40 g/m^2 NFP 1 in trigger spray. The concentration was found to reach around 1.4 mg/m^3 immediately after treatment (cf. Appendix 2 section 2.2.1). Taking in to account that Vernez et al. used a Two-zone model and Nørgaard et al. assumes instantaneous distribution of the spray in the room this indicates that SprayExpo (and ConsExpo 4.1 with evaporation) is better at estimating the mean event concentration of the < 10 µm fraction than ConsExpo 4.1. When comparing SprayExpo to measured exposure values it should, furthermore, be taken into account that Koch et al. (2012) found that, on average, the exposure concentrations are slightly overestimated by SprayExpo. In about 70 % of cases the model is in agreement with the measurements within a factor of 4-5.

According to Eickmann et al. (2007) ConsExpo 4.1 underestimates the mean event concentration significantly and therefore it is not used for risk characterisation in section B.9.1.1.2. “Modifying” ConsExpo 4.1 to take solvent evaporations into account gives mean event concentrations that are in the same order of magnitude as the mean event concentrations estimated by SprayExpo. Therefore only SprayExpo is used for risk characterisation. However, with the uncertainties of this model taken in to account

The estimation of the consumer exposure to hydrolysates and condensates of polyfluorooctyl triisopropoxysilane from using a NFP 1 like product 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 (cf. Appendix 2 section 2.2.1). The parameter assumed to account for the largest uncertainty is the choice of initial droplet/particle size distribution. Therefore SprayExpo calculations have been performed with available minimum and maximum initial droplet/particle size distribution. For an aerosol dispenser the minimum initial droplet/particle size distribution (Min MMD) used is a distribution with MMD = 15.1 µm and GSD = 1.8 and the maximum initial droplet/particle size distribution (Max MMD) used is a distribution with MMD = 44 µm and GSD = 1.6. For trigger- and pump the Min MMD used is a distribution with MMD = 57 µm and GSD = 2.1 and pump the Max MMD used is a distribution with MMD = 164 µm and GSD = 2.1 (cf. Appendix 2 section 2.2.3.1). Mean event concentrations of particles with a diameter < 10 µm for these calculations are shown in Table 8. This table is identical to Table 2-11 in Appendix 2.

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[10] The author who performed the ConsExpo 4.1 calculations in Koch et al. (2012) has retired but (one of) the other authors suggested that a re-calculation of droplet/particle distribution has been performed. A set of ConsExpo 4.1 calculations has been performed in order to reproduce the results presented in table 3.3 in Koch et al. (2012). The results could only be reproduced if droplet/particle distribution were re-calculated after evaporation of the solvent.

TABLE 8 EXPOSURE ESTIMATES FROM SPRAYEXPO FOR A NFP 1 LIKE PRODUCT IN AEROSOL, PUMP- AND TRIGGER SPRAY SCENARIO 1-4 WITH MIN, MAX AND RWC INITIAL DROPLET/PARTICLE DISTRIBUTIONS AND ALL OTHER PARAMETERS KEPT FIXED

			Mean event concentration [mg/m³]		
Scenarios	**Model**	**Spray type**	**Min MMD**	**RWC**	**Max MMD**
1) Impregnation of 3.4 m² tiles in a 10 m³ bathroom (use approximately 40 g/m²)	SprayExpo	Aerosol	118.9	**97.1**	59.6
		Trigger	45.5	**39.2**	6.2
		Pump	16.3	**14**	2.2
2) Impregnation of 3.4 m² tiles in a 10 m³ bathroom (use approximately 10 g/m²)	SprayExpo	Aerosol	33.2	**27.3**	16.7
		Trigger	12.8	**11.1**	1.8
		Pump	4.4	**3.8**	0.7
3) Spraying of a 0.3 m² mirror in a 10 m³ bathroom (use approximately 40 g/m²)	SprayExpo	Aerosol	9.4	**7.5**	4.7
		Trigger	3.4	**3.1**	0.4
		Pump	1.2	**1.1**	0.16
4) Spraying of a 0.3 m² mirror in a 10 m³ bathroom (use approximately 10 g/m²)	SprayExpo	Aerosol	3.0	**2.5**	1.6
		Trigger	1.2	**1.1**	0.13
		Pump	0.46	**0.37**	0.065

The intervals seen for each spray type in Table 8 is not the overall uncertainty intervals for SprayExpo but only the uncertainty intervals for the initial droplet/particle distribution (based on the available distributions available). This is used for the risk characterisation along with fact that Koch et al. (2012) found that, on average, the exposure concentrations are slightly overestimated by SprayExpo. In about 70 % of cases the model is in agreement with the measurements within a factor of 4-5.

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. Furthermore, small amounts of unbound TDFAs or hydrolysates may be released during curing.

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 environmental issues from using consumer spray products containing TDFAs are related to the possible release of per- or polyfluoroalkyl substances present either as trace content of raw materials and intermediates or release of non-hydrolysed TDFAs during production and use.

When cured, the TDFAs mixtures form a siloxane polymer with polyfluorinated side-chains. As the self-cleaning effect of the impregnated surface weaken over time it may be necessary to repeat the treatment. This indicates that either the polyfluorinated side-chains are released from the polymer or the polymer is abraded and released as small polymer particles.

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. Furthermore, unbound TDFAs or hydrolysates may be released during curing.

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.

RAC Assessment

The risk depends on a respirable fraction (< 10 µm) of the mixture being generated. This is dependent by the application method (pressurised can, pump or trigger spray) of the spray (impregnating/proofing) product. Data from the Koch study supports 20% of particles < 10 µm for aerosol products and a lower particle concentration of respirable fraction for pump sprays (less than 0.9%). No information was available in the dossier or was obtained during the public consultation that provided technological information on how nozzle design impacts on the MMAD of particles. During the opinion making process the dossier submitter refined the exposure scenarios and the model used to estimate exposure. The refinements to input parameters were considered appropriate and RAC agreed that while there is uncertainity with the use of models the use of the SprayExpo model is more appropriate to this exposure estimate than the spray use in the ConsExpo model.

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 a product like the product named NFP 1 in the articles by Nørgaard et al. The active substances are hydrolysates and condensates of TDFAs in 2-propanol. Chemical analysis of NFP 1 using electrospray ionization mass spectrometry (ESI-MS) showed that it contained 1.1 ± 0.1 % active substances.

The acute 1 hour DNELs was calculated to 0.068 mg/m^3 and 0.21 mg/m^3 (see B.5.11).

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

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

Table 9 shows the calculated exposure concentrations along with the risk characterisation ratios. A risk characterisation ratio above 1 shows that the risk is not adequately controlled.

TABLE 9 RWC SPRAYEXPO EXPOSURE ESTIMATES AND RISK CHARACTERISATION RATIOS FOR A NFP 1 LIKE PRODUCT IN FOUR DIFFERENT SCENARIOS

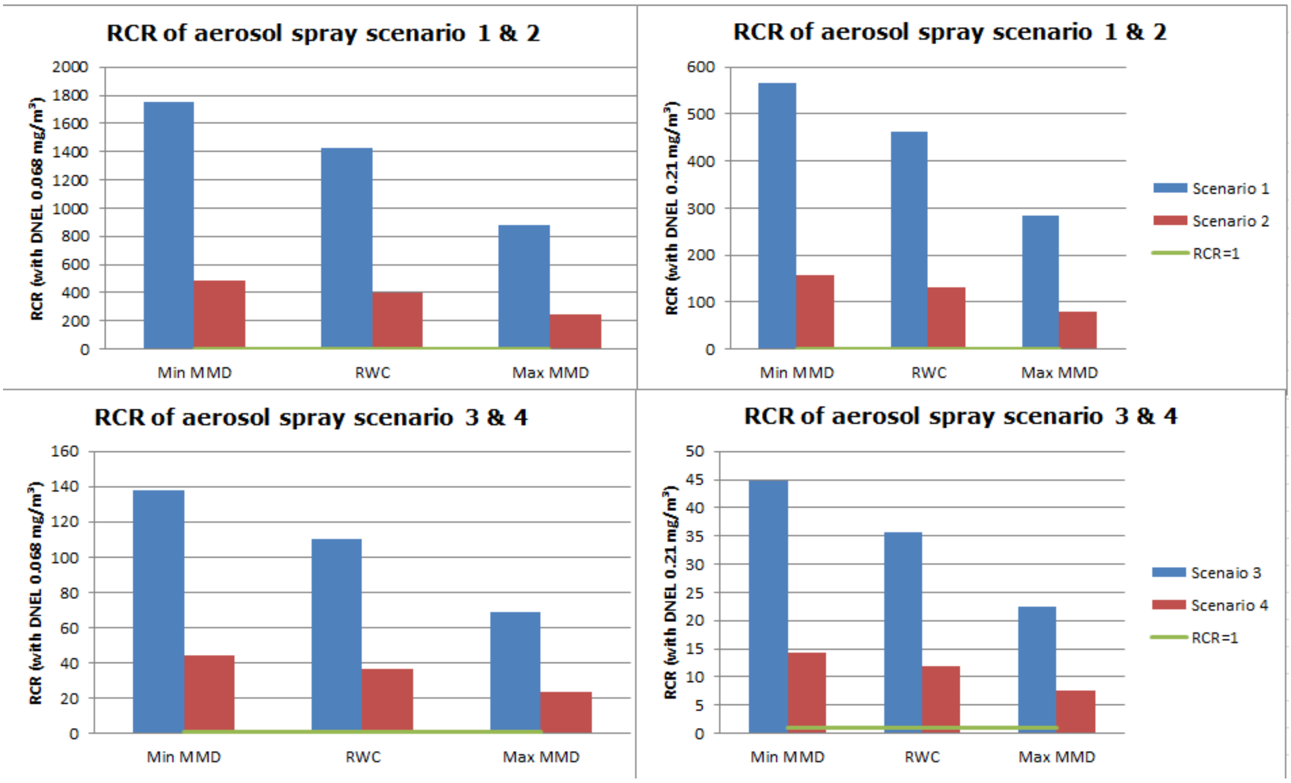
Scenarios	Spray type	Mean event concentration [mg/m³]	RCR (with DNEL 0.068 mg/m³)	RCR (with DNEL 0.21 mg/m³)
1) Impregnation of 3.4 m² tiles in a 10 m³ bath-room (approx. use 40 g/m²)	Aerosol	97.1	1428	462
	Trigger	39.2	576	187
	Pump	14	206	67
2) Impregnation of 3.4 m² tiles in a 10 m³ bath-room (use ap-prox. 10 g/m²)	Aerosol	27.3	401	130
	Trigger	11.1	163	53
	Pump	3.8	56	18
	Aerosol	7.5	110	36

3) Spraying of a 0.3 m² mirror in a 10 m³ bath-room (use ap-prox.40 g/m²)	Trigger	3.1	46	15
	Pump	1.1	16	5.2
4) Spraying of a 0.3 m² mirror in a 10 m³ bath-room (use 10 g/m²)	Aerosol	2.5	37	12
	Trigger	1.1	16	5.2
	Pump	0.37	5.4	1.8

Table 9 shows that when using SprayExpo there is a risk that is not adequately controlled for all of the RWC scenarios when applying mixtures containing TDFAs and 2-propanol by both aerosol dispenser, pump- and trigger spray independent of the DNEL used.

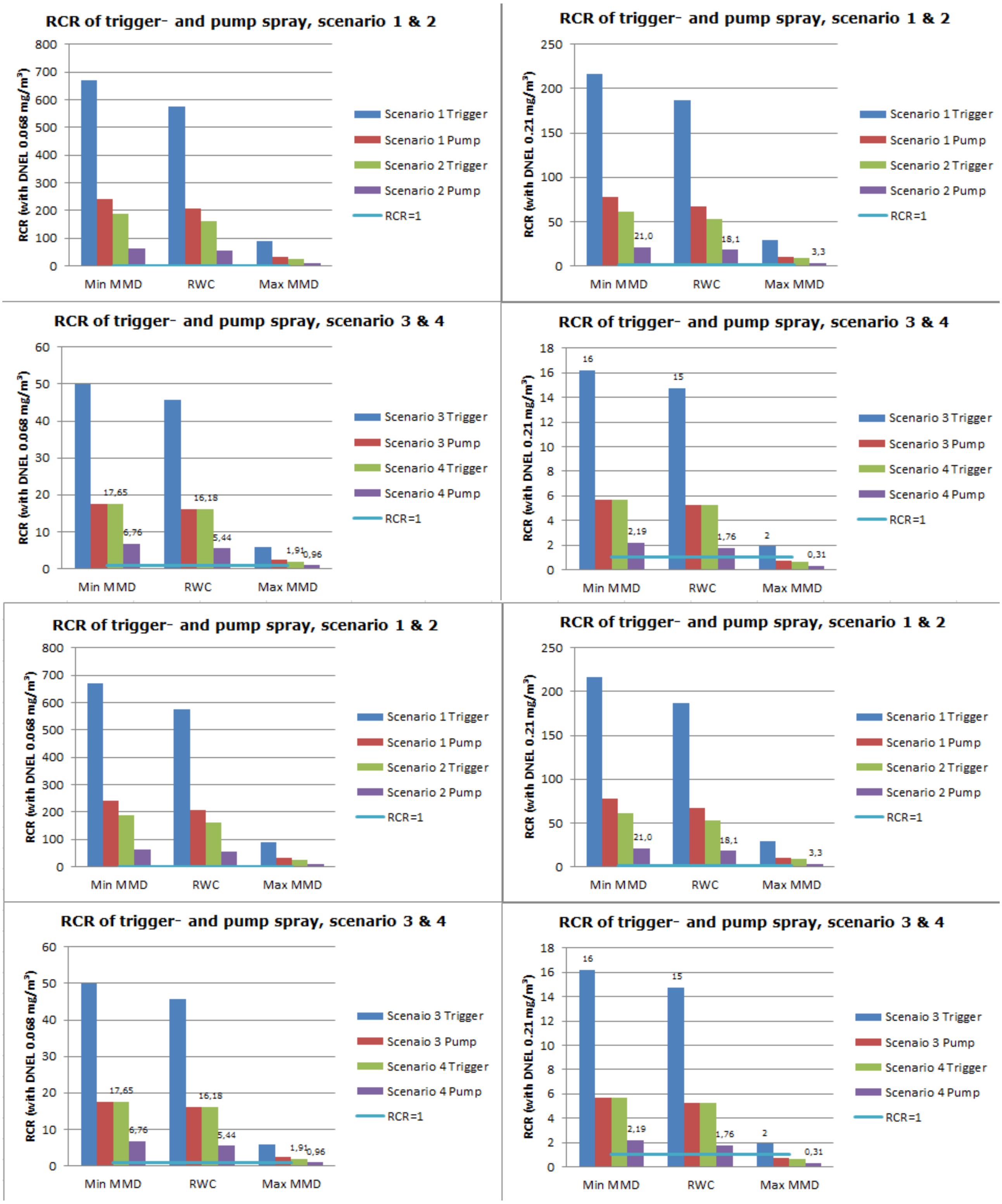
Table 9 should be interpreted very carefully, as the expected exposure values calculated by SprayExpo are based on a number of assumptions (cf. B.8.3.2 and Appendix 2).Especially the choices for mass generation and initial droplet/particle size distribution can have a huge impact on the estimated mean event concentrations. Uncertainty intervals for the initial droplet/particle distribution (based on the available distributions available) are shown in Table 8. The inclusion of these uncertainties in RCR calculations can be seen in Figure 1 and Figure 2.

