# Committee for Risk Assessment (RAC)

# Committee for Socio-economic Analysis (SEAC)

Opinion

on an Annex XV dossier proposing restrictions

# 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

**ECHA/RAC/RES-O-0000001412-86-142/F**

**ECHA/SEAC/[reference code to be added after the adoption of the SEAC opinion]**

**Adopted**

10 March 2017

**Agreed**

16 March 2017

*10 March 2017*

**ECHA/RAC/RES-O-0000001412-86-142/F**

*16 March 2017*

**ECHA/SEAC/[reference code to be added after the adoption of the SEAC opinion]**

# Opinion of the Committee for Risk Assessment

# and

# Opinion of the Committee for Socio-economic Analysis

## on an Annex XV dossier proposing restrictions of the manufacture, placing on the market or use of a substance within the EU

Having regard to Regulation (EC) No 1907/2006 of the European Parliament and of the Council 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (the REACH Regulation), and in particular the definition of a restriction in Article 3(31) and Title VIII thereof, the Committee for Risk Assessment (RAC) has adopted an opinion in accordance with Article 70 of the REACH Regulation and the Committee for Socio-economic Analysis (SEAC) has adopted an opinion in accordance with Article 71 of the REACH Regulation on the proposal for restriction of

**Chemical name(s):** ***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***

**EC No.:** N.A. (group entry)

**CAS No.**: N.A. (group entry)

This document presents the opinions adopted by RAC and SEAC and the Committee's justification for their opinions. The Background Document, as a supportive document to both RAC and SEAC opinions and their justification, gives the details of the Dossier Submitters proposal amended for further information obtained during the public consultation and other relevant information resulting from the opinion making process.

## PROCESS FOR ADOPTION OF THE OPINIONS

Denmark has submitted a proposal for a restriction together with the justification and background information documented in an Annex XV dossier. The Annex XV report conforming to the requirements of Annex XV of the REACH Regulation was made publicly available at: http://echa.europa.eu/web/guest/restrictions-under-consideration on **15 June 2016**. Interested parties were invited to submit comments and contributions by **15 December 2016**.

## ADOPTION OF THE OPINION

ADOPTION OF THE OPINION OF RAC:

**Rapporteur, appointed by RAC: *Yvonne MULLOOLY***

**Co-rapporteur, appointed by RAC: *Agnes SCHULTE***

The opinion of RAC as to whether the suggested restrictions are appropriate in reducing the risk to human health and/or the environment was adopted in accordance with Article 70 of the REACH Regulation on ***10 March 2017***.

The opinion takes into account the comments of interested parties provided in accordance with Article 69(6) of the REACH Regulation.

The opinion of RAC was adopted ***by consensus.***

## ADOPTION OF THE OPINION

ADOPTION OF THE OPINION OF SEAC

**Rapporteur, appointed by SEAC: *Åsa THORS***

**Co-rapporteur, appointed by SEAC: *João ALEXANDRE***

The draft opinion of SEAC

The draft opinion of SEAC on the proposed restriction and on its related socio-economic impact has been agreed in accordance with Article 71(1) of the REACH Regulation on **16 March 2017*.***

The draft opinion takes into account the comments from the interested parties provided in accordance with Article 69(6) (a) of the REACH Regulation.

The draft opinion takes into account the socio-economic analysis, or information which can contribute to one, received from the interested parties provided in accordance with Article 69(6)(b) of the REACH Regulation.

The draft opinion was published at ***https://echa.europa.eu/restrictions-under-consideration*** on ***22 March 2017***. Interested parties were invited to submit comments on the draft opinion by ***22 May 2017***.

The opinion of SEAC

The opinion of SEAC on the proposed restriction and on its related socio-economic impact was adopted in accordance with Article 71(1) and (2) of the REACH Regulation on ***[date of adoption of the opinion]***. **[**The deadline for the opinion of SEAC was in accordance with Article 71(3) of the REACH Regulation extended by ***[number of days]*** by the ECHA decision ***[number and date]*****]**.

**[**The opinion takes into account the comments of interested parties provided in accordance with Article[s 69(6) and][5] 71(1) of the REACH Regulation.**] [**No comments were received from interested parties during the public consultation in accordance with Article[s 69(6) and][3] 71(1)**]**[6].

The opinion of SEAC was adopted ***by* [*consensus*.][*a simple majority*]** of all members having the right to vote. [The minority position[s], including their grounds, are made available in a separate document which has been published at the same time as the opinion**.]**[6].

## Contents

# OPINION OF RAC AND SEAC

The restriction proposed by the Dossier Submitter is:

| | |
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| (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:<br><br>(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)trimethoxysilane<br>CAS No. 85857-16-5<br>EC No. 288-657-1<br><br>(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)triethoxysilane<br>CAS No. 51851-37-7<br>EC No. 257-473-3<br><br>(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)triisopropoxysilane<br>– CAS No. 1240203-07-9 | Conditions of the restriction<br>1. Shall not be used in the formulation of mixtures with organic solvents in spray products intended for supply to the general public<br>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.<br>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.<br>4. Organic solvents mentioned in paragraph 1 and 2 include organic solvent used as aerosol propellants. |

## THE OPINION OF RAC

RAC has formulated its opinion on the proposed restriction based on an evaluation of information related to the identified risk and to the identified options to reduce the risk as documented in the Annex XV report and submitted by interested parties as well as other available information as recorded in the Background Document. RAC considers that the proposed restriction on **mono-, di- or tri-O-(alkyl) derivatives of 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanetriol *(TDFAs)*** and **3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanetriol** is the most appropriate Union wide measure to address the identified risk in terms of the effectiveness, in reducing the risk, practicality and monitorability as demonstrated in the justification supporting this opinion, provided that the [scope and/or conditions] [is/are][1] modified, as proposed by RAC.