FIGURE 1 RCRS FOR A NFP 1 LIKE PRODUCT IN FOUR DIFFERENT SCENARIOS BASED SPRAYEXPO EXPOSURE ESTIMATES FOR AN AEROSOL DISPENSER WERE INITIAL DROPLET DISTRIBUTION IS CHANGES AND ALL OTHER PARAMETERS KEPT FIXED . TWO DIFFERENT DNELS IS USED.



From Figure 1 it is seen that all RCRs is well above 1 independent of the DNEL used in all of the four scenarios for an aerosol dispenser - even when taking the uncertainty in initial droplet/particle distribution in to account. These scenarios shows that there is a risk that is not adequately controlled when applying mixtures containing TDFAs and 2-propanol by an aerosol dispenser.

Figure 2 RCRs for a NFP 1 like product in four different scenarios based SprayExpo Exposure estimates for trigger- and pump spray were initial droplet distribution is changes and all other parameters kept fixed . Two different DNELs used.



From Figure 2 it is seen that when using a pump spray with Max MMD (MMD of 164 and GSD of 2.1) in scenario 4 a RCR < 1 is found independent of the DNEL used (0.068 or 0.21 mg/m^3). The same is true when using a trigger spray in scenario 4 and a pump spray in scenario 3 when the

DNEL is 0.21 mg/m^3. For the rest of the scenarios in Figure 2 a RCR > 1 is found. However, this changes when taking in to account that Koch et al. (2012) found that, on average, the exposure concentrations are slightly overestimated by SprayExpo. In about 70 % of cases the model is in agreement with the measurements within a factor of 4-5.

When (as an extreme) all the RCRs in Figure 2 is divided by 5 it is seen that when using a pump- or trigger spray with Max MMD in scenario 4 or a pump spray in scenario 3 a RCR < 1 is found independent of the DNEL used. The same is true when using a trigger spray in scenario 3 and a pump spray in scenario 2 when the DNEL is 0.21 mg/m^3. Furthermore a RCR < 1 is seen when using a pump spray with Min MMD in scenario 4 when the DNEL is 0.21 mg/m^3. For the rest of the scenarios a RCR > 1 is found.

In other words, it is possible that there are pump- and trigger sprays on the market that would not pose a risk that is not adequately controlled in a few scenarios. However, calculations with SprayExpo indicates risk for both pump- and trigger spray in one or more of the four scenarios even when uncertainties is taken in to account.

If using ConsExpo 4.1 and taking evaporation of solvents into account comparable result as those seen for SprayExpo in Figure 1 and Figure 2 is expected as the RWC mean event concentrations is comparable in Table 7. ConsExpo 4.1 (without evaporation taken into account) is expected to underestimate the mean event concentration as seen in Eickmann et al., 2007, and therefor also to underestimate the RCRs.

The 1 hour NOAEC and LC$_{50}$ used for calculating the DNELs is based on TDFAs with 2-propanol as a solvent. As described in section B.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 NOAEC and LC$_{50}$ and therefore higher DNELs. Mixtures containing TDFAs and methanol are expected to have a NOAEC and LC$_{50}$ that is only slightly higher than mixtures containing TDFAs and 2-propanol (see B.5.11). Mixtures of TDFAs and solvents that are more lipophilic than 2-propanol are expected to have a lower NOAEC and LC$_{50}$. 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 an aerosol dispenser containing mixtures of TDFAs and organic solvent. This is also likely to be the case for pump- and trigger spray containing mixtures of TDFAs and organic solvent.

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- and trigger spray. This is in line with the much bigger number of incidents reported with use of aerosolised products. This risk characterization ratio also shows that the risk is higher for the mixtures containing TDFAs and 2-propanol when the product is applied by a trigger spray than by a pump spray. This difference is related to the choice of mass generation rate in the calculations (cf. section B.8.3.2) and is therefore somewhat uncertain.

If no other parameters are changed a NFP 1-like product with a concentration of hydrolysates and condensates of TDFAs and 2-propanol at 0.0008 % or 0.002 % (1428 or 462 times less, respectively, than the NFP 1 concentration of 1.1 %) that is applied on 3.4 m^2 in a 10 m^3 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 0.0008 %.

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 risk based limit value of 0.00008 % (800 ppb) in RMO 2 (see, E.2.2).

Product specific acute 1 hour DNELs for "Magic Nano Glass & Ceramic" was calculated to 0.13 mg/m^3 and 0.24 mg/m^3 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 these DNELs is the true rat DNELs 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 m^3 resulted in an exposure concentration of non-volatile components of 11.5 mg/m^3 which were able to reach the bronchioles and/or alveoli. From this RCRs of 88 and 48 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/m^3. 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 RCRs of approximately 2 and 1, 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/m^3. 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/or hydrolysates and condensates of TDFAs and organic solvents via the environment is not expected to be frequent or to involve high levels of exposure. However, exposure may occur if bystanders are close to a person performing outdoor spraying with impregnation sprays. Furthermore, small amounts of unbound TDFAs or hydrolysates may be released during curing.

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.4.

B.10 Summary on hazard and risk

Recent research has 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 a spray product like the floor sealant product NFP 1 (by Nørgaard et al.), were carried out for the hydrolysates and condensates of TDFAs and 2-propanol. Four different scenarios indicated that spray application of a NFP 1 like product presents an unacceptable risk of serious injury when using the SprayExpo model. The risk assessment based on exposure values calculated by SprayExpo contains a number of uncertainties as the exposure values are based on a number of assumptions. The calculations show a risk that is not adequately controlled for aerosol dispensers in all scenarios. They also show that it is possible that there are pump- and trigger sprays on the market that would not pose a risk that is not adequately controlled in a few scenarios. However, calculations with SprayExpo indicates risk for both pump- and trigger spray in one or more of the four scenarios even when uncertainties is taken in to account.

The difference seen in RCR between trigger and pump spray are e.g. due to the assumption that trigger spray has a higher mass generation rate than pump spray.

Based on the risk assessment of NFP 1 like product (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. This is also likely to be the case for pump- and trigger spray containing mixtures of TDFAs and organic solvent – at least for the reasonable worst case scenarios (based on SprayExpo calculations).The environmental risk is expected to be very limited due to limited environmental exposure from these products.

RAC ASSESSMENT

The exposure modelling supports a risks to consumers and the general public from the use of impregnating aerosol sprays containing TDFAs and 2-propanol are not properly controlled when used under worse case conditions. This is also supported by the number of cases reported to EU poison centres. The modelling also demonstrates a risk for pump and trigger sprays under RWC conditions when the product is used to treat a larger surface areas e.g. bathroom floor/wall. As the toxic effect is dependent on the fraction of spray which becomes respirable during or following application, a restriction on the maximum respirable fraction (e.g. 0.6%) that a pump or trigger spray can generate might be a way to control potential risks from pump and trigger spray products. However, it is not clear which concentrations of the ingredients will result in a limit fraction of primary aerosol particles below 0.6%, how technical or design parameters influence the size distribution or how the ageing process (reducing the aerosol particle sizes) may affect the hazardous effects of the mixtures of TDFAs and organic solvents.

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
- Polyfluorioalkyl 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 6, 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 trigger 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 indicates 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.

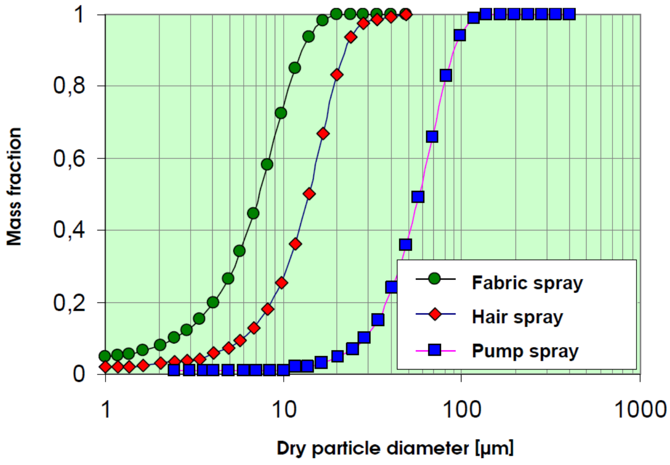
The Cosmetic Ingredients Review (CIR) Expert Panel has issued a document on aerosols (CIR, 2012), describing the typical particles released from a pump spray. According to CIR (2012), the median d_{ae} of the airborne droplets/particles of pump hair sprays range from 60 µm to 80 µm and typically less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

It should be noted that particle size distributions are product specific and time dependent. Numerous factors determine the initial size distribution of droplets or particles released from a spray product, including the product formulation (e.g., volatile or non-volatile solvent), can size, propellant and differential pressure through the nozzle for propellant sprays, and formulation and nozzle characteristics for pump sprays. After release to the air, 3 the particle size distribution can change rapidly through aggregation, agglomeration, sedimentation, evaporation of volatile components, or hygroscopic absorption of water. For example, all of the water and other volatile solvents and propellants in droplets with d_{ae} <40 µm will evaporate within 1 second of release from a spray can, so that the remaining particles will contain non- or low-volatile constituents (e.g., polymers with little or no biological activity in hair sprays). Accordingly, a wide spectrum of particle size distributions can be released from cosmetic sprays (CIR, 2012).

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 3. The fabric spray and the hair spray are aerosol sprays.

FIGURE 3 MASS FRACTION AS A FUNCTION OF PARTICLE DIAMETER (AFTER COMPLETE EVAPORATION OF THE SOLVENT) FOR THREE TYPES OF SPRAY



For spray impregnation products it is relevant to take overspray[11] in to account. The overspray 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. 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). In 2004 Vernez et al. tested two different proofing/impregnation with the same type of trigger spray. Using a two-zone model, with the near field volume defined to be $2m^3$, the mean inhalable overspray concentration for the two formulations were calculated to 12 mg/m^3 and 7 mg/m^3, respectively, in a room of 43 m^3. The fraction of droplets/particles with a diameter < 10µm were found to be 3.4 mg/m^3 (28%) and 2.6 mg/m^3 (37%) for the two formulations, respectively. In a 12 m^3 room the inhalable overspray for the two formulations were calculated to 60 mg/m^3 and 34 mg/m^3, respectively. In this room the fraction of droplets/particles with a diameter < 10µm were found to be 40 mg/m^3 (67%) and 45 mg/m^3 (75%) for the two formulations, respectively.

No pulmonary risk can be expected from application of mixtures containing TDFAs and organic solvents by cloth, roller or brush, since parent substances are volatile whereas hydrolysates and condensates are not (personal communication with Nørgaard). This means that that non-spray applications such as brush or roller are safe, since parent substances do not interact with the lung surfactants (Nørgaard et al. 2010 and Larsen et al. 2014).

C.2.2 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.

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 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.

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[11] 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.

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 10.

TABLE 10 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.

SEAC assessment

The Dossier Submitter has identified a number of alternatives to the use of mixtures containing TDFAs and organic solvent in consumer sprays, including:

a) Alternative application methods (such as brush, roller or cloth);

b) Water-based mixtures containing TDFAs (mainly for non-adsorbing surfaces);

c) Mixtures based on non-fluorinated active substances. E.g. non-fluorinated alkylsilanes and organic solvents

d) Mixtures based on polyfluorioalkyl trialkoxysilanes chain different from octyl; and

e) Mixtures based on fluorinated active substances except fluorotrialkoxysilanes.

There is a lack of information on the hazards or risks of these alternatives but it is assumed that options a), b) and c) have a much lower impact. With alternatives d) and e), the uncertainties related to impact are higher.

SEAC does not have any information whether concentrations of TDFAs as impurities occur in polyfluoroalkyl trialkoxysilanes with polyfluoroalkyl chain different from octyl. Thus, it cannot be fully excluded that a restriction for TDFAs used in a concentration of 2 ppb, like RMO1 and RMO3, will impose a ban also for polyfluoroalkyl trialkoxysilanes other than TDFAs as acknowledged by the Dossier Submitter. However, no information confirming or denying the presence of TDFA impurities was submitted in the SEAC Draft Opinion Public Consultation. Regarding the risk reduction potential of the proposed restriction options, RMO 1 might not be more effective than RMO 2, as both of the two RMOs impose TDFAs concentration limits, 2 ppb and 800 ppb respectively, to ensure that risks are adequately controlled for the general public. However, RMO1 and RMO3 could imply a restriction also for the use of mixtures with polyfluoroalkyl trialkoxysilanes with polyfluoroalkyl chain different from octyl, if TDFAs are present as impurities in its composition. RMO2 might not imply any reformulation for spray products based on polyfluoroalkyl trialkoxysilanes, other than TDFAs and could allow the use of drop in alternative substances for the ones based on TDFAs and organic solvents. However, SEAC does not have any evidence that the content of TDFAs as impurity in polyfluoroalkyl trialkoxysilanes with polyfluoroalkyl chain different from octyl are below of 800 ppb or even if they are present. Furthermore, SEAC does not have information about the inherent risks of the uses of such alternative substances and other less hazardous alternatives are available.

Formulators of products that currently contain TDFAs may need to reformulate their products or change the application method prior to the deadline, i.e. by the end of the transition period or to change the application method. They may also need to seek confirmation from their supplier about the content of TDFAs in the polymers or mixtures they purchase. Retailers of aerosol and spray products may request declaration from their suppliers that none of their products contains TDFAs. The authorities may, for enforcement purposes, request information about product composition from the suppliers of the consumer products.

Compliance tests are expected to be undertaken as spot test campaigns to assess the level of compliance. The Dosser Submitter claims that at present there are no adequate EU standards or analytic standard method available. The TOP Assay method is currently being implemented by a commercial laboratory for analysing PFOA and PFOA precursors. This method could according to the information in the dossier be adapted to analyse the targeted substances (limit of detection: 2 ppb). However further information provided after the submission indicates that the TOP assay method might not be applicable for TDFAs analysis.

As alternative application methods could be used and similar products without TDFAs exist on the market, SEAC finds it possible to replace TDFAs with the alternatives that seem to be both technically and economically feasible. However SEAC does not exclude the possibility that replacing TDFAs in the proofing/impregnation spray products might result in some product performance loss, but still SEAC concludes that the restriction proposal is implementable and manageable.

SEAC lack information about the specific length of time required to perform a reformulation to remove TDFAs, and thus cannot conclude on whether it is manageable for the involved actors to reach compliance within the proposed 18 months’ compliance period or not. Additionally, there is no information on the relation between the compliance period and the development of any analytical test.

If the targeted products are not put on the market the discussion about reformulation is irrelevant. Notwithstanding, there is no discussion for the relation between the compliance period and the development of any analytical test or to develop a standardized method to enforce consistently the restriction. SEAC has therefore no ground to justify 18 months of compliance period but agrees that it could be sufficient to deplete stocks.

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 Nano-Cover (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 Dynasylan 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 are 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 clots.

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 (C_4 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 chemistries (such as PFOA, PFOS and 8:2 FTOH)[12] toward the use of C_{4-6} 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 (C_8 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 re-

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[12] 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)

viewed 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 polyfluorinoalkyl triethoxysilanes with polyfluoroalkyl chain length different from octyl

Only little effect on pulmonary function were seen in mice following short term exposures to aerosolised non-hydrolysed 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 human health endpoints is available for the polyfluorioalkyl 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 polyfluorinoalkyl 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 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. However, short-chain PFCAs and PFSAs have been seen to accumulate in crops like e.g. maize, Krippner et al., 2015. Based on available information short chain PFCAs and PFSAs appear to have low ecotoxicity (Kjølholt et al., 2015).

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 C_8 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 alkoxysilanes.

The formulator indicates that the final coating may by 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 formulator[13] suggest that prices increase with increasing chain length of the polyfluoroalkyl alkoxysilanes. 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 11 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
Non-fluorinated alternatives			
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).

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[13] 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 non-fluorinated alkylsiloxanes (See Appendix 1, Greenland).

It is not clear to what extent the incidents reported in Table 6 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 (C_{4-6}) 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 (cf. section B.7).

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, fluorpolymer, acrylate fluorpolymer, 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, C_{4-6} 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 (< C_8). 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 12 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 12 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 alkoxysiloxane 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 Swizz 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 13. 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 13 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	Maybe a bit more expensive 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 polyfluorotrialkoxysilane	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	Generally less expensive, 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

RAC ASSESMENT

As the risk is not relevant for these mixtures where a respirable fraction is not generated this means that mixtures of TDFA's & organic solvent can be used when applied using alternative techniques such as brush, roller or cloth.

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 indicate 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 risk assessment based on reasonable worst case scenarios involving a floor sealant indicates 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 may be placed on the market and 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.

RAC ASSESSMENT

There is currently no restriction under REACH on the placing on the market of mixtures of TDFA’s and organic solvents in consumer products. There is also no provision in Annex

II part 3 of CLP that prohibits the placing on the market, for the general public, substances or mixtures classified as acute toxic in Category 1 or 2 by inhalation in aerosol packaging.

SEAC assessment

Based on the key principles of ensuring a consistent level of protection across the EU and of maintaining the free movement of goods, SEAC supports the view that any necessary action to address risks associated with TDFAs, (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 should be implemented on an EU-wide basis. This restriction will prevent that such spray products would be placed on the EU market now or in the future. This action would also guarantee the free movement of goods within the EU to ensure that the internal market works properly. This further underpins the necessity of implementing a union wide action.

SEAC recognises that action is required to avoid the risks for consumers' pulmonary distress from the use of the targeted products, since it cannot be excluded that the targeted products are (or could be put) on the EU market as intended for use by the general public. It is not known if aerosolised mixtures containing TDFAs and organic solvents in consumer products are actually placed on the EU market. During the public consultation no information about aerosolised mixtures containing TDFAs and organic solvents currently on the market for use by the general public was submitted. Sweden provided information verifying that proofing/impregnation spray products based on mixtures of TDFAs and organic solvents intended for consumer use were registered in the Swedish Product Registry from 2010 to 2013. However, since 2014 no consumer products based on mixtures of TDFAs and organic solvents have been registered. According to the dossier submitter spray products likely to contain mixtures of TDFAs and organic solvents linked to incidents due to exposure from proofing/impregnation sprays have been identified in several cases, but when the incidents have occurred the products have subsequently been withdrawn from the market. One of the manufacturers of TDFAs claims not to know of any current use of TDFAs in the targeted products. The same manufacturer also claims that the use of TDFAs in some of the spray products involved in the reported incidents have not been conclusively proven. This statement is corroborated by the information available in the dossier.

Since the composition of the spray products on the market is not known to a sufficient detail, as the chemical description on labels or in SDS of the fluoralkylsilanes when used as ingredient is not sufficiently detailed, it is not possible to identify these substances as TDFAs. Therefore, proofing/impregnation spray products intended for supply to the general public cannot be excluded.

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.

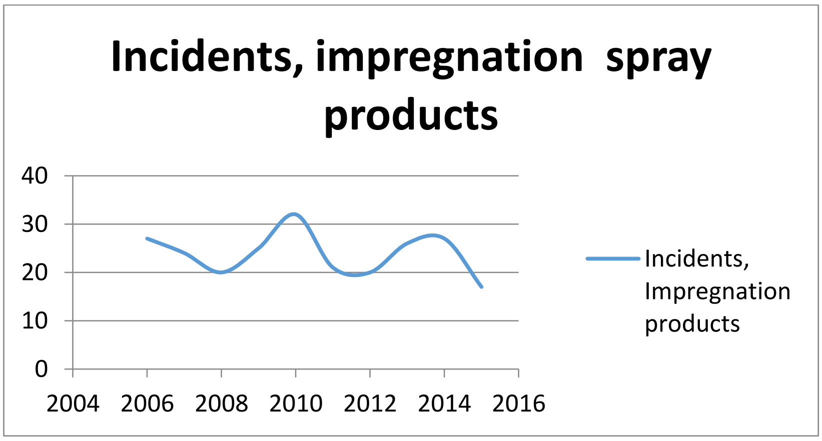
E.1.1 Risk to be addressed – the baseline

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 6 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 6 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 4 shows the number of such calls over the years.

FIGURE 4 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 population[14], would correspond to 2200 calls (range 1500 - 2900 calls). Assuming that in line with Table 6 that 20 to 40% is related 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 0.00008 % (0.8 mg/kg, 800 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

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[14] EUROSTAT, 2015: Danish population 2014: 5.6 M, EU population 2014: 507.4 M.

- 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 specials 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. For the products classified as mentioned above, the effect for the general population would be the same, while for products without classification would be allowed even if they could still impose a risk. Therefore, this is not considered a relevant stand-alone RMO in the context of this proposal. However, in order to reduce the risk that products for professional or industrial use are supplied to the general public such a supplementary RMO could be considered. It is noted, however, that it looks as for none of the incidents reported, the products were labelled as acute toxic to humans.

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.

SEAC Assessment

SEAC finds that a restriction with a specific scope as in RMO1 would be a more appropriate and implementable measure for the industry and enforcement authorities, as it clearly identifies the mixture, the ingredients and the application methods that lead to a risk. Therefore, SEAC concludes that a restriction is the most appropriate EU-wide measure to address the concern for human exposure to spray products containing a mixtures of TDFAs and organic solvents

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 incidents. 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 prices[15] 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 sprays[16]. 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 11.

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 0.00008 % (800 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.

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.

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[15] 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

[16] According to one producer of a nano film product

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 dispersers.

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.

Nørgaard et al. (2010b and 2010c) have tested various analytical techniques for analysis of products containing organo-functionalized silanes including NFP1 that contains TDFAs and 2-propanol. The content of organo-functionalized silanes 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 non-hydrolysed and hydrolysed silanes, while the corresponding di-, tri- and tetrasiloxanes were common in ESI, APCI and TM-DESI. LTP seems superior in showing the substances in their pristine, unreacted state. ESI and APCI are applicable for fast and simple analysis of organosilane/siloxane mixtures and represent the most straightforward approach since both ion sources are standard equipment on most commercial mass spectrometers with an atmospheric pressure inlet instruments and thus commonly accessible.

None of the five techniques can be designated as being universal for analysis of reactive organofunctionalized silanes since each of them is somewhat biased, thus suggesting the use of more than one ionization technique in future analyses of similar reactive samples (Nørgaard et al., 2010c).

LTP-tests are not available from commercial laboratories. A Danish research laboratory has suggested using a combination of direct infusion ESI-MS and APCI-MS for the analysis of the parent substances (TDFAs). According to Nørgaard (personal communication) the detection limit (LOD) of this method is expected to be 1-2 ppb for the parent substances as this is achievable for modern mass spectrometers.

According to Nørgaard (personal communication) an extra analytical technique has to be added for quantification. This could e.g. be elemental determination of the total amount of silicon by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) The Instrumental Detection Limit (IDL) for silicon using ICP-MS[17] is 0.1-1 ppb. The Practical Quantitation Limit (PQL) will generally be 2-10 times higher than the IDL.

Costs of analysis - The Danish research laboratory that suggested to use a combination of direct infusion ESI-MS and APCI-MS 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.

Limit value - To keep costs and analytical complexity as low as possible for compliance testing the limit value of the individual substances belonging to the group of TDFAs is set to 2 ppb as this is the expected LOD of the combination of direct infusion ESI-MS and APCI-MS for the parent substances.

It cannot be excludes that some commercial laboratory will currently have a higher LOD (e.g. 5-10 ppb) due to factors such as available instrument, sample matrix, sample collection and preparation methods, and operator skill level. To not exclude such laboratories from performing compliance testing forming enforcement authorities could choose to not enforce below 10 ppb. This would be acceptable as 10 ppb does not pose a risk.

Conclusion - For enforcement purposes, an indication whether the product contains one or more substances meeting the target formula above the LOD 2 ppb would be sufficient.

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[17] http://crustal.usgs.gov/laboratories/icpms/intro.html

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. The German Magic Nano case and the NanoCover product (NFP 1) voluntarily removed from the Danish market were reported in RAPEX.

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 0.00008 % (0.8 mg/kg, 800 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 0.00008 % (0.8 mg/kg; 800 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 likely 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 ppb and 800 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 ppb and 800 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 1and 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 0.00008 % (800 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 this would require that an extra analytical technique has to be added (e.g. elemental determination for quantifying the total amount of silicon).

As the handling of the mixtures would highly influence the results (the formation of condensation products before analysis) if would be necessary to develop a standard to be used for the analysis.

The extra costs and the possible time needed for development 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 800 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 indicated that the same mixture applied by pump- or 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 trigger/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 form 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 indicated 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.

SEAC assessment

SEAC finds that among the restriction options, RMO1 and RMO2 would be more effective than RMO3 as they cover trigger and pump spray products. Therefore, SEAC concludes that a restriction with a specific scope as in RMO1 or RMO2 would be a more appropriate and implementable measure for the industry and enforcement authorities, as it clearly identifies the mixture, the ingredients and the application methods that lead to a risk. Regarding the risk reduction potential of the proposed restriction options, RMO 1 might not be more effective than RMO 2, as both of the two RMO impose TDFAs concentration limits, 2 ppb and 800 ppb respectively, to ensure that risks are adequately controlled for the general public. SEAC also does not have any evidence that the content of TDFAs as impurities in polyfluoroalkyl trialkoxysilanes with polyfluoroalkyl chain different from octyl are below of 800 ppb or even if they are present, so the scope of this two RMOs could be the same.

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 0.00008% (800 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 alkoxysilanes from the restriction. As mentioned above this 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 trialkoxysilanes 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.

SEAC assessment

The assessment and comparison of the risk management options carried out by SEAC could be summarised in the tables below:

Table A - Comparing the impacts of different RMOs using qualitative, quantitative and monetised data.

RMO	Advantages:	Drawbacks:
RMO1: (proposed restriction – ban mixtures of TDFAs and organic solvents in spray products for use by general public)	2.5-100 fewer consumers with severe incidents. 3-115 fewer consumers with moderate incidents. 3-115 fewer consumers with mild incidents.	The eventual content of TDFAs as impurities in polyfluoroalkyl trialcoxy silanes with polyfluoroalkyl chains different from octyl could make the use of these substances as drop in alternatives impossible. Therefore, higher reformulation costs per formula might be foreseen. However, there is not any information available regarding this matter. Fewer consumer benefits due to the poor performance of the alternatives products and alternative application methods. Possible social impacts in terms of unemployment. However irrelevant due to the small market of the targeted products. Administrative costs. Some distributional impacts might be foreseen but still irrelevant due to the small market of the targeted products. Blacklist effect.
RMO2: (ban of mixtures of TDFAs and organic solvent in spray products for general public uses in a concentration of TDFAs equal to or greater than 800 ppb)	2.5-100 fewer consumers with severe incidents. 3-115 fewer consumers with moderate incidents. 3-115 fewer consumers with mild incidents.	Polyfluoroalkyl trialkoxy silanes with polyfluoroalkyl chains different from octyl could be used as alternatives, which foresees lower reformulation costs – drop in alternatives. There is no information on this matter. Fewer consumer benefits due to the poor performance of the alternative products and alternative application methods. However, it is possible to keep using polyfluoroalkyl trialcoxy silanes with different chain length in sprays. Possible social impacts in terms of unemployment, however still irrelevant due to the small market of the targeted products. Administrative costs. Higher costs to ensure compliance (higher testing costs). Some distributional impacts might be foreseen but still irrelevant due to the small market of the targeted products. Blacklist effect.

RMO3: (ban mixtures of TDFAs and organic solvents in aerosol products for use by general public)	Less than 2.5 -100 fewer consumers with severe incidents. Less than 3-115 fewer consumers with moderate incidents. Less than 3-115 fewer consumers with mild incidents.	Higher reformulation costs per formula might be foreseen if the companies will not change from the aerosol production to pump and trigger sprays, provided polyfluoroalkyl trialkoxysilanes with chain length different from TDFAs could not be used as drop-in alternatives. Fewer consumer benefits due to the poor performance of the alternative products and alternative application methods. It is possible to keep using pump and trigger spray products filled with mixtures of TDFAs and organic solvents with the same level of performance. Possible social impacts in terms of unemployment, however still irrelevant due to the small market of the targeted products. Administrative costs. Some distributional impacts might be foreseen but still irrelevant due to the small market value of the targeted products. Blacklist effect.

Table B - Comparing the main impacts of different RMOs using qualitative, quantitative and monetised data.

	Health impacts (per year)	**Reformulation costs (per year)**	**Administrative costs include tests**
RMO 1	€75 000 - €110 000	€8 000 – 12 000 (€10 000)	€ 300/test
RMO 2	€75 000 – €110 000	Drop in alternatives at the same price level – irrelevant reformulation costs	More than € 1000/test
RMO 3	Less benefits than RMO1 and RMO2	Reformulation costs between RMO1 and RMO2	€ 300/test

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 members[18]. 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 is 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 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 mixtures containing TDFAs and 2-propanol shows a risk that is not adequately controlled for these mixtures applied by aerosol dispenser, and indicates that such a risk also exists for trigger- and pump spray. The calculated risk characterisation ratios for aerosol dispensers, trigger- and pump spray drops in the order: aerosol dispensers > trigger spray >

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[18] The statement from FEA was linked to aerosol dispensers.

pump spray, which indicates the highest risk for application by aerosol dispenser and the lowest for application by pump spray.

Evidence of consumer exposure – In the EU, 725 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 6). 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 spray products (aerosol dispensers, pump and trigger sprays and mixtures marketed for spray application) and spray products produced in the EU. A Union-wide ban is justified by the fact that risks can arise in all Member States due to free movement of goods across borders and to avoid different legislative requirements in Member States with the risk of creating unequal 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 both with and without TDFAs have been reported. Animal experiments have demonstrated similar effects from the application of aerosolised mixtures with TDFAs and organic solvents. A risk assessment for hydrolysates and condensates of TDFAs and 2-propanol shows that a risk exists for these mixtures applied by aerosol dispensers, and indicates that a risk exists when the mixtures are applied by pump- or trigger sprays. The risk seems to be higher for aerosol dispensers than for pump and trigger sprays. Other risk management options have been evaluated but none were considered to provide 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.