[1] Delete or keep parts as needed.

The conditions of the restriction proposed by RAC are:

| 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:<br>(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)trimethoxysilane<br>CAS No. 85857-16-5<br>EC No. 288-657-1<br>(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)triethoxysilane<br>CAS No. 51851-37-7<br>EC No. 257-473-3<br>(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)triisopropoxysilane<br>– CAS No. 1240203-07-9 | 1. Shall not be (formulated/used) with organic solvents in the manufacture of spray products which are for supply to the general public.<br><br>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.<br><br>3. Organic solvents referred to in paragraph 1 and 2 also include organic solvents used as aerosol propellants.<br><br>4. For the purpose of this restriction spray products should be interpreted as any aerosol cans, pump or trigger (impregnation/proofing) spray.<br><br>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"<br><br>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".<br><br>7. This restriction shall entry into force on the "date" |

## THE OPINION OF SEAC

See opinion of SEAC.

# JUSTIFICATION FOR THE OPINION OF RAC AND SEAC

## IDENTIFIED HAZARD, EXPOSURE/EMISSIONS AND RISK

### Justification for the opinion of RAC

#### Description of and justification for targeting of the information on hazard and exposure/emissions (scope)

***Summary of proposal:***

The main objective of the proposal is to reduce or prevent consumers' exposure to mixtures containing (3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanetriol/TDFAs and organic solvents in spray products intended for use by consumers across all EU Member States. The main risk is not related to (3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanetriol and its TDFA derivatives but is associated with the hydrolysis and condensation products of (3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanetriol and its TDFA derivatives in combination with organic solvents.

The scope of the restriction proposal is targeted at all spray products containing organic solvents and (3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanetriol and its TDFA derivatives on the market for supply to consumers and the general public which are manufactured in the EU or imported into the EU. The mixtures are sold in different forms of packaging, one packaging type allows application in spray form (aerosol cans, pump or trigger spray) and the other packaging type allows for alternative methods of application such as a brush or a cloth. The proposal only targets the forms sold in packaging that permits spray application i.e. aerosol cans, trigger and pump sprays and not the form that is sold for brush or cloth application. Inhalation of aerosol particles in the respirable range is the exposure route of concern. Using alternative application methods e.g. application by brush, roller or using a cloth will not result in the formation of respirable or inhalable particles.

The concern presented in the proposal relates to mixtures of (3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanetriol and its TDFA derivatives and organic solvents that are used to provide water, stain and oil repellent properties to different surfaces when applied as a spray by aerosol dispensers, pump or trigger spray. These products are often referred to as 'stain proofing', 'water proofing', 'impregnating" or "sealing" sprays. Note: For the purposes of the opinion RAC has used the term "impregnating" to describe these group of uses/products.

The active substances in the mixtures are hydrolysed (3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanetriol and its TDFA derivatives monomers dissolved in a solvent. After spraying, the solvent vaporises and the (3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanetriol and its TDFA derivatives remain on the treated surface by forming a polysiloxane-based (polymer) coating with polyfluorooctyl as a side-chain which provides the water and oil-proofing coating.

Mixtures of (3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanetriol and its TDFA derivatives and organic solvents appear to account for a minor part of the total consumption of impregnating sprays. It is estimated that 20-40% of the 725 incidents reported in the EU were most likely related to spray products that contained (3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanetriol and its TDFA derivatives and organic solvents intended for use by the general public. While professionals are expected to be the main group of users of these

impregnating mixtures, consumers are expected to account for a higher share of the users of these impregnating mixtures sold in spray product form. Spray impregnating products containing mixtures of TDFAs and organic solvents are marketed for application to non-absorbing surfaces.

The Dossier Submitter considers the risks of lung injury from spray "impregnating" products, containing mixtures of (3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanetriol and its TDFA derivatives and organic solvents, as potentially high and likely to occur in every EU country because "impregnating" spray products are distributed in several Member States.

The type of spray containers can be divided into two classes:

(i) aerosol spray cans, which use the expansion of a prepressurized propellant gas to drive out the aerosol, and
(ii) pump and trigger sprays, which operate by means of mechanical force.

Over the last three to four decades many cases involving spray "impregnation" products resulting in respiratory effects were observed in several Member States. The incidents have ranged from single occurrences to larger outbreak occurrences. The "impregnation" products associated with the incidents were marketed for either non-absorbing and/or absorbing surfaces. Very little information is available on the chemical identity of the polymeric active ingredients, as their active ingredients are usually present in low concentrations and the products have in general only been classified and labelled by the formulator according to the organic solvent properties and its content in the product.

While a number of incidents involving proofing sprays among the general public have occurred, where respiratory effects and hospitalisation were observed, unfortunately data from the national poison centres on the composition of the products involved (including identification of the active ingredient) was not confirmed. Nor has, data on the exact composition of the substance been obtained from the manufacturers of these products or during the public consultation.