RAC assessment

As the acute toxicity to humans effect only occurs when both substances are used together and aerosolised into a mist with a respirable concentration <10 um, this information would not always be evident to formulators based on the test data of the parent substances in the mixture. Information would have generally only been available to the importers or formulators if the mixture was tested before the product was placed on the market or if this information is contained in Section 2.3 of SDS "Other Hazards". In the absence of an appropriate provision for the testing of final impregnating/proofing products before they are placed on the market a REACH restriction is an appropriate risk management measure addressed at consumers which will specifically reflect the particular concerns of the use of TDFAs and solvents in mixtures placed on the market in spray products.

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, 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. However, some of the incidents[19] described in Appendix 1, Table 1 - 2, last for much longer time.

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.

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[19] It is noted that it is not documented that the actual cases in the Appendix, table 1-3, is triggered by TDFAs in combination with organic solvents

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 distributes as follows:

TABLE 14 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 2011[20]. 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

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

standard rates by diagnosis. The 2014 rate for one incident of "Observation of respiratory disease"[21] 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 salaries[22] 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 here[23].

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

TABLE 15 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. [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.

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[21] Covers all expenses related to hospital sector distributed on specific diseases. Stationære DRG takster 2015 http://sundhedsdatastyrelsen.dk/da/afregning-og-finansiering/takster-drg/takster-2015 (Stationære DREG-takster 2015 - table row 146 (1€=7,5 DKK)
Harmonised indices of consumer prices (HICP): http://appsso.eurostat.ec.europa.eu/nui/show.do?dataset=prc_hicp_aind&lang=en
PPP: http://ec.europa.eu/eurostat/tgm/table.do?tab=table&init=1&language=en&pcode=tec00120&plugin=1

[22] 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. Newer updated labor cost survey has later become available - http://ec.europa.eu/eurostat/documents/2995521/6313539/3-15122014-AP-EN.pdf/36ae8443-6a22-429a-8e05-6b59088e3155, confirming the assumed projection s – the figures are not changed as the 2008 figures were already price adjusted by 10% (up to 2013), quite close to the 11% increase in the labor cost survey (EU28) (2012). Actually, as a secondary source https://www.destatis.de/EN/PressServices/Press/pr/2014/05/PE14_164_624.html - the average labor cost in EU(27) is estimated to €24 per hour which with the assumed numbers of working hours per day of 7.5, makes an estimate of a working day to be 180 €, exactly the value mentioned in table 15

[23] RICARDO-AEA 2014 *"Update of the Handbook on External Costs of Transport"*

TABLE 16 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 17 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. In addition to this an individual welfare loss due to less activity, inconvenience or pain should be taken into account. Therefore the €49 is considered as being a minimum.

For the mild incidents the costs have been assumed to 10€. This only covers the individual welfare loss, and is estimated to be 20% of the value for a minor restriction day due to air pollution. Even that no supporting evidence for this value is available, it is considered to be in the lower end, as it does not include other elements like fear of what it may be the severity of the symptoms.

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 18.

TABLE 18 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.

SEAC assessment

SEAC concludes that the benefits estimation can be based on the number of avoided incidents. SEAC agrees with the estimation of health costs in the range of €1 520 - €2 220 as well as with the costs related to production and welfare losses and to the annual estimation of benefits of the avoided number of incidents. However SEAC disagrees with the estimation of the number of EU incidents based on a simple extrapolation of the Danish data. SEAC acknowledges that it is highly likely that the number of registered incidents might not indicate the real number of incidents in the EU, thereby resulting to an underestimation of benefits. SEAC does not have any ground to take the Danish data as representative for all Member States. The available information from some EU countries indicate that most of the Member States do not have any reported incidents related to the use of the targeted products. Therefore SEAC concludes that the Danish data might not be representative for all EU, and an estimation based on such extrapolation would result in an overestimation. Also, considering the uncertainty regarding the presence of the targeted products on the market for the general public, the assumption that 40% of the estimated incidents could be related to the use of spray products based on TDFAs and organic solvent does not seem to be realistic. SEAC estimates that the number of human incidents related to the targeted products is in the range 8.5 - 360, which lead, using the central value estimate for the yearly average number of incidents in the EU, to an estimation of benefits in the range of €75 000 – €110 000 per year.

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

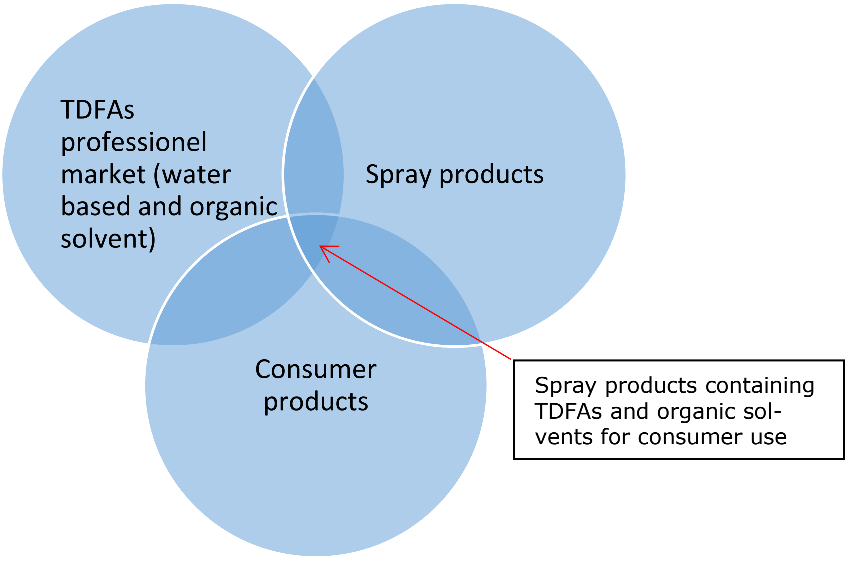
F.2.1 Compliance costs

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 5. 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 5 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 polyfluoralkyl 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 2002 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 alkoxysilane is substituted by another polyfluoroalkyl alkoxysilane 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 reppellency (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 19.

TABLE 19 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 million – 58 million[24], equivalent to €5 500 - 16 100 per formula for which formulation is required.

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 formula[25]. 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.

The main problem is, however, that no information is available on the number of formulas that need to be changed to other substances than polyfluroalkyl 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.

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[24] It should be noted that this dossier on TDFAs was submitted before the SEAC opinion on D4/D5 was agreed. The opinion questions the assumptions on possibilities for coordination and has a medium scenario, assuming 10 years of coordination and no cost savings due to less minor reformulations of a value 2.5 times higher (€50 - 90M instead of $20-58 M), equivalent to €13,300 - 24,000 per formulation for which formulation is required.

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

SEAC assessment

An important part for the compliance costs are the reformulation costs. For producers that may have to develop more complex reformulations, the Dossier Submitter concludes that the annual costs of reformulation per formula should be 30% of the estimated value for D4/D5 substitution, which is €8 000- €12 000 (SEAC assumes that for this type of products, produced essentially by small companies with a small market share, it is unlikely that companies would have regular reformulation activities that could be coordinated with this demand). Although the reasoning given for that range is weak, SEAC may consider this estimation of the reformulation costs as indicative. The Dossier Submitter is not able to estimate the total number of products facing reformulation, and so the estimation of the total costs of reformulation was not carried out.

SEAC's approach to overcoming this lack of information is to apply different scenarios and to focus on the credibility of the estimated reformulation costs to arrive at an indicative value. Therefore, SEAC assumes four scenarios to describe the general public market of the targeted products market, where there are 0, 2, 5 and 8 targeted spray products available for non-professional users, each of them with its own producer. In addition, SEAC assumed that the market share is equal for all the companies, since the differences among the formulations of the mixtures to be used in pump or trigger or aerosol spray products, based in TDFAs and organic solvents, are irrelevant and half of the products have the same formulation. These scenarios are underpinned by the following information:

- SEAC is not aware of if any proofing/impregnation spray products based on mixtures of TDFAs and organic solvents, intended for supply to the general public, are put on the market.
- It is known that there are eight proofing/impregnation spray products with TDFAs and organic solvents put on the market for professional use in Spain. Therefore, it is unlikely that there is a larger product diversity on the market for use by the general public.
- Information received during the public consultation from the Swedish Product Registry, verifies that mixtures containing organic solvents and TDFAs were used in two spray products for non-absorbing surfaces by consumers between the years 2010 and 2013.

For the first scenario, where it is assumed that there are no targeted spray products on the market for consumers use, RMO1 and RMO3 could be more costly for the industry than RMO2. These two options may imply a restriction for the use of mixtures with polyfluoroalkyl trialkoxysilanes with polyfluoroalkyl chain different from octyl if the content of TDFAs as impurities would occur. RMO2 does not involve any product reformulation because the limits of the TDFAs content might be sufficient to avoid the need for reformulation to comply with this RMO. However, there is no information on the content of TDFAs as impurities in such substances or even if TDFAs as impurities occur in such products.

For the scenario with eight companies sharing the market, assuming an equal share of a total annual turnover of €50 000 and €1 200 000, that roughly accounts an annual turnover between €6 250 and €150 000 for each company. From SEAC's view, it is not credible that a company produces one product with this annual turnover, for sales throughout the EU.

For the scenario with five companies on the market, each of them would have an annual turnover between €10 000 and €240 000, which is more plausible but perhaps still not credible.

Finally, if there are only two companies on the market, their annual turnover would be €25 000 and €600 000. SEAC finds this to be the more realistic scenario.

According to the SEAC assumptions, industry will only have to reformulate one formula, and therefore the annual costs for reformulation will be an indicative value of €10 000 (central range estimate of the range estimated by the DS for the reformulation costs of one formula).

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.

SEAC assessment

No costs for ensuring compliance have been identified by the Dossier Submitter if a substitution would occur to alternative application methodologies like brushes, rollers or cloth.

Furthermore the Dossier Submitter does not discuss the necessary steps for ensuring compliance for the different actors (manufacturers, importers, formulators, producers, retailers). Therefore SEAC is not able to assess whether this information in the supply chain will be achieved and able to use for enforcement purposes.

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 polyfluroalkyl 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 in 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.

SEAC assessment

SEAC concludes that the above mentioned impacts (social impacts, wider economic impacts and distributional impacts) are highly likely to be irrelevant and that the resulting change is likely to be largely distributional. SEAC arrived at this conclusion by considering: the small size of the market, the estimated costs and benefits, the availability of alternatives (products, substances, application methods) on the market and the absence of claims in the industry consultation and the public consultation.

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 polyfluroalkyl trialkoxysilanes of TDFAs in organic solvents is considered, the annualised cost of reformulation per formula is € 8 000 – 12 000.

Table 20 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 20 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 TDFA	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[26]" 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 **Reconsile 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 Reconsile 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.

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[26] http://echa.europa.eu/documents/10162/13641/bd_call_for_evidence_pfas_en.pdf

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.

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 Brancheforening)** 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, B2.2.1, 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 6. Spain had information on 13 phone calls related to incidents related to polyfluorinated silanes or fluorinated compounds and organic solvents (aromatic or isoparafinic hydrocarbons). Of the 13 incidents 5 were due to inhalation. These 5 incidents are included in Table 6. Call for Evidence is included in Appendix 3 and follow up to the Call for Evidence is included in the confidential Appendix 4 (removed from the public version of the BD).

Lithuania, Slovenia and Cyprus has responded to the Public Consultation (2016) that their National Poison Control Centers do not have any cases of poisoning incidents related to TDFAs substances in spray product. Industry (manufacture of polyfluorooctyl triethoxysilane) informed that they have got no hints or information of cases with pulmonary effects with TDFAs.
Sweden added that according to a Swedish survey on PFASs from 2015 a lack of available information is substantial for the whole PFAS-group.
During Public Consultation Ireland submitted information of 16 case stories with 21 human incidents elated to proofing/impregnation product from 2006 to 2016. Of these 21 incidents 12 (4 consumers and 8 occupational) were due to inhalation. These 12 incidents are included in Table 6.

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 disperser 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 disperser 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 6 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	<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. <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.		
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	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 salbutamoland IV corticosteroids. All were discharged within 24 hours.		

1992-1993	**Canada**
	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. 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	Laliberté M., Sanfaçon G, Blais R. 1995. Acute pulmonary toxicity linked to use of a leather protector. Ann Emerg Med. 1995 Jun;25(6):841-4.

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

<table>
<tr><th>2002-2003</th><th colspan="3">Switzerland</th></tr>
<tr><td>Product name</td><td colspan="3">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.</td></tr>
<tr><td>Product description</td><td colspan="3">Three commercial spray cans intended for domestic or light occupational waterproofing.</td></tr>
<tr><td rowspan="2">Product ingredients</td><td>Active substances</td><td>Solvents</td><td>Other substances</td></tr>
<tr><td>Fluorinated acrylate polymer</td><td>Isoparaffinic hydrocarbons</td><td>No information</td></tr>
<tr><td>Application (intended)</td><td colspan="3">Aerosol spray cans
Patina-Fala: Paintbrush</td></tr>
<tr><td>Application (actual)</td><td colspan="3">Aerosol spray cans
Patina-Fala: Trigger spray</td></tr>
<tr><td>Treated area/object</td><td colspan="3">Different water proofing sprays. No details.
Patian-Fala: Tiled surface</td></tr>
<tr><td>Exposure concentration</td><td colspan="3">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 $0.2 \cdot 10^{1}$ 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.</td></tr>
<tr><td>Exposure period</td><td colspan="3">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.</td></tr>
<tr><td>Exposure conditions</td><td colspan="3">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.</td></tr>
</table>

2002-2003	**Switzerland**
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 recorded 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 connclude 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. *Journal of Occupational and Environmental Hygiene* 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. *Journal of Occupational and Environmental Hygiene*, 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.		

2005 (reporting year)	**Scotland**
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.
Number of affected	Four workers in the horse rug cleaning company were referred to a chest clinic with cough and dyspnoea over a 15 month period. 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	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 apyrexial. 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 withtreatment. 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%;

2005 (reporting year)	**Scotland**
	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	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 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.		

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.**
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. Duration 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, 2005-2006. 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	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. Detailed characteristics of exposed patients available.		

2005	**US: 30 incidents of pulmonary toxicity from 6 regional poison control centers from June 1, 2005 to December 1, 2005**
	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.
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.

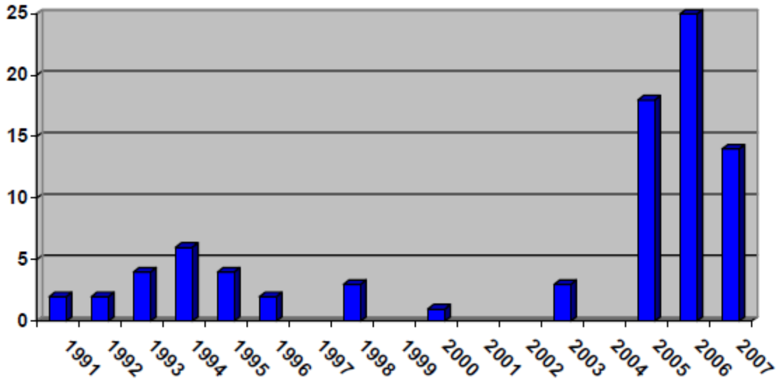
2006, Germany: Exposure to sealing sprays for glass and ceramics and for hygienic facilities "The Magic Nano case"

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	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. • Magic Nano Bath & WC: - 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. • Magic Nano Glass & Ceramic: 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. - Person 4: Severe shortness of breath. - Person 5: Violent cough and shortness of breath. Cought 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 cought. 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.		