While a number of the products contained fluorinated or fluorocarbon compounds (silanes, polymers, others) no robust information about the occurrence of fluorinated compounds in combination with a solvent could be derived to explain the observed intoxications. Thus, other fluorinated compounds were not included in the scope of this restriction proposal. The reported human incidents demonstrates a relationship between short-term exposure to certain proofing/impregnation sprays and the development of respiratory illness.

It has been shown that aerosolised mixtures of (3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanetriol and its TDFA derivatives and organic solvents can cause serious acute lung injury in mice. 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 their lipophilicity) facilitates contact between hydrolysates and condensates of (3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanetriol and its TDFA derivatives and the SP-B proteins. This may also explain why no effect on the lungs are seen for spray products based on hydrolysed (3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanetriol and its TDFA derivatives where water is the solvent when these mixtures reach the bronchioles (particle size <10 µm). Thus, the toxicity of the products in rats and mice depends on hydrolysates and condensates of (3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanetriol and its TDFA derivatives, the solvents, particle size distribution and particle concentration. This rationale can explain numerous cases where consumers have experienced acute pulmonary distress following proofing/impregnation spray products containing fluorinated substances. The Dossier Submitter has justified the proposed

restriction on the basis of risks to human health from such impregnating products containing mixtures of (3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanetriol and its TDFA derivatives and organic solvents.

The restriction proposal notes, that at present, no consumer spray product appears to be on the EU market that contain mixtures of (3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanetriol and its TDFA derivatives and organic solvents. Information from the Swedish Product Registry obtained during the public consultation identified that (3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanetriol and its TDFA derivatives were used in 4 spray products for non-absorbing surfaces, three of these were reported between 2010-13 and three contained organic solvents. Since 2014 monomers dissolved in a solvent. After spraying, the solvent vaporises and the (3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanetriol and its TDFA derivatives consumer impregnation products are no longer registered in Sweden.

The Dossier Submitter has confirmed that the intention of the use of the term "spray" is to cover all types of spray products containing (3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanetriol and its TDFA derivatives and organic solvent (not just impregnating products) for supply to the general public. The justification provided by the Dossier Submitter is that if at some time in the future other product uses were identified and placed on the market in spray products they would pose the same risk as impregnation/proofing sprays. This would be a precautionary restriction approach for other potential but currently unknown uses.

***RAC conclusion:***

**RAC agrees that the scope of the proposal in the dossier is clear, however, RAC has suggested some amendment to the proposed legal text to provide additional clarity that the focus of the restriction proposal is to address both the EU manufacture/formulation of sprays products along with the import of spray products from outside the EU.**

**RAC notes the only reported uses of (3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanetriol and its TDFA derivatives and organic solvents mixtures in the restriction proposal is for 'stain proofing', 'water proofing', 'impregnating" or "sealing" sprays.**

**RAC agrees that the risks associated with pump sprays are likely to be lower based on the lack of supporting human cases involving pump sprays including the NFP1 product that was studied in animals whose results are the basis for the proposed restriction.**

**RAC recommends that Safety Data Sheets (SDS) for 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanetriol and its TDFA derivatives should in Section 2.3 (Other Hazards) contain the following information: Mixtures of TDFAs and organic solvents, intended for professional use, shall be labelled *"fatal if inhaled"* to ensure workers and professionals are aware of the hazards associated with using these mixtures.**

**Following advice from the Forum, RAC supports that professional products of 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanetriol and its TDFA derivatives and organic solvents should be labelled "for professional use only".**

**Following advice from the Forum, RAC supports a clear indication of an entry into force date in the legal text entry of Annex XVII.**

***Key elements underpinning the RAC conclusion:***

While the cases reported involving impregnation products are likely to be linked to their use, the cause of sudden outbreaks of respiratory disorders associated with impregnation products remains unknown. The dossier has indicated that such outbreaks have been linked to changes in the aerosol nozzle spray design in products that were previously on the market with no effects reported, and/or associated with a change in the type of organic solvent used.

Toxicity is dependent on the concentration of aerosol in the respirable range (conc. of mist with an MMAD (Mass Median Aerodynamic Diameter) <10 µm) (Yamashita et al 1997b2). Parameters such as application pressure, type of nozzle and volatility of the mixture influence mist aerodynamic particle size. The importance of the concentration of MMAD particles <10 µm to toxicity for impregnation/proofing sprays was also recognised in some countries around the world. A Japanese Aeorosol Industry Association voluntary guidance recommended that the ratio of aerodyamic particles <10 µm should not exceed 0.6% (Kawakami et al. 2015, based on measurements at 15 cm distance from the nozzle). Studies on different aerosol sprays have also documented variations in the percentage of particles <10 µm in different types of aerosol sprays, ranging between 0.1% to 18% (Delmaar & Bremmer, 2009) [3]

RAC agrees that the dossier has provided evidence of acute inhalation toxicity from impregnation/proofing aerosol products but the incidence data alone is not robust. RAC agrees to the use of the evidence from animal data, as the test mixtures of TDFA and isopropanol used in the animal study by Norgaard was nebulised and therefore available for inhalation in the respirable range. The data indicates that based on the most conservative DNEL of 0.068 mg/m³, the fraction of particles with an MMAD <10 µm should not exceed 0.6%. However no data is available to inform about the concentration limits of the ingredients in the formulation that produces less than 0.6% of <10 µm particles.

While evidence has been provided that aerosol sprays achieve sufficient concentrations in the MMAD range (<10 µm) (Magic Nano cases), limited evidence has been provided to support that mists generated from pump sprays reach low level concentrations in the MMAD range <10 µm. Losert et al. 2015 indicated that impregnation spray applications using pump spray generate particles in nanometer sizes.

Koch et al. (2009) estimated that about 0.9% of particles in the pump spray were <10 µm however the analytical methods used by Koch et al. (2009) were not appropriate to characterise particles in the nanosize scale. No human incidents were reported in the pump spray product (NFP1) that was studied intensely in the animal studies by Norgaard et al. before it was removed from the Danish market in 2010. In addition, no human incidents were reported for the pump spray form of the "Magic Nano Bath & WC" product and only limited effects were seen in an inhalation study in rats.

While the reported consumer incidents, both in the EU and outside, are linked to aerosol dispensers one product reported in Canada (1992-1993) which resulted in two incidents of respiratory problems and 14 calls to the poison centre is described as a "pump spray". However, this pump sprays contained Stoddard solvent which RAC notes is classified to cause respiratory effects which places doubts as to whether the incidents involving these pump sprays are relevant to the presented risk associated with TDFA's and organic solvents.

Two occupational cases with three incidents were reported from trigger sprays containing fluoroacrylates in Switzerland (2002-2003) suggesting the potential for respirable particle generation from trigger sprays but also noting the causative agent belonged to the chemical

[2] Yamashita M., Yamashita M., Tanaka J., et al(1997b) Toxicity of waterproofing spray is influenced by the mist particle size.VetHum Toxicol39, 332-33

[3] Delmaar J.E., & Bremmer H.J. (2009) The ConsExpo spray model; Modelling and experimental validation of the inhalation exposure of consumers to aerosols from spray cans and trigger sprays.

group of fluoroacrylats, Vernex et al. (2004)

As no robust information is available to establish a concentration limit based on a particle concentration with an MMAD <10 µm. Therefore, any consumer spray products containing 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanetriol and its TDFA derivatives and organic solvents are expected to result in inadequately controlled risks.

As the risk is associated with the hydrolysis and condensation products formed it is also important that those involved in the manufacture, import and use of 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanetriol and its TDFA derivatives are aware of the inhalation hazards generated when 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanetriol and its TDFA derivatives are mixed with organic solvents and sprayed. Therefore, RAC recommends that the associated Safety Data Sheets (SDS) for 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanetriol and its TDFA derivatives should in Section 2.3 (Other Hazards) contain the following information: Mixtures of TDFAs and organic solvents, intended for professional use, shall be labelled "Fatal if inhaled" (where the concentration of TDFAs is equal to or greater than 2ppb).

RAC notes that the Dossier Submitter has indicated that the scope of the restriction is not intended to cover the formulation of TDFAs and organic solvents for export. However, RAC notes that such formulations would present a risk to non EU consumers if applied by consumers as a spray. The Annex XVII text should address the EU manufacture of sprays product mixtures containing TDFAs and organic solvents offered for sale to consumers or the general public, as well as, imported spray products. Both EU manufacturers of impregnating/proofing sprays and importers will need to demonstrate compliance with the proposed restriction.

**Information on hazard**

***Summary of proposal:***

This restriction proposal targets the placing on the market of spray products[4] containing mixtures of 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanetriol and its TDFA derivative and organic solvents intended for use by the general public. Inhalation is the exposure route of concern.

Animal studies have shown that 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanetriol and its TDFA derivatives alone were not able to induce lung injury and mortalities, the fatal effect became obvious only in combination with organic solvents. Thus the Dossier Submitter concluded that 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanetriol and its TDFA derivatives and organic solvents in the aerosol products were involved in the cases of lung injury and fatalities observed in consumers.

Evidence that supports the information from the animal studies comes from data on a previous outbreak involving impregnation products in 2006. The outbreak consisting of 154 cases of intoxication 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 ingredient data available for these two products and therefore no data on the concentrations of 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanetriol and its TDFA derivatives in the mixtures used but analytical investigations at the time of the incidents did identify fluorosilanes and organic solvents in these products.

Nørgaard et al. (2010b) tested 10 impregnation spray products ("nanofilm spray products") from three Danish suppliers and found TDFAs with organic solvent in two spray products for

[4] Aerosol dispensers, pump and trigger sprays

non-absorbing materials.

In an animal study (Nørgaard et al., 2010a) which tested the effects of TDFAs and 2-propanol on mice, it was found that exposure to the aerosolised mixture had decreased the tidal volume (VT) of the mice following short term exposure. Higher toxicities (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>ethanol>methanol) (Nørgaard et al. (2014). In vitro tests demonstrated that the lipophilicity of the solvent determined the toxicity of TDFA's on the surfactant function.

The hypothesis regarding the toxicity of mixtures of 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanetriol and its TDFA derivatives and organic solvents is that in the deeper parts of the lung, the organic solvent (depending on its lipophilicity) facilitates contact between the hydrolysates and condensates of 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanetriol and its TDFA derivatives 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 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanetriol and its TDFA derivatives with organic solvents that reaches the deeper parts of the lungs.