2006	**Germany**
	Of the total of 154 persons affected there were 13 severe cases of pulmonary edema according to Pauluhn et al. 2008.
Treatment	Some patients treated with glucocorticoid spray
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. *Tagungsbericht VIII. Potsdamer BK-Tage.* 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. Inhal Toxicol. 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.		

<table>
<tr><td>2005</td><td>DK: 84 incidents of respiratory effects following exposure to proofing sprays from 1991 to 2007</td></tr>
<tr><td>Number of exposed</td><td>In addition to the 84 exposed, information on exposure of bystanders included: 2 pets, 4 children below 10 years, and 1 adult (accidental exposure).</td></tr>
<tr><td>Number of affected</td><td>Respiratory effects present in most patients (92%).</td></tr>
<tr><td>Symptoms and effects</td><td>Clinical data on 84 incidents accidentally exposed to proofing sprays:
<table>
<tr><th>Parameter</th><th>Number of incidents</th><th>Percent (%)</th></tr>
<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>
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.</td></tr>
<tr><td>Treatment</td><td>No information available via this source.</td></tr>
<tr><td>Other information</td><td>Distribution of incidents in the period from 1991 to 2007:

</td></tr>
<tr><td>Source</td><td>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.</td></tr>
</table>

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	Hydrogenated naphtha C_9-C_{13}. (50–100%) (MSDS and MS)	No information

2010	**Maniitsoq, Greenland**		
	(MS and WD-XRF)		
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 m² of the 300 m² tile floor was sprayed with 30 L (22.8 kg) of the tile coating product, Stain Repellant Super®		
Exposure concentration	The ground area of the building was 900 m² with a ceiling hight of 4 m. Total volume 7200 m³.		
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.		

2010	**Maniitsoq, Greenland**
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., Lynggard 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. Clinical Toxicology (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 m², 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	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. 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. 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. Moreover, the resuts showed bronchoalveolar lavage with cellular differentiation in the acute phase of a toxic alveolitis due to a water repellent spray.		
Treatment	The patient was treated supportively with supplemental oxygen and anti-emetics. Corticosteroids and bronchodilators initiated as an outpatient were discontinued. 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.		
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		

2011	**Netherlands**
	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	repiratory 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:

$$Total\_NFP1 = \frac{(Inlet\ \ flow)x(density)}{Airflow}$$

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/m^2 NFP 1 is used in the standard room with a floor of 7 m^2 and a volume of 17.4 m^3 the total amount of NFP 1 sprayed pr. m^3 equates to 16.1 g/m^3.

As can be seen form 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/m^3. This result is used in section B. 8.3.2.

2.2 Detailed information on exposure estimation

A lot of different parameters related to spray characteristics, room size, time of exposure to the spray etc. are important for the exposure. For calculation of the reasonable worst case (RWC), two exposure models, with substantial different approaches, are used: The "well-mixed room" ConsExpo 4.1 model and the more advanced "turbulent diffusion" SprayExpo model. SprayExpo contains a droplet impaction module for calculating the overspray during spraying onto a surface and it includes options for different release patterns with detailed information about the target of the spraying process and the sprayer's position (wall line, wall area, ceiling, floor, or room), Koch et al., 2012. The program assumes that the created overspray spreads evenly throughout the room in all directions by means of turbulent diffusion, Eickmann et al., 2007.

ConsExpo 4.1 offers only two release patterns (‘spraying towards exposed person’ or not). In ConsExpo 4.1 it is assumed that the particle size distribution specified in the input remains constant (i.e. particles will not shrink due to evaporation) and the model does not compute the share of droplets that are not deposited on the wall. It is possible, though, to define an ‘airborne fraction’ in ConsExpo, to allow for the share that is deposited on the wall to be neglected for the airborne concentration. If this airborne fraction is assumed to be 100 %, the computed values correspond exactly to the values that would be obtained for room spraying under otherwise identical conditions.
Furthermore when not spraying towards exposed person in ConsExpo 4.1 (when e.g. spraying on to a wall) an instantaneous distribution of the spray in the room is assumed, so that the concentration will be the same everywhere in the room. To determine the decrease in concentration, the air exchange rate and particle sedimentation to the ground are taken into account. Deposition on the walls through diffusion is neglected. This strong simplification regarding the dispersion of the spray cloud by instantaneous diffusion dramatically differs from the actual physical dispersion behavior, in particular in high or very large rooms, Koch et al., 2012.

The RWC exposure of consumers is estimated using SprayExpo and ConsExpo 4.1 in four scenarios with a NFP 1 like product:

1) Large area with high amount of product used pr. area: Impregnation of 3.4 m² floor/wall tiles in a bathroom of 10 m³ with aerosol, pump and trigger spray. Use of 40 g/m^2 is assumed.

2) Large area with low amount of product used pr. area: Impregnation of 3.4 m² floor/wall tiles in a bathroom of 10 m³ with aerosol, pump and trigger spray. Use of 10 g/m^2 is assumed.

3) Small area with high amount of product used pr. area: Impregnation of 0.3 m² (0.6 m x 0.48 m) mirror in a bathroom of 10 m³ with aerosol, pump and trigger spray. Use of 40 g/m^2 is assumed.

4) Small area with small amount of product used pr. area: Impregnation of 0.3 m² (0.6 m x 0.48 m) mirror in a bathroom of 10 m³ with aerosol, pump and trigger spray. Use of 10 g/m2 is assumed.

2.2.1 Input parameters for ConsExpo 4.1 and SprayExpo

General exposure parameters
In ConsExpo 4.1 the inhalation model "exposure to spray" is selected, with "spraying" chosen as release mode. The different general input parameters entered in SprayExpo and ConsExpo 4.1 is shown in Table 2 - 1.

TABLE 2 - 1 GENERAL INPUT PARAMETERS USED FOR EXPOSURE CALCULATION

Parameter	**Explanation**	**RWC Input value in scenarios**	**Reference**
Spray duration (Duration of application)	The amount of time between start and finish of the spraying. The spray duration depends on recommended amount of product to be used per area.	1) 4 min 2) 2 min 3) 20 sec 4) 10 sec	RWC Assumption
Exposure duration	The total amount of time spent in the room where the spraying takes place	1) 10 min 2) 5 min 3) 380 sec 4) 40 sec	RWC Assumption
Room volume	The volume of the room where the spraying takes place	1) 10 m³ 2) 10 m³ 3) 10 m³ 4) 10 m³	ECHA, 2012b
Room height	The height of the room where the spraying takes place. Minimum height in SprayExpo is 3 m. Therefore this is also chosen for ConsExpo	1) 3 m 2) 3 m 3) 3 m 4) 3 m	Koch et al., 2012
Area of treated object	Even though NFP1 is floor treatment product wall treatment chosen in scenario 1) and 2). This is in order to be able to compare output from SprayExpo and ConsExpo. In SprayExpo it is also possible to choose floor, ceiling or wall lining. When choosing floor treatment it is not possible to set exposure duration different from spray duration The treated area is set through mass generation rate and spray duration	1) Wall tiles 3.4 m³ 2) Wall tiles 3.4 m³ 3) Mirror 0.3 m³ 4) Mirror 0.3 m³	RWC Assumption
Ventilation rate	The number of total air changes in the room per time	1) 0.2 h^{-1} 2) 0.2 h^{-1} 3) 0.2 h^{-1} 4) 0.2 h^{-1}	ECHA, 2012b

Product specific input parameters

In ConsExpo 4.1 the inhalation model "exposure to spray" is chosen. This model is used in case a non-volatile compound is released as an aerosol from an aerosol dispenser or a pump- or trigger spray. NFP1 is a floor treatment product for non-absorbing floors. However, in SprayExpo wall area is selected for the NFP 1 like product under application pattern to be able to compare the output (mean event concentrations) to the output from ConsExpo 4.1. Furthermore it is not possible to set the RWC parameter “Time spend in room after application” when floor treatment is chosen in SprayExpo.

Chemical analysis using electrospray ionization mass spectrometry (ESI-MS) showed that NFP 1 contained hydrolysates and condensates of polyfluorooctyl triisopropoxysilane. Total concentration of non-volatile was found to 1.1±0.1 %, Nørgaard et al. (2009).

The RWC 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	RWC Input values	Reference
Mass generation rate/rate of release	The amount of compound that will be released from the spray container during the spraying per unit of time See further explanation on choice on input values below this table.	1) Aerosol and trigger spray: 0.55 g/s. Pump spray 0.2 g/s 2) Aerosol and trigger spray: 0.3 g/s. Pump spray 0.1 g/s 3) Aerosol and trigger spray: 0.55 g/s. Pump spray 0.2 g/s 4) Aerosol and trigger spray: 0.3 g/s. Pump spray 0.1 g/s	Delmaar et al., 2009 Feilberg et al. 2008 Nørgaard 2015 (pers. comm.)
Airborne fraction (only used in ConsExpo)	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. See further explanation on choice on input values below this table.	Aerosol dispenser: 0.4 Trigger spray: 0.014 Pump spray: 0.014	Delmaar et al., 2009
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/cm³	Density of perfluorooctyl triisopropoxysilane is used
Vapour pressure solvent (only used in SprayExpo)	The solvent used in NFP 1 is 2-propanol	In all scenarios: 44 hPa	Nørgaard et al. 2010
Diameter of nozzle (only used in SprayExpo)	The chosen nozzle diameter is for an aerosol spray	In all scenarios: 0.5 mm	Eickmann et al., 2007
Spray angle (only used in SprayExpo)	The chosen spray angle is for an aerosol spray	In all scenarios: 30 °	Eickmann et al., 2007
Initial droplet/particle distribution	The normalized mass distribution of the particles (droplets) immediately after they are ejected. The parametric distribution function: lognormal are chosen. In SprayExpo the input parameters are therefore mass median diameter (MMD) and the geometric standard deviation (GSD) In ConsExpo 4.1 the input parameters are MMD and the arithmetic coefficient of variation (CV) See further explanation on choice on input values below this table.	Aerosol dispenser: MMD: 25 µm GSD: 1.8 CV: ~0.6 Trigger- and pump spray: MMD: 65 µm GSD: 2.2 CV: ~0.8	Koch et al., 2012 Delmaar et al., 2009 Kawakami et al., 2015

Parameter	Explanation	RWC Input values	Reference
Turbulent diffusion Coefficient (only used in SprayExpo)	The diffusion constant K primarily depends on the temperature gradient in the room (possible heat sources) and increases with increasing room size. Furthermore, movements of workers or machines will increase the air exchange. The selected value of K = 0.1 m^2/s should be valid for room heights from 3 m to 10 m, as long as there exist no other extraordinary influences such as heat sources etc.	In all scenarios: 0.1 m^2/s	Koch et al., 2012
Distance nozzle to wall (only used in SprayExpo)		In all scenarios: 0.3 m	Koch et al., 2012
Distance sprayer to wall		In all scenarios: 1.0 m	Koch et al., 2012
The inhalation cut-off diameter	The diameter below which the spray droplet can be inhaled and reach the lower areas of the lungs.	10 µm	Default value ConsExpo

Mass generation rate/rate of release

Both ConsExpo and SprayExpo uses mass generation rates instead of applied amount. Nørgaard et al. (personal communication) measured the mass generation rate of the trigger spray NFP 1 to 0.2 g/s. This is rather low compared to the mass generation rates available for trigger sprays in Delmaar et al., 2009. However, this is, as can be seen from Table 2-3, for other product categories than impregnation products.

TABLE 2-3 MASS GENERATION RATES AVAILABLE FROM THE LITERATURE

Product category	Sub category	Spray type	Mass generation rate [g/s]	Reference
Pesticides	Air space spray	Aerosol spray	0.5 – 2.3	Delmaar et al., 2009.
	On surfaces	Aerosol spray	1.5 – 2.6	
	Ready to use on surfaces	Trigger spray	1.2 – 1.6	
	Plant spray	Trigger spray	1.4 – 2.2	
Cosmetics	Deodorant	Aerosol spray	0.6 – 0.9	
	Hairspray	Aerosol spray	0.6 – 0.8	
	Toilet water[1]	Pump spray	0.09 – 0.1	
Cleaning products	All purpose cleaner	Trigger spray	1 – 1.2	
	Bathroom and anti-grease cleaner	Trigger spray	1.3 – 1.7	
Paints	Spray paint	Aerosol spray	0.5 – 0.9	
Furniture polishes	Furniture polish	Aerosol spray	0.8 – 1.8	
Cockpit sprays	Cockpit spray	Aerosol spray	0.8 – 1.0	
Lubricants	Silicone spray	Aerosol spray	0.9 – 1.2	
	Penetrating spray	Aerosol spray	1.1 – 1.5	
Air fresheners	Air freshener	Aerosol spray	0.5 – 2.0	
Water-repellent making products	Anti-rain spray	Aerosol spray	0.6	
Textile impregnation sprays		Aerosol spray	0.1 – 1.46	Feilberg et al. 2008
		Pump/Trigger spray[2]	0.26 – 1.7	

Waterproofing	For tile surfaces made of natural porous stone	Trigger spray[3]	0.55 - 1.1[4]	Vernez et al., 2004

[1] Eau de toilette/eau de perfume

[2] From the report it is not possible to distinguish between pump- and trigger spray

[3] Intendet to be applied by paintbrush. Applied by trigger spray to save time resulting in 3 occupational incidents in Switzerland (product contained a fluoroacrylate polymer in combination with an organic solvent)

[4] Spray output pr. stroke 1.1g ± 0.2g with distilled water. 1-2 strokes pr. second is assumed

A mass generation rate of 0.55 g product/sec is used for the aerosol dispenser and trigger spray when use of 40 g product per m^2 is assumed in the RWC scenarios. When use of 10 g product per m^2 is assumed a mass generation rate of 0.3 g product/sec is used for the aerosol dispenser and trigger spray. For the pump spray 0.2 g product/sec is used when use of 40 g product per m^2 is assumed and 0.1 g product/sec is used when use of 10 g product per m^2 is assumed. This change in mass generation rate when going from 40 to 10 g product per m^2 is introduced to have realistic duration of application (spray duration) as the mass generation rate are used to calculate the duration of application, based on the surface area of the object being treated. To make sure that the calculated duration of application is realistic it has to be compared to the actual physical process of spraying 1 m^2 that takes approximately 25 sec.