***RAC conclusion:***

- **RAC agrees that the dossier has provided evidence of acute inhalation toxicity in animal studies following exposure to TDFA's an organic solvents and from impregnation/proofing aerosol products but that the cause of sudden outbreaks of respiratory disorders associated with impregnation products remains unknown.**
- **RAC agrees on the link between the 154 cases reported to occur after the use of two aerosol spray products ('Magic Nano Bath & WC', 'Magic Nano Glass & Ceramic) and mixtures of fluorosilanes formulated with organic solvents. It appears to be plausible that fluorosilanes were the active substances that have contributed to the lung injury.**
- **RAC agrees that the proposed mechanism behind the effects observed as presented in the dossier is plausible and the risk depends on the mixture having a concentration in the respirable range to reach the alveolar/bronchiolar regions of the lungs**.
- **RAC concluded that mixtures of TDFAs in combination with organic solvents with a particle MMAD <10 µm are necessary to cause acute lung injury.**
- **RAC agrees that pulmonary toxicity depends on the ability of the reaction products and solvent reaching the respirable area of the lungs. The lipophilicity of the solvent facilitates contact between the hydrolysates and condensates of TDFAs and the SP-B proteins in the lung. Solvents that are less lipophilic than 2-propanol, are shown to have a slightly lower toxicity whereas mixtures of TDFAs and more lipophilic solvents are expected to have a higher toxicity (in terms of earlier onset of the effect).**
- **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.**

**In addition, following assessment of the available evidence RAC concludes the following:**

- **Inhalation toxicity testing of each individual substance is not sufficient to assess the hazards from formulated products of TDFAs and organic solvents.**
- **To derive a DNEL 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 $LC_{50}$-value more appropriate (in comparison to the expected application by consumers) than the extrapolation to a 4-hour value. In line with the Background Document (revised accordingly by the Dossier Submitter) two approaches – the $LC_{50}$-value in combination with a large assessment factor and the NOAEL as a starting point - are taken forward for DNEL derivation. The two DNELs (0.068 mg/m³ and 0.21 mg/m³) are used for risk calculation:**
- **At present no specific (TDFAs-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 (Kawakami et al. 2015) or in the nanometer sizes in pump and trigger sprays (Losert et al., 2015), the generation of respirable particles <10 µm cannot be excluded. The percentage of particles <10 µm is likely to be lower for trigger and pump sprays than from aerosol. The potential risk for trigger and pump spray applications have been quantified based on the limited information on the generation of particles <10 µm from trigger and pump spray products.**

***Key elements underpinning the RAC conclusion:***

**Hazardous effect linked to exposure to spray products**

The restriction proposal identified two aerosol spray products ('Magic Nano Bath & WC', 'Magic Nano Glass & Ceramic[5]) containing fluorosilanes and organic solvents as the responsible agents that induced acute lung injury in 154 cases in 2006. The Dossier Submitter considered the ingredients in both products as probable of being TDFAs and organic solvents.

At the time of the outbreak in 2006 no information on the composition was available. In 2009, Koch et al. published information on the ingredients of the Magic Nano aerosol spray products which indicated the presence of (w/w) 0.46-2.3 % of silanes and 26.2 % ethanol.

The aerosol fraction in the spray was low (1-3%) indicating that a large fraction of the spray is volatile. X-ray emission spectroscopy revealed high peak concentrations of silicium and fluor in the Magic Nano Glass & Ceramic aerosol spray that justified the assumption that fluorosilanes were the toxic agents. As a corrosion inhibitor (0.83% w/w) was not found in the aerosol spray Magic Nano Bath & WC, it was not likely to be the cause of the intoxications.

Measurements with ICP-MS on the suspension revealed low concentrations of tin in the Magic

[5] The name was referring to the thickness of the waterproofing film on the surface rather than on nano-sized particles (Pauluhn, 2008).

Nano products (37-50 µg/g in Glass & Ceramic, 18-29 µg/g in Bath & WC, 0.01-0.03 µg/g in the pump spray); no evidence on tin was found in the aerosol analysis using X-ray emission spectroscopy (Koch et al., 2009). A commenter (PC Comment No. 1488) raised the assumption that organotins produced in the formulation were responsible for the inhalation toxicity. Tin (like other metals) were found in (other) spray product formulations and their aerosol and thought to originate from the spray can (Losert et al., 2015). However, production of organotin compounds has not been demonstrated for impregnation sprays and is considered unlikely to result from metallic tin (this would require a strong acid or base). Several conditions such as surfactant/alveolar surface active chemicals (as a result from combined exposure to TDFAs and organic solvent), respirable particle sizes and the relevant concentrations (at the site of effect) seem to be necessary in causing acute lung injury. However, no information is available on threshold concentrations.

There may be other fluorosilanes than TDFAs (other fluorinated compounds) in mixtures used for spray products that are not covered by the restriction proposal since information on the ingredients in spray products along with evidence on specific links to effects in consumers is insufficient. No confirmative studies using the relevant (fluorsilane-based) products in animals are available either except one study in mice using a commercial spray product (based on fluororesin, silicone resin and organic solvents) that observed alveolar atelectasis and inflammation responses after inhalation of repeated 20 sec spray application (Yamashita and Tanaka, 1995[6]). However, neither the formulation nor the aerosol were analysed with regards to their compositions and the particle size distribution.

**Clinical signs**

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 severe cases.

**Animal studies**

TDFAs alone do not cause lung injury. This evidence comes from animal studies showing that mixtures of TDFAs in combination with organic solvents are essential to cause acute lung injury.

Mice exposed to aerosolised mixtures containing (polyfluorinated silanes) 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 (60 min) (Nørgaard et al., 2010). A significant concentration-dependent decrease of the tidal volume (VT) was seen, which was still significantly suppressed in the 18.4 mg/m³ group one day after exposure. Three out of 20 mice died at 18.4 mg/m$^3$ and 10 out of 10 died at 24.4 mg/m$^3$. Histological examinations revealed atelectasis (collapsed alveoli), haemorrhage, and emphysema or lung over-distension (emphysema) because of maldistribution of ventilation.

Nonfluorinated alkylsilanes in combination with organic solvents were unable to induce the

[6] Yamashita M, Tanaka J (1995) Pulmonary collapse and pneumonia due to inhalation of a waterproofing aerosol in fmale CD-1 mice. Clinical Toxicology 33(6), 631-637.

toxic effects in mice. It was also shown that water-based products containing hydrolysates and condensates of TDFAs were unable to cause lung effects. The effect on the tidal volume increased with the length of the carbon chain/lipophilicity of the alcoholic solvents methanol, ethanol and 2-propanol (Nørgaard et al., 2014) or by adding 0.5, 0.75 or 1.0 mol water leading to more free hydroxyl groups (Nørgaard et al., 2010).

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 by the Dossier Submitter as 10 mg/m$^3$ (dry weight) (Pauluhn et al., 2008).

Inhalation of organic solvents alone did not cause pulmonary disorder (Norgaard et al. 2010a, Yamashita & Tanaka, 1995).

The lack of toxicologically significant changes in rats exposed to the 28 100 mg/m³ aerosol spray 'Magic Nano Bath & WC' (Pauluhn et al., 2008) appears to be inconsistent to the observed cases in humans. Although the authors demonstrated that the aerosol particles were in the respirable size (aerosol concentration 30%, calculated concentration at MMAD 5.81 was 148 mg/m³), neither they nor the Dossier Submitter could explain the unexpected negative outcome in rats.

**Mode of action**

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 when 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.

**Supporting evidence from other spray products**

Symptoms consistently reported after the exposure to other spray products (than the Magic Nano products), which most contained fluorinated polymers are: cough, dyspnoea, pulmonary oedema, nausea, fever, shivers and headache. The Dossier Submitter noted that respiratory symptoms have been reported to appear shortly after exposure or with some delay. Symptoms usually resolved within a few days, but sometimes supportive treatment with oxygen, bronchodilators or corticosteroids was needed.

The restriction proposal suggested that the presence of substances/monomers for polymers, with per- or polyfluoroalkyl side-chains as ingredients in mixture with organic solvents are a common characteristic of many of the spray products that caused acute lung injury (Page. 37). However detailed information on ingredients were lacking for these products. The lack of detailed information justified the narrow scope of this restriction proposal.

No human cases of lung injury were observed for the 'Magic Nano Bath & WC' pump spray which contained even higher fractions of silanes (1-5%) and ethanol (57.5%) than the two Magic Nano aerosol sprays. This may be explained by a low aerosol fraction of <0.9% of respirable particles (<10 µm) from the pump spray (which was 20 fold below those of the two Magic Nano aerosol sprays in a model room of 60 m³ without ventilation following the release

of a 200 g spray within 5 min).

Most outbreaks on other spray products resulted from using aerosol dispensers. Some incidents in 1992 resulting from the use of a pump spray were reported from cases in Canada. The active substances in these formulation did however included stoddard solvent, heptane, fluorinated polymer resin, silicon and polymerised C10 alkanes which could be the causative agents responsible for the effects. Based on the cases linked to pump sprays (with limited knowledge on the ingredients) the evidence is weaker for including pump sprays in the restriction proposal.

In rats exposed for 4 h to the pump (Magic Nano Bath) spray following nebulization the tested concentration (81 222 mg/m$^3$, aerosol conc. 5-7%, calculated concentration at MMAD 4.59 µm 21 mg/m$^3$) was in the beginning lethal range (Pauluhn, et al., 2008). The authors stated that this concentration is markedly above the recommended maximum concentration recommended for animal welfare reasons. The rats exposed to the nebulised pump spray displayed clinical signs including breathing abnormalities, neurobehavioral changes and lower rectal abnormalities that were interpreted by the authors as indicative for upper respiratory tract sensory irritants. Broncheoalveolar lavage (BAL) revealed significant higher fraction of polymorphnuclear neutrophils (PMN), a non-significant decrease of the fraction of alveolar macrophages and a tendency for higher protein content and increased lactat dehydrogenase (LDH, indicating cell damage). All these effects were also observed in the rats exposed to Magic Nano Glass & Ceramic aerosol spray using an intermittent generation during 120-240 min exposure duration, at more pronounced significant effect levels.