The mass generation rates used for aerosol dispenser and trigger spray are in the lower end of the table values of mass generation rates available in Delmaar et al., 2009 and Feilberg et al., 2008 as seen in Table 2-3. The mass generation rates used for trigger spray, though, corresponds reasonably well with the mass generation rates of 0.2 g/s measured for the trigger spray NFP 1. For pump sprays only one value is available - 0.1 g/s for perfume products, Delmaar et al., 2009. Feilberg et al., 2008 gives mass generation rates for 'hand pump sprays', but it is not known if this covers pump sprays, trigger sprays or both. These uncertainties in choosing the mass generation rates for the calculations have an impact on the validity of the resulting estimates. The choices are, though, seen as relative conservative.

Airborne fraction

SprayExpo contains a droplet impaction module for calculating the overspray during spraying onto a surface.

ConsExpo 4.1 does not compute the share of droplets that are not deposited on the wall. It is possible, though, to define an 'airborne fraction' in ConsExpo, to allow for the share that is deposited on the wall to be neglected for the airborne concentration. If this airborne fraction is assumed to be 100 %, the computed values correspond exactly to the values that would be obtained for room spraying under otherwise identical conditions. It is, furthermore, in ConsExpo 4.1 assumed that the particle size distribution specified in the input remains constant (i.e. particles will not shrink due to evaporation) and when spraying an object (like e.g. a wall) an instantaneous distribution of the spray in the room is assumed, so that the concentration will be the same everywhere in the room. To determine the decrease in concentration, the air exchange rate and particle sedimentation to the ground are taken into account. Deposition on the walls through diffusion is neglected. These strong simplifications dramatically differ from the actual physical dispersion behavior, in particular in high or very large rooms, Koch et al., 2012.

To compensate for these simplifications in ConsExpo 4.1 the airborne fraction was redefined. According to Delmaar et al., 2009 the "new" airborne fraction is defined as Airborne $fraction_{new} = f_{airborne\_old} \times f_{scale}$. The "old" airborne fraction ($f_{airborne\_old}$) is set to 1 for MMD < 50 µm and to 0.2 for MMD ≥ 50 µm for surface sprays. The scaling factor f_{scale} represents the mass fraction of the droplets/particles with a MMD < 22.5 µm. In this way only the fraction of droplets/particles with an initial MMD less than 22.5 µm are taken in to account. Delmaar et al., 2009 offers some default values for pesticides, cosmetics and cleaning agents (from 0.006 – 0.9). Nørgaard, 2015 (personal communication) assumed that the fraction of active compound (hydrolysates and condensates of polyfluorooctyl triisopropoxysilane) that will be airborne is 10 % from the NFP 1 trigger spray and 25 % for an aerosol dispenser.

Initial droplet/particle distribution

Due to the evaporation of volatile components in the droplet, the particle diameter can change significantly, and thus influence both the steady state settling velocity as well as the overspray fraction of the spray. At the same time, the evaporation process generally lowers the temperature in a droplet. Describing these complex processes in a calculation model would require a great deal of computing power. The result of such calculations still remains unsure to a certain extent because the droplet size distribution of an actual spray is rarely known exactly in practice, Eickmann et al., 2007. Nevertheless, initial droplet/particle distribution is still required as an input parameter for both ConsExpo 4.1 and SprayExpo. SprayExpo, though, contains some default values.

Nørgaard et al., 2009 tested the number of particles generated and particle size distribution by the trigger spray containing NFP 1 by spraying on a target plate at a distance of 35 cm and measuring the particles 20 cm behind the trigger spray in a spray chamber. The number of particles generated was approximately 4×10^2 particles/cm^3 per g applied product. The particle number size distribution for two other trigger sprays (NFP 2 and NFP 3) was comparable to NFP 1. For NFP 4 that was applied by an aerosol spray the number of particles generated was approximately 3×10^5 particles/cm^3 per g applied product under similar test conditions.

Nørgaard (2010d) extrapolated these NPF1 data to the spraying 7 m^2 in a 17.4 m^3 room using 40 g/m^2 NFP in trigger spray. The concentration of TDFAs and 2-propanol (hydrolysates and condensates) was found to reach around 1.4 mg/m^3 (≈ 6×10^3 particles/cm^3) immediately after treatment. Nørgaard states that this concentration may be overestimated, since the high air velocity in the test chamber enhances the external diffusion from the coated surface. On the other hand, Nørgaard et al., assumes instantaneous distribution of the spray in the room (like ConsExpo 4.1), which could lead to an under prediction of the concentration in the near field of the person spraying.

The droplet/particle size distribution for NFP 1 from Nørgaard et al, 2009 cannot be used as input in ConsExpo 4.1 and SprayExpo calculations as this droplet/particle size distribution is measured after spraying on a plate which means that the measured distribution is the overspray rather than the initial droplet/particle size distribution.

The high-pressure nebulization of the NFP 1 in the study by Nørgaard et al. (2010a) generated significantly higher particle concentrations (1.4×10^5 – 4.6×10^6 particles/cm^3) than observed in spray chamber experiments with trigger 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/m^3 – 42.4 mg/m^3 (dry weight). This is the concentrations that mice are exposed to in the animal study, Nørgaard et al., (2010a).

A report by the Danish EPA, Feilberg et al. (2008), gives information on 29 textile impregnation sprays – 10 pump- or trigger sprays and 19 aerosol sprays. 3 pump/trigger sprays are water-based, for 3 pump/trigger[27] sprays there are no information on solvents and the rest of the products (23) contains organic solvents. For 16 of these textiles impregnation sprays the number of particles generated and particle size distribution is tested after spraying on a piece of fabric in a spray chamber (set up not exactly the same as in Nørgaard et al. (2009) but comparable). The results are shown in Table 2-4 below were product no. 4, 11, 15, 16 and 24 pump/trigger sprays and the rest are aerosol sprays.

TABLE 2-4 MEASURED DROPLET/PARTICLE SIZE DISTRIBUTION 1 MINUTE AFTER SPRAYING ON FABRIC (FROM PAGE 56 IN FEILBERG ET AL., 2008)

Product no.	**Spray type**	**Liberated amount of proofing spray pr. 10 s [g]**	**Aerosols 20-650 nm [10^3 per cm^3]**	**Mean aerosol size [nm]**
1	Aerosol spray	5.0	3000	104
3	Aerosol spray	4.3	4500	171
4	Pump/trigger spray	5.0	4	
6	Aerosol spray	6.7	3200	93
8	Aerosol spray	14.6	230	38
9	Aerosol spray	7.3	3100	98
11	Pump/trigger spray	17.0	2	
14	Aerosol spray	7.0	5000	105
15	Pump/trigger spray	4.3	17	79
16	Pump/trigger spray	16.7	1	
18	Aerosol spray	1.0	2500	114
20	Aerosol spray	9.3	100	83
21	Aerosol spray	5.9	26	136
24	Pump/trigger spray	2.6	1	
25	Aerosol spray	12.0	170	99
26	Aerosol spray	12.7	3400	74

Feilberg et al., 2008 finds no clear connection between the chemical composition and number or aerosol size. Instead they find that aerosol exposure is first and foremost determined by whether aerosol or pump/trigger spray products are in question.

As can be seen from Table 2-4 the particle number generated is comparable to those seen in Nørgaard et al., 2009 (when dividing the number of aerosols with the amount of product used). It can also be seen that the NFP 1 particle concentrations generated by the high-pressure nebulizer in Nørgaard et al., 2010a are comparable to those seen for aerosol sprays in Table 2-4 – that is for aerosol sprays after being sprayed against a surface (fabric). Therefore one should be careful by using the particle size distribution measured by the high-pressure nebulizer in Nørgaard et al. (2010a) as input parameter for ConsExpo 4.1 and SprayExpo.

For comparison, the particle number concentrations rarely exceed 1×10^6 particles/cm^3 in high-traffic streets and reported indoor concentrations of sub-µm particles are usually below 10^5 particles/cm^3 (Nørgaard 2010d).

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[27] From the report it is not possible to distinguish between pump- and trigger spray

None of the above mentioned droplet/particle size distributions can be used as input parameters in ConsExpo and SprayExpo. However, Delmaar et al. (2009) contains some default initial droplet/particle size distributions. One of these is for an aerosol dispenser - Anti-rain spray (MMD 28.5 µm and CV 1.7). The median of this spray is also relatively close to the median of the available default aerosol spray in SprayExpo (MMD 25 µm and GSD 1.8). The product category of this SprayExpo aerosol spray is not known but the distribution seems to be closely related to primary droplet distribution referred to in the Magic Nano report, (figure 2 in Koch et al., 2009). It is not known if this figure actually represents the aerosol spray products "Magic Nano Glass & Ceramic" and "Magic Nano Bath & WC" and "Magic Nano Bath & WC" pump spray.

For the RWC calculations default aerosol spray in SprayExpo (MMD 25 µm and GSD 1.8) is chosen. This is more conservative than choosing data for the Anti-rain spray in Delmaar et al. (2009) as the ratio of droplet/particles with a diameter <10 µm from the default aerosol spray in SprayExpo is around 5.6% whereas the ratio for the Anti-rain spray is around 17.5 %

To get more information on the initial droplet/particle size distributions of pump and trigger sprays the author of Kawakami et al., has provided the actual spray data. In Table 2-5 the ratio of particles with a diameter below 9 and 11 µm is shown for the 13 trigger sprays and 3 pump sprays.

Table 2-5 Ratio of fine particles (%) of 13 trigger sprays and 3 pump sprays (from Table 2 in Kawakami et al., 2015)

Product Name	Usage	Country	Type of spray	Ratio of fine particles [%]	
				< 9 µm	< 11 µm
A1	Fabric	UK	Trigger	0.1	0.4
A2	Fabric	UK	Trigger	0.2	0.5
A3	Leather and fabric	Japan	Trigger	0.8	1.4
A4	Leather and fabric	UK	Pump	0	0.1
A5	Ceramic products, bathroom	Unknown	Trigger	0	0
A6	Kitchen and bathroom	Japan	Trigger	0	0.2
A7	Kitchen and bathroom	Japan	Trigger	0.3	0.6
A8	Kitchen and bathroom	Unknown	Pump	0.4	0.8
B1	Iron	South Korea	Trigger	0	0
B2	Iron	South Korea	Trigger	0	0
B3	Clothing care	Unknown	Trigger	0.6	1.2
B4	Clothing care	Unknown	Trigger	1.7	2.7
B5	Preventing pollen adhesion to masks and clothing	South Korea	Trigger	0	0
B6	Preventing pollen adhesion to masks and clothing	Japan	Trigger	2.1	3
B7	Preventing pollen adhesion to masks and clothing	Japan	Trigger	1.6	2
B8	Preventing pollen adhesion to masks and clothing	Japan	Pump	0.2	0.4

Table 2-5 shows that the aerosol particles sprayed from five trigger spray products (A5, A6, B1, B2 and B5) contained few or no particles with a diameter smaller than 11 µm. In five trigger spray products (A3, B3, B4, B6 and B7) the ratio of particles with diameter <9 µm exceeded 0.6% and the ratio of particles with diameter <11 µm exceeded 1%. For three trigger spray products (A1, A2 and A7) the ratio of particles with diameter <11 µm were below or equal 0.6%. The product B3 with a droplet/particle size distribution estimated to MMD of 65 µm and a GSD of approximately 2.2 is chosen for the RWC calculations as this represents the group of products with the ratio of particles with diameter <9 µm exceeding 0.6%.

From Table 2-5 and the spray data provided Kawakami it is difficult to distinguish the initial droplet/particle size distributions of the three pump sprays from the trigger sprays. Therefore the B3 data will also be used for RWC calculations for pump sprays. It should though be noted that the statistical justification for this choice is limited with only three pump spray products.

2.2.2 Exposure estimates from ConsExpo 4.1 and SprayExpo

The resulting exposure estimates from running ConsExpo 4.1 and SprayExpo with the input parameters given in Table 2-1 and 2-2 can be seen in Table 2-6 - Table 2-9 (results summarized in Table 7 in B.8.3.2).

TABLE 2-6 CONSEXPO 4.1 AND SPRAYEXPO INPUT PARAMETERS AND EXPOSURE ESTIMATES FOR A NFP 1 LIKE PRODUCT IN SCENARIO 1 (SPRAY OF A LARGE AREA WITH HIGH AMOUNT OF PRODUCT USED PR. AREA)

Parameters	Aerosol	Pump	Trigger
Room size- Bathroom (3m x 2m x 1.66m) with shower (0.8m x 0.8m) [m^3]	10	10	10
Area treated per container with 40g/m^2 product used [m^2]	3.4	3.4	3.4
Spray duration/Duration of application [min]	4	4	4
Amount of product used [g]	144	48	144
Time in room after application [min]	6	6	6
Ventilation rate [1/h]	0.2	0.2	0.2
Release rate/Mass generation rate [g/s][1]	0.55	0.2	0.55
Airborne fraction$_{new}$[2]	0.4	0.014	0.014
Vapour pressure solvent [hPa] (Isopropanol)	44	44	44
Weight of non–volatile (ratio)	0.011	0.011	0.011
Density non-volatile [g/ml]	1.3	1.3	1.3
Spray angle [degrees]	30	30	30
Distance to wall [m]	0.3	0.3	0.3
Distance consumer to wall [m]	1	1	1
Inhalation cut off	<10µm	<10µm	<10µm
Nozzle diameter [mm]	0.5	0.5	0.5
RWC Initial droplet/particle size distribution	MMD 25 µm GSD 1.8 (CV ~ 0.6)	MMD 65 µm GSD 2.2 (CV ~ 0.8)	MMD 65 µm GSD 2.2 (CV ~ 0.8)
Mean event concentration			
RWC ConsExpo Ver. 4.1 [mg/m^3]	1.9	0.0016	0.0043
RWC SprayExpo [mg/m^3]	97.1	14.0	39.2

[1] SprayExpo uses release rate in ml/s. Assumption used: Density product ≈ density volatile (isopropanol=0.79 g/ml).
[2] The fraction below 22.5 µm (approx. 40 %) in the particle/droplet distribution for the aerosol spray is used as the scaling factor f_{scale} for calculation of the Airborne fraction$_{new}$ (0.4x1 = 0.4) in the ConsExpo calculations. For the pump- and trigger spray distribution the fraction below 22.5 µm is found to 168pprox.. 7 % which gives Airborne fraction$_{new}$ = 0.014 (0.07x0.2).

TABLE 2-7 CONSEXPO 4.1 AND SPRAYEXPO INPUT PARAMETERS AND EXPOSURE ESTIMATES FOR A NFP 1 LIKE PRODUCT IN SCENARIO 2 (SPRAY OF A LARGE AREA WITH LOW AMOUNT OF PRODUCT USED PR. AREA)

Parameters	Aerosol	Pump	Trigger
Room size- Bathroom (3m x 2m x 1.66m) with shower (0.8m x 0.8m) [m^3]	10	10	10
Area treated per container with 10g/m^2 product used [m^2]	3.4	3.4	3.4
Spray duration/Duration of application [min]	2	2	2
Amount of product used [g]	36	12	36
Time in room after application [min]	3	3	3
Ventilation rate [1/h]	0.2	0.2	0.2

Release rate/Mass generation rate [g/s][1]	0.3	0.1	0.3
Airborne fraction$_{new}$[2]	0.4	0.014	0.014
Vapour pressure solvent [hPa] (Isopropanol)	44	44	44
Weight of non–volatile (ratio)	0.011	0.011	0.011
Density non-volatile [g/ml]	1.3	1.3	1.3
Spray angle [degrees]	30	30	30
Distance to wall [m]	0.3	0.3	0.3
Distance consumer to wall [m]	1	1	1
Inhalation cut off	<10μm	<10μm	<10μm
Nozzle diameter [mm]	0.5	0.5	0.5
RWC Initial droplet/particle size distribution	MMD 25 μm GSD 1.8 (CV ~ 0.6)	MMD 65 μm GSD 2.2 (CV ~ 0.8)	MMD 65 μm GSD 2.2 (CV ~ 0.8)
Mean event concentration			
RWC ConsExpo Ver. 4.1 [mg/m^3]	0.56	0.00043	0.0013
RWC SprayExpo [mg/m^3]	27.3	3.8	11.1

[1] SprayExpo uses release rate in ml/s. Assumption used: Density product ≈ density volatile (isopropanol=0.79 g/ml).

[2] The fraction below 22.5 μm (approx. 40 %) in the particle/droplet distribution for the aerosol spray is used as the scaling factor f_{scale} for calculation of the Airborne fraction$_{new}$ (0.4x1 = 0.4) in the ConsExpo calculations. For the pump- and trigger spray distribution the fraction below 22.5 μm is found to approx. 7 % which gives Airborne fraction$_{new}$ = 0.014 (0.07x0.2).

TABLE 2-8 CONSEXPO 4.1 AND SPRAYEXPO INPUT PARAMETERS AND EXPOSURE ESTIMATES FOR A NFP 1 LIKE PRODUCT IN SCENARIO 3 (SPRAY OF A SMALL AREA WITH HIGH AMOUNT OF PRODUCT USED PR. AREA)

Parameters	Aerosol	Pump	Trigger
Room size- Bathroom (3m x 2m x 1.66m) with shower (0.8m x 0.8m) [m^3]	10	10	10
Area treated mirror (0.6 m x 0.48m) with 40 g/m^2 product [m^2]	0.3	0.3	0.3
Spray duration/Duration of application [sec]	20	20	20
Amount of product used [g]	11	4	11
Time in room after application [min]	6	6	6
Ventilation rate [1/h]	0.2	0.2	0.2
Release rate/Mass generation rate [g/s][1]	0.55	0.2	0.55
Airborne fraction$_{new}$[2]	0.4	0.014	0.014
Vapour pressure solvent [hPa] (Isopropanol)	44	44	44
Weight of non–volatile (ratio)	0.011	0.011	0.011
Density non-volatile [g/ml]	1.3	1.3	1.3
Spray angle [degrees]	30	30	30
Distance to wall [m]	0.3	0.3	0.3
Distance consumer to wall [m]	1	1	1
Inhalation cut off	<10μm	<10μm	<10μm
Nozzle diameter [mm]	0.5	0.5	0.5
RWC Initial droplet/particle size distribution	MMD 25 μm GSD 1.8 (CV ~ 0.6)	MMD 65 μm GSD 2.2 (CV ~ 0.8)	MMD 65 μm GSD 2.2 (CV ~ 0.8)
Mean event concentration			
RWC ConsExpo Ver. 4.1 [mg/m^3]	0.20	0.00017	0.00046
RWC SprayExpo [mg/m^3]	7.5	1.0	2.9

[1] SprayExpo uses release rate in ml/s. Assumption used: Density product ≈ density volatile (isopropanol=0.79 g/ml).

[2] The fraction below 22.5 μm (approx. 40 %) in the particle/droplet distribution for the aerosol spray is used as the scaling factor f_{scale} for calculation of the Airborne fraction$_{new}$ (0.4x1 = 0.4) in the ConsExpo calculations. For the pump- and trigger spray distribution the fraction below 22.5 μm is found to approx. 7 % which gives Airborne fraction$_{new}$ = 0.014 (0.07x0.2).

TABLE 2-9 CONSEXPO 4.1 AND SPRAYEXPO INPUT PARAMETERS AND EXPOSURE ESTIMATES FOR A NFP 1 LIKE PRODUCT IN SCENARIO 4 (SPRAY OF A SMALL AREA WITH SMALL AMOUNT OF PRODUCT USED PR. AREA)

Parameters	Aerosol	Pump	Trigger
Room size- Bathroom (3m x 2m x 1.66m) with shower (0.8m x 0.8m) [m^2]	10	10	10
Area treated mirror (0.6 m x 0.48m) with 10 g/m^2 product [m^2]	0.3	0.3	0.3
Spray duration/Duration of application [sec]	10	10	10
Amount of product used [g]	3	1	3
Time in room after application [min]	0.5	0.5	0.5
Ventilation rate [1/h]	0.2	0.2	0.2
Release rate/Mass generation rate [g/s][1]	0.3	0.1	0.3

Airborne fraction$_{new}$[2]	0.4	0.014	0.014
Vapour pressure solvent [hPa] (Isopropanol)	44	44	44
Weight of non–volatile (ratio)	0.011	0.011	0.011
Density non-volatile [g/ml]	1.3	1.3	1.3
Spray angle [degrees]	30	30	30
Distance to wall [m]	0.3	0.3	0.3
Distance consumer to wall [m]	1	1	1
Inhalation cut off	<10µm	<10µm	<10µm
Nozzle diameter [mm]	0.5	0.5	0.5
RWC Initial droplet/particle size distribution	MMD 25 µm GSD 1.8 (CV ~ 0.6)	MMD 65 µm GSD 2.2 (CV ~ 0.8)	MMD 65 µm GSD 2.2 (CV ~ 0.8)
Mean event concentration			
RWC ConsExpo Ver. 4.1 [mg/m^3]	0.056	0.000043	0.00013
RWC SprayExpo [mg/m^3]	2.5	0.35	1.0

[1] SprayExpo uses release rate in ml/s. Assumption used: Density product ≈ density volatile (isopropanol=0.79 g/ml).

[2] The fraction below 22.5 µm (approx. 40 %) in the particle/droplet distribution for the aerosol spray is used as the scaling factor f_{scale} for calculation of the Airborne fraction$_{new}$ (0.4x1 = 0.4) in the ConsExpo calculations. For the pump- and trigger spray distribution the fraction below 22.5 µm is found to approx. 7 % which gives Airborne fraction$_{new}$ = 0.014 (0.07x0.2).

2.2.3 Uncertainties in exposure estimates from ConsExpo 4.1 and SprayExpo

From Table 2-6 to Table 2-9 it is seen that the RWC mean event concentrations from SprayExpo are much higher than the once estimated using ConsExpo 4.1. No measured data exist that can be used for direct comparison of an NFP 1 like spray product in a 10 m^3 bathroom. However, results from Vernez et al. (2004) and Nørgaard et al. (2010d) indicates that for a trigger spray the mean event concentration of particles in the < 10 µm fraction should be expected to be above 1 mg/m^3. Vernez et al. (2004) predicted the mean overspray concentration in the < 10 µm fraction to be 40 mg/m^3 and 45 mg/m^3 for two different proofing/impregnation formulations using the same type of trigger spray in a 12 m^3 (cf. C.2.1). Nørgaard (2010d) extrapolated measured NPF 1 data to the treating of 7 m^2 in a 17.4 m^3 room using 40 g/m^2 NFP 1 in trigger spray. The concentration was found to reach around 1.4 mg/m^3 immediately after treatment (cf. Appendix 2 section 2.2.1). Taking in to account that Vernez et al. used a Two-zone model and Nørgaard et al. assumes instantaneous distribution of the spray in the room this indicates that SprayExpo is better at estimating the mean event concentration of the < 10 µm fraction than ConsExpo 4.1.

The two models, ConsExpo 4.1 ("well mixed room") and SprayExpo ("turbulent diffusion") were compared to each other and to experimental exposure values in Eickmann et al. (2007) and Koch et al. (2012). Eickmann et al. (2007) found that the values calculated by ConsExpo 4.1 are way below the experimental data in every case. The differences increase from the respirable through the thoracic to the inhalable fraction and also grow as the MMD increases. In the worst case (large fan nozzle, water) ConsExpo 4.1 calculates a low, disappearing concentration, although the measurement results are over 1 mg/m^3. In most cases, the calculation results from ConsExpo 4.1 and the measured data are separated by several orders of magnitude. Eickmann et al. (2007) further adds that: "*only 1 in 69 calculations is within a factor of 2 of the results, 10 % of the measurement results are in the correct order of magnitude, 6 % of the values are falsely stated as disappearing and the median of the quotient measurement/calculation result is 250 000. ConsExpo 4.1 thus calculates values which cannot be compared to the measurement results.*"

According to Eickmann et al. (2007) the large deviations in the calculations from the actual measurements point to the fact that the model simplifications in ConsExpo 4.1 (solvent evaporation not taken into account) do not allow for a comparison between measurements and model calculations for particle distributions with a diameter clearly greater than 50 µm.

It should be noted that Eickmann et al. (2007) does not use the 'new' Airborne fraction as defined by Delmaar et al. (2009) (cf. Appendix 2 section 2.1.1). Eickmann et al. (2007) uses 0.3 for an aerosol spray and 0.1 for most other sprays. For aerosol spray this is relatively close to the airborne fraction used in Table 2-6 to Table 2-9 but for pump- and trigger spray it is a factor of 10 higher.

Eickmann et al. (2007) found that 63 % of the values calculated by SprayExpo do not deviate from the measurement result by more than a factor of 2 (when results from the large fan nozzle are excluded). All the calculated values were in the correct order of magnitude.

It should be noted that SprayExpo subsequently has been updated. This update was taken into account when Koch et al. compared SprayExpo to ConsExpo 4.1 and experimental values in 2012. The SprayExpo model used in Koch et al., 2012 is identical to the one used for the calculations in Table 2-6 to Table 2-9.

From comparing experimental exposure values to calculated mean event concentrations calculated by SprayExpo, Koch et al. (2012) found that, on average, the exposure concentrations are slightly overestimated by the model. The geometric standard deviations of 2.3 (assuming lognormal distribution) mean that in about 70 % of cases the model is in agreement with the measurements within a factor of 4-5.

The difference in the calculated mean event concentrations between ConsExpo 4.1 and SprayExpo were also seen in Koch et al., 2012. However, the differences in the mean event concentrations in Table 2-6 to Table 2-9 is considerably higher than in Koch et al., 2012 were the maximum difference were 19 times for wall spraying with particles with a small MMD in a larger room. Personal communication with one of the authors of Koch et al. (2012) revealed that in order to compare the two models droplet/particle distribution were re-calculated[28] the after evaporation of the solvent for ConsExpo 4.1. When not doing so two significantly different distributions of the droplets/particles will be compared as SprayExpo takes evaporation into account whereas ConsExpo 4.1 do no. To test this approach a set of ConsExpo 4.1 calculations has been performed using the same set-up as in Table 2-6 to Table 2-9 but except for the droplet/particle size and the Airborne fraction$_{new}$.

Evaporation of the droplets continues until they have reached a minimum diameter (d_{min}). This minimum diameter depends on the non-volatile volume concentration (C) and the initial droplet diameter d_0 as: $d_{min} = C^{1/3} \cdot d_0$, SprayExpo 2.0 Program description[29]. Assuming a concentration of non-volatile of 1.1% like in Table 2-6 to Table 2-9 the initial droplet/particle size of 25 µm used for the aerosol spray calculations will shrink to 5.5 µm. The initial droplet/particle size of 65 µm used for the pump- and trigger spray calculations will shrink to 14.5 µm. Using the same

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[28] The author who performed the ConsExpo 4.1 calculations in Koch et al. (2012) has retired but (one of) the other authors suggested that a re-calculation of droplet/particle distribution has been performed. A set of ConsExpo 4.1 calculations has been performed in order to reproduce the results presented in table 3.3 in Koch et al. (2012). The results could only be reproduced if droplet/particle distribution were re-calculated after evaporation of the solvent.

[29] SprayExpo 2.0 Program description: http://www.baua.de/en/Topics-from-A-to-Z/Hazardous-Substances/pdf/F2137-1.pdf;jsessionid=318CD18E7A68D70D14E2646602895BB4.s1t1?__blob=publicationFile&v=4

coefficient of variation as in Table 2-6 to Table 2-9 the percentage of particles with a diameter < 22.5 µm will be 100% for the aerosol spray and approximately 70% for the new pump- and trigger spray. This is used for Airborne fraction$_{new}$.

The approach described above is the same a used in Koch et al. (2012) except for the use of for Airborne fraction$_{new}$. In Table 2-10 the mean event concentrations from Table 2-6 to Table 2-9 is compared to a new set of ConsExpo 4.1 calculations were evaporation of the solvents is taken into account.

TABLE 2-10 EXPOSURE ESTIMATES FROM SPRAYEXPO AND CONSEXPO 4.1 WITH AND WITHOUT EVAPORATION OF THE SOLVENTS TAKEN IN TO ACCOUNT. SET-UP IS IDENTICAL TO TABLE 2-6 TO 2-9 EXCEPT FOR CONSEXPO 4.1 WITH EVAPORATION WERE DROPLET/PARTICLE SIZE AND AIRBORNE FRACTION$_{NEW}$ HAS BEEN CHANGED

		Mean event concentration [mg/m³]		
Scenarios	**Spray type**	**ConsExpo 4.1**	**ConsExpo 4.1 with evaporation**	**SprayExpo**
1) Impregnation of 3.4 m² tiles in a 10 m³ bathroom (use approximately 40 g/m²)	Aerosol	**1.9**	89.6	**97.1**
	Trigger	**0.0043**	20.7	**39.2**
	Pump	**0.0016**	7.5	**14**
2) Impregnation of 3.4 m² tiles in a 10 m³ bathroom (use approximately 10 g/m²)	Aerosol	**0.56**	25.7	**27.3**
	Trigger	**0.0013**	6.1	**11.1**
	Pump	**0.00043**	2.0	**3.8**
3) Spraying of a 0.3 m² mirror in a 10 m³ bathroom (use approximately 40 g/m²)	Aerosol	**0.20**	9.3	**7.5**
	Trigger	**0.00046**	2.2	**2.9**
	Pump	**0.00017**	0.79	**1.0**
4) Spraying of a 0.3 m² mirror in a 10 m³ bathroom (use approximately 10 g/m²)	Aerosol	**0.056**	2.5	**2.5**
	Trigger	**0.00013**	0.6	**1.0**
	Pump	**0.000043**	0.2	**0.35**

From Table 2-10 it is seen that the mean event concentrations of ConExpo 4.1 changes significantly when evaporation of the solvents is taken into account and that the results is comparable to the mean event concentrations estimated by SprayExpo. As seen from Koch et al. (2012) larger differences than the once seen in Table 2-10 can be expected for other scenarios.