In conclusion, observations in rats exposed to a high concentration of the Magic Nano Bath nebulised pump spray (mainly the occurrence of breathing abnormalities and similarities of the BAL parameters) can be interpreted as supporting that mixtures of TDFAs and organic solvents contained in pump sprays cause lung injury[7] if the spray mist is in respirable range. However, this information on its own does not give sufficient evidence to support the inclusion of pump sprays in the conditions of the restriction as the test pump spray was nebulised in the rat study and particle size distribution results of the nebulised spray (NFP 1, ethanol, 2-propanol) had a large fraction that can end up in the bronchioles and alveoli. As no human cases of lung injury were seen with the pump spray 'Magic Nano Bath & WC' that was characterised by a low aerosol fraction of <0.5% (<4.5 µm) and of < 0.9% of respirable particles <10 µm (Fig. 8 in Koch et al., 2009), the question raises whether pump sprays in general are able to produce relevant amounts of mixtures as respirable particles.

A study by Yamashita et al. (1997b)8 tested four identical waterproofing sprays but with different mist particle sizes supported suggestions that the toxicity of waterproofing sprays is influenced by mist particle size generated. The study also highlighted that while there are many brands on the market only few are associated with respiratory effects.

The U.S. Silicones Environmental, Health and Safety Council (SEHSC) recommends that when considering a consumer aerosol application for any silicone-based material, regardless of the method of aerosol generation, the particle size MMAD should be at least 30 µm with no more than 1% of the particles having an aerodynamic diameter of 10 µm or less. Following this

[7] This conclusion takes the uncertainties into account (high dose tested only, no data on single animal findings, mode of action may differ (at least partly) as the tidal volume was not reduced and inspiration time was prolonged and followed by a post inspiratory apnoea, but two modes may also run in parallel). The mortality (1/16 rats died) is not considered to be kick-off criteria, as mortality may result from the primary lung injury and was also observed in rats exposed to Magic Nano Glass & Ceramic spray.

[8] Yamashita M., Yamashita M., Tanaka J., et al (1997b) Toxicity of waterproofing spray is influenced by the mist particle size.VetHum Toxicol39, 332-33

guidance should ensure that virtually all aerosol particles will be trapped in the nasopharyngeal region and very few if any particles will be deposited in the tracheobronchial region. However, this recommendation should be taken with care since it does not take into account that spray droplets released into the air may shrink due to solvent evaporation. This leads to a considerable shift of the size distribution towards smaller particles and an increase of the respirable fraction.

In December 2008 authorities from Germany, The Netherlands, Japan and Switzerland published a safety guideline limit on waterproof aerosol sprays to improve product safety by avoiding acute lung injury from fluorine-based or silicone based compounds. The guidance given by Aerosol Industry Association of Japan recommends to limits aerosol particles of diameter less than 10 µm to less than 0.6% of the sprayed aerosol particles[9]. Another voluntary guidance document from the IKW (Industrieverband Körperpflege und -Waschmittel e.V)[10] remains open with regards to the critical concentration of particles <10 µm. Losert et al. (2015)[11] showed that in two pump sprays analysed the water-based impregnation pump sprays for glass (like propellant aerosol spraying) resulted in mean particle sizes in the nanometer range. Also, the particle numbers were comparable to the aerosol for a propellant spray with alcohols or even higher than for the tested water-based propellant spray. The authors concluded that pump sprays also can release nanoparticles. The analytical methods in the Koch study, performed a decade earlier with less developed techniques than those used by Losert et al., were not expected to characterise the distribution and numbers of aerosol particles in the lower nano ranges. This could be interpreted as supporting evidence to include pump sprays in the restriction.

While there were no reported cases of acute lung injury due to inhalation of aerosols from hand pump sprays containing fluorine or silicone based compounds in Japan, a second study[12] investigated the aerosol particle size distribution of 16 household hand-pump sprays. The samples surveyed included sprays for waterproofing textiles, and kitchen and bathroom (8 samples), ironing sprays (two samples), clothing care sprays (two samples), and sprays to prevent adhesion of pollen to masks and clothing (four samples). Although the constituents were not described for three product types these products were selected because a waterproofing effect was expressed on the product label. Three of the products tested came from the EU (UK). In seven samples, the ratio of fine particles (<11 µm) in aerosols exceeded 0.6% of the voluntary guidance recommendation. This study confirmed that hand-pump sprays available in the Japanese market can spray fine particles (<11 µm). However, personal communication of the Dossier Submitter with the authors revealed that six out of the seven sprays assumed to be pump sprays were in fact trigger spray products (see Table 2-5 in Appendix 2 of the Background Document). Regarding the limited database on pump and trigger sprays in general, more data is needed to characterise the particle size in pump and trigger sprays and the effects of technical design of sprays such as nozzle type.

DNEL calculations

Point of departure

The available human data show that the lung injury manifested shortly after application of

[9] Kawakami et al. 2015 https://www.ncbi.nlm.nih.gov/pubmed/26821469

[10] http://www.ikw.org/fileadmin/content/downloads/Haushaltspflege/HP_Example-impregnation-spray.pdf

[11] Online Characterisation of nano- aerosols released by commercial spray products using SMPS-ICPMS

[12] Particle size distribution of aerosols sprayed from household hand-pump sprays containing fluorine-based and silicone-based compounds. Tsuyoshi Kawakami, Kazuo Isama. Yosluaki Ikaraslu. Bull. Nati Inst. Health Sct, 133, 3741 (2015) Tcchnical Data

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.

The observed effects are acute toxicity effects, only in exceptional cases exposure durations longer than 15 min/day (for which ECHA Guidance, Chapter R. 8 recommends to derive a long-term DNEL) are to be expected.