Overall Eickmann et al. (2007) and Koch et al. (2012) finds SprayExpo to be more suitable than ConsExpo 4.1 for producing mean event concentrations that are comparable to experimental values. Koch et al. (2012) finds that SprayExpo slightly overestimates (on average) and Eickmann et al. (2007) finds that the simplifications in ConsExpo 4.1 don’t allow for a comparison between measurements and model calculations for particle distributions with a diameter clearly greater than 50 µm. In order to compare ConsExpo 4.1 and SprayExpo Koch et al. (2012) took shrinking of particles due to evaporation of the solvents into account in the ConsExpo 4.1 calculations. Therefore mean event concentrations are more comparable in Koch et al. (2012) than in Eickmann et al. (2007). From Table 2-10 it is seen that for the four scenarios in a 10 m^3 room the mean event concentrations estimated by ConsExpo 4.1 with evaporation taken in to account is comparable to mean event concentrations estimated by SprayExpo. Adjustment of droplet/particle size due to solvent evaporation as a way of improving ConsExpo 4.1 is, however, not described in the ConsExpo 4.1 manual (Dalmaar et al., 2009). It is therefore questionable if the mean event concentrations calculated by ConsExpo 4.1 – with or without evaporation of the solvents - in Table 2-6 to Table 2-10 can be used for risk characterisation.

2.2.3.1 Uncertainties from different parameters

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.

Mass generation rate: This parameter influences both the total amount of product applied and the exposure time entered in the model. From Table 2-6 to 2-9 it can be seen that the amount of product used and mean event concentration is approximately three time higher for trigger spray than for pump spray. This is due to the fact that the mass generation rate chosen for the calculations are approximately three times higher for trigger spray than for pump spray. From Table 2-3 it can be seen that mass generation rates usually are higher for trigger sprays than for pump sprays and in most cases more than three times. From Table 2-3 is can also be seen that the data available for pump sprays is limited and that there large variation in mass generations for aerosol dispensers and trigger sprays. The mass generation rates chosen for the SprayExpo and ConsExpo 4.1 can very well be an underestimation which means that the mean event concentrations will be underestimated – especially in scenarios large spray containers with high mass generation rates are used, as the size of the spray container sets an upper limit for the total amount of product used (assuming that consumers doesn’t use more spray containers during the same spray event).

Airborne fraction: The Airborne fraction$_{new}$ were calculated to 0.4 for the aerosol dispenser in Table 2-6 to Table 2-9 and to 0.014 for the pump- and trigger spray following the approach defined by Delmaar et al. (2009) (cf. Appendix 2 section 2.2.1). Mean event concentration is linearly proportional to the airborne fraction in ConsExpo 4.1. If airborne fraction is set to 0.2 for the aerosol dispenser in scenario 1) the RWC mean event concentration are found to 0.923mg/m^3 (compared to 1.85 mg/m^3 when the airborne fraction are 0.4). The airborne fraction is therefore subject to large uncertainties. However, as seen from Table 2-10 the fact that evaporation of the solvents are not taken into account in ConsExpo 4.1 are subject to much larger uncertainties.

Initial droplet/particle distribution: This is the normalized mass distribution of the droplets or particles immediately after they are ejected. When measuring initial droplets/particles distributions there is a distance between the nozzle of the spraying equipment and the measuring devise. This means that the droplets are airborne for a certain time before they are measured. In this time (some of) the solvent can evaporate and the particle droplet/diameter can change significantly. Therefore the measuring of droplet/particle sizes is subject to uncertainties. No exact data on average particle diameter are available for the aerosols generated from NPF 1 (cf. Appendix 2 section 2.2.1).

Data (measured under the same circumstances) from Kawakami et al., 2015 Table 2-5 shows that there is a huge variability in the initial droplet/particle size distribution for especially trigger spray but also for pump spray. Product B1 (MMD 164 and GSD 2.1) in Table 2-5 can be chosen to represent the group (Max MMD) of sprays with the highest MMD (i.e. the group of products expected to give the lowest mean event concentration). In a similar way the product B4 (MMD

57 and GSD 2.1) can be chosen to represent the group (Min MMD) of sprays with the smallest MMD (i.e. the group of products expected to give the highest mean event concentration).

The chosen Min MMD for aerosol dispensers spray paint (MMD 15.1) from Dalmaar et al. (2009). GSD is set to 1.8. The aerosol Max MMD is for a hairspray (MMD 44 and GSD 1.6).

A SprayExpo calculation with Min and Max initial droplet/particle size distribution is set up for the four aerosol, pump- and trigger spray scenarios (keeping all other parameters fixed) to see the variability in mean event concentrations.

TABLE 2-11 EXPOSURE ESTIMATES FROM SPRAYEXPO FOR A NFP 1 LIKE PRODUCT IN AEROSOL, PUMP- AND TRIGGER SPRAY SCENARIO 1-4 WITH MIN, MAX AND RWC INITIAL DROPLET/PARTICLE DISTRIBUTIONS AND ALL OTHER PARAMETERS KEPT FIXED

			Mean event concentration [mg/m³]		
Scenarios	**Model**	**Spray type**	**Min MMD**	**RWC**	**Max MMD**
1) Impregnation of 3.4 m² tiles in a 10 m³ bathroom (use approximately 40 g/m²)	SprayExpo	Aerosol	118.9	**97.1**	59.6
		Trigger	45.5	**39.2**	6.2
		Pump	16.3	**14**	2.2
2) Impregnation of 3.4 m² tiles in a 10 m³ bathroom (use approximately 10 g/m²)	SprayExpo	Aerosol	33.2	**27.3**	16.7
		Trigger	12.8	**11.1**	1.8
		Pump	4.4	**3.8**	0.7
3) Spraying of a 0.3 m² mirror in a 10 m³ bathroom (use approximately 40 g/m²)	SprayExpo	Aerosol	9.4	**7.5**	4.7
		Trigger	3.4	**3.1**	0.4
		Pump	1.2	**1.1**	0.16
4) Spraying of a 0.3 m² mirror in a 10 m³ bathroom (use approximately 10 g/m²)	SprayExpo	Aerosol	3.0	**2.5**	1.6
		Trigger	1.2	**1.1**	0.13
		Pump	0.46	**0.37**	0.065

The large variability in the initial droplet/particle size distribution, as seen in e.g. Table 2-5, results in large variations in mean event concentration as seen in Table 2-11. This shows the importance of initial droplet/particle size distribution and the difficulties in choosing the correct initial distribution. The choice of initial droplet/particle size distributions is subject to large uncertainties if no experimental data is available on the spray being studied.

When comparing mean event concentrations estimates in Table 2-11 to estimates from ConsExpo 4.1 in Table 2-10 it is seen that when evaporation of the solvents is taken into account the ConsExpo mean event concentrations falls in the interval between Min MMD and Max MMD in all scenarios. When evaporation is not taken into account the ConsExpo mean event concentrations falls below the Max MMD mean event concentrations (the lowest values in Table 2-11). This is also true when all the Max MMD mean event concentrations is divided by 5 to take into account that Koch et al. (2012) found that, on average, the mean event concentrations are slightly overestimated by SprayExpo. In about 70 % of cases SprayExpo is in agreement with the measurements within a factor of 4-5.

Room size: Koch et al. (2012) found that the size of the room has little impact on the mean event concentrations estimated by SprayExpo for spraying onto a surface when compared to measurements. According to Eickmann et al. (2007) "well mixed room" approach has proved itself in interior rooms, providing these rooms do not exceed a volume of some 150 to 200 m³. However, it leads to an underestimation of the exposure if a worker is constantly very close to the source of a substance. Where large rooms or halls are concerned, the diffusion approach of SprayExpo produces more realistic values because the spread of the substance cloud around the nozzle is taken into account, Eickmann et al. (2007).

Ventilation rate: The effect of changing the ventilation rate can be seen in Table 2-12 where the ventilation rate in scenario 1) is changed and all other parameters kept fixed. From Table 2-12 it can be seen that both SprayExpo are relatively insensitive to minor changes in the ventilation rate (0.2 to 1.2 1/h). However, when the ventilation rate is changed by a factor of 100 (from 0.2 to 20) is more than halved.

TABLE 2-12 AEROSOL DISPENSER RWC EXPOSURE ESTIMATES FROM SPRAYEXPO FOR A NFP 1 LIKE PRODUCT IN SCENARIO 1 WITH DIFFERENT VENTILATION RATES AND ALL OTHER PARAMETERS KEPT FIXED

			Mean event concentration [mg/m³]
	Spray type	**Ventilation rate [1/h]**	**SprayExpo**
Spraying of 3.4 m² tiles in a 10 m³ bathroom	Aerosol dispenser	0.1	97.7
		0.2	**97.1**
		1.2	91
		20	35

Exposure time and floor treatment: NFP 1 is a floor treatment product. By setting application pattern to 'floor' in SprayExpo the model offers the opportunity to choose floor as a target (this is not possible in the ConsExpo 4.1 model). When treating a floor one would most likely not spend time in the room after application. This means that the exposure time will be identical to the spay duration. The effect of setting the time in the room after the application to zero and using floor treatment in SprayExpo can be seen in Table 2-13 were Scenario 1) is used and all other parameter are kept fixed.

TABLE 2-13 AEROSOL DISPENSER RWC EXPOSURE ESTIMATES FROM SPRAYEXPO FOR A NFP 1 LIKE PRODUCT IN SCENARIO 1 WITH FLOOR TREATMENT AND DIFFERENT TIMES SPEND IN THE ROOM AFTER APPLICATION AND ALL OTHER PARAMETERS KEPT FIXED

			Time in room after application [min]	**Mean event concentration [mg/m³]**
	Spray type	**Treated object**		**SprayExpo**
Spraying of 3.4 m² tiles in a 10 m³ bathroom	Aerosol dispenser	Wall	0	64.8
	Aerosol dispenser	Floor[1]	0	64.7
	Aerosol dispenser	Wall	3	95.6
	Aerosol dispenser	Wall	6	**97.1**
	Trigger spray	Wall	0	26.6
	Trigger spray	Floor[1]	0	25.8
	Trigger spray	Wall	3	38.2
	Trigger spray	Wall	6	**39.2**

[1] SprayExpo defaults: Sprayer to wall (horizontal): 0.3 m; Nozzle to floor (vertical): 0.5 m

From Table 2-13 it can be seen that the effect of choosing floor treatment in SprayExpo instead of wall treatment is limited for the RWC initial droplet/particle distributions. It cannot be excluded that one would see a larger effect for larger droplets, as it must be expected that larger droplets will settle faster. From the Table it can also be seen that the first 3 min spend in the room after treatment has a large impact on the mean event concentration whereas the next 3 min (from 3 to 6 min) has only a minor effect.

Overall: Because of the many uncertainties described above the resulting exposure estimates should be interpreted very carefully and the results can only be seen as indicative of the expected exposure values. It should furthermore be kept in mind that Koch et al. (2012) found that, on average, the exposure concentrations are slightly overestimated by SprayExpo. In about 70 % of cases the model is in agreement with the measurements within a factor of 4-5. This needs to be taken in to consideration when calculating risk characterization ratios based on SprayExpo exposure estimations.

Appendix 3 Call For Evidence/Information

(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

Start of the consultation: 01.04.2015

Deadline for providing input: 28.05.2015

Subject of the call: The objective of this call is to gather information from as many relevant stakeholders as possible for the preparation of an Annex XV restriction dossier on polyfluorinated silanes in combination with one or more organic solvents in aerosol spray cans sold to the general public.

Objective of the call: The DK Competent Authority (DK-CA) is preparing a restriction proposal for the placing on the market of sprays for proofing purposes sold to the general public containing specific types of polyfluorinated silanes as well as one or more organic solvents. There have been several cases across Europe where the use of proofing sprays have caused serious health problems for people either using them or people staying in rooms where the sprays have been used. The exact identity of the chemical agents causing the effect are unknown but many of the involved products have been reported to contain per- and/or polyfluorinated compounds.
Recent research has shown that spray products containing a combination of certain polyfluorinated substances (polyfluorinated silanes) and organic solvents can cause respiratory disorders in experimental animals. These disorders are similar to the ones observed in human cases after inhalation of aerosols from proofing spray products. The toxicity is mainly caused by the hydrolysis products of polyfluorooctyl trilalkoxysilanes (mono hydrolysed, di hydrolysed and fully hydrolysed) which, in theory, may be formed from different parent compounds.
In addition, the restriction should only be targeted at spray products which contain one or more organic solvents.

Background note: Denmark has made a Registry of Intention (RoI) for a restriction concerning use of polyfluorooctyl trialkoxysilanes in spray cans for proofing purposes and intended for the general public.
Polyfluorooctyl trialkoxysilanes have been shown to cause serious acute lung injury in mice exposed to aerosolized mixtures containing hydrolysates of these substances at certain concentration levels. These findings are supported by numerous cases across the EU where consumers have experienced acute pulmonary distress following exposure to proofing sprays in aerosol cans containing fluorinated polymers.

Detailed information on the fluorinated constituents is typically not available as the fluorocarbon monomers alone do not require hazard classification under CLP and are included in low concentrations.
At present, the provisions on chemicals and consumer protection legislation are insufficient to protect consumers from experiencing acute respiratory distress when using proofing sprays containing hydrolysates of polyfluorooctyl trialkoxysilanes. Thus the Danish CA is investigating whether it would be appropriate to propose a restriction on the content of polyfluorooctyl trial-

koxysilanes in spray cans sold to the general public. It also seems that alternatives are available and a restriction is therefore considered to have limited negative economic and social impacts.

The objective of this call for evidence is to get more information on cases of health effects connected to exposure to polyfluorooctyl trialkoxysilanes in sprays, information on production, import and placing on the market of such mixtures or sprays cans as well as information on alternatives both in term of other substances and application methods, especially where the fluorinated substances are combined with organic solvents. Some specific questions have been given in the call for evidence.
Therefore, anyone who could be affected by this possible restriction or who holds relevant information is kindly invited to provide responses to the specific questionnaire before 28 May 2015.

Target Groups:

- All manufacturers of polyfluorooctyl trilalkoxysilanes
- All suppliers (producers, importers, distributors) of especially proofing sprays (both in "pressurized" spray cans (aerosol spray cans) and as pump sprays)
- Trade associations and other stakeholders
- Poisoning Centers
- Member States
- Other stakeholders, individuals

Specific questions: All information about polyfluorooctyl trilalkoxysilanes in spray cans and pump sprays used for proofing purposes is welcomed.
However, detailed information regarding the following subjects is especially welcomed:

- Any knowledge of pulmonary diseases (or any other health effects) related to the use of polyfluorooctyl trilalkoxysilanes in spray cans;
- Any data available to National Poison Centers concerning poisoning incidents caused by the use of polyfluorooctyl trilalkoxysilanes in spray cans;
- Occurrence of polyfluorooctyl trilalkoxysilanes in spray cans and pump sprays to be used by the general public (any available info on exposure patterns/quantities of used substances/spray cans and pump sprays manufactured or imported to the EU)
- "What is the concentration of polyfluorooctyl trilalkoxysilanes used in different aerosol spray?"
- Types of solvents used in combination with polyfluorooctyl trilalkoxysilanes in spray cans and pump sprays; what are the advantages and disadvantages of use of organic solvents instead of water-based impregnating sprays?
- Other application methods where polyfluorooctyl trilalkoxysilanes are used for treatments of articles with effects similar to those achieved by using spray cans and pump sprays (by the general public)
- Use of alternatives to polyfluorinated trilalkoxysilanes in spray cans and pump sprays
- Costs of substituting polyfluorinated trilalkoxysilanes in spray cans and pump sprays