As a starting point to derive the DNEL, the Dossier Submitter in his initial proposal suggested to take the $LC_{50}$-value in mice from the study of Nørgaard et al. (2010a). Based on this the Dossier Submitters estimated 1-hour $LC_{50}$ of 20.4 mg/m$^3$ (after correction to a 4-hour exposure), 5 mg/m$^3$ was estimated as the starting point to derive the DNEL. Comparing the LOAEC and the 4-hour $LC_{50}$ values the mouse was more sensitive than the rat in the study on Magic Nano products by Pauluhn et al. (2010).

Assessment factors

The Dossier Submitter in his initial dossier proposal suggested using an assessment factor (AF) of 100 for the severity of effect to the $LC_{50}$-value. According to the ECHA Guidance (Chapter R.8) using mortality as a starting point to derive a DNEL ignores the possibility of serious sub lethal effects and substantial uncertainty regarding the toxicity at lower doses remains. The guidance recommends to determine the size of an additional severity factor to be applied to the $LC_{50}$-value (without giving any further suggestions or examples) to cover the significant inherent uncertainties. The Dossier Submitter's proposal to take an AF of 100 coherent with the guidance is noted; no specific reasoning was given for its size or derivation from the default AF 100. RAC accepted to take the AF of 100.

In addition, an AF of 3 is used because of the very steep concentration-response curve. The derived 4 hour no-effect concentration (DNEL) for TDFAs and 2-propanol is calculated using the total assessment factor of 300:

DNEL (as initially proposed by the Dossier Submitter)

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

**DNEL estimate 1 based on 1hr $LC_{50}$ and AF 300**

RAC considered that the use of the 1 h $LC_{50}$-value of 20.4 mg/m$^3$ is more appropriate than the 4 h $LC_{50}$-value suggested by the Dossier Submitter.

$$DNEL\ (acute) = \frac{20.4\ mg/m^3}{300} = 0.068\ mg/m^3$$

**DNEL estimate 2 based on NOAEC and AF 75**

Other starting points to derive a DNEL such as the NOAEC or LOAEC for the effects of concern should also be considered.

The guidance notes (R.8.2) recommend that in the case of a steep curve the derived NOAEL can be considered as more reliable (the greater the slope, the greater the reduction in response to reduced doses); in the case of a shallow curve, the uncertainty in the derived NOAEL may be higher and this has to be taken into account in the DNEL derivation.

Neither an effect on the tidal volume nor on the BAL was observed in mice exposed to 16.1 mg/m³ (Nørgaard et al. (2010a); this concentration based on specific effects on the respiratory system is considered as a NOAEC to be used for DNEL calculation.

Weight loss within 22-24 h was the most sensitive effect that increased concentration-dependently from 15.7 mg/m³. The corresponding NOAEC of 3.3 mg/m³ is considered less robust and will not be selected as the effect on body weight may be an unspecific effect.

Allometric scaling to correct for the impact of interspecies differences of inhalation volume on (systemic) kinetic processes is not appropriate for local effects on the respiratory tract. The default AF of 2.5 for remaining interspecies differences and the default AF of 10 for interspecies differences are proposed. An AF of 3, as suggested by the Dossier Submitter, is applied for the steepness of the dose-response.

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

**Information on emissions and exposures**

***Summary of proposal:***

There are two types of surfaces that water, stain proofing, impregnating or sealing spray products are designed to treat (1) absorbing surfaces such as textiles e.g. shoes or clothing and (2) non-absorbing surfaces such as ceramic tiles or shower doors.

Spray products for consumers containing TDFAs in mixtures with organic solvents are used for non-absorbing surfaces. Exposure depends on the product's ability to reach the deep lung tissue; so is dependent on the particle size distribution which depends on the application method of the product.

The exposure scenarios presented in the dossier are based on

(a) exposure modelling under realistic worst case conditions where mixtures of TDFAs and 2-propanol are sprayed onto different surface types to be treated.

(b) data from studies involving Magic Nano glass and ceramic/formulations of NFP 1 and

(c) evidence of reported incidents involving proofing sprays in EU Member States and non EU Member States.

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

More detailed information on manufacture and uses of TDFAs and related sprays, as well as on the exposure assessment (particle sizes and distributions from animal and spray chamber experiments, summary of human exposure incidents and exposure modelling calculations) are presented in the Background document.

***RAC conclusion:***

- **RAC agrees that the risk depends on the respirable fraction (<10 µm) generated with an ability to reach the deep lung tissue which is dependent by the application method (pressurised aerosol can, pump or trigger spray) of the spray (impregnating/proofing) product. Therefore, RAC agrees that the % of spray that is respirable is important when considering potential exposure concentration.**

- **RAC agrees that 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.**

- **As data from the Koch study supports 20% of particles <10 µm for aerosol products and a lower particle fraction of particles <10 µm for pump sprays (less than 0.9%) RAC agrees that the Dossier Submitter initial exposure assessment over estimated the risk as it assumed that all generated aerosols have relevant fractions of MMAD <10 µm.**

- **Based on limited information for pump and trigger sprays products (not specific to TDFAs) RAC have assessed in a quantitative way from modelled exposure information whether the use of pump or trigger sprays under realistic worst case or normal realistic use conditions present a risk that is not controlled and concluded that mixtures containing TDFAs and organic solvents in pump and trigger sprays may also pose a risk, although at a lower level than the aerosol spray products**.

- **Spray products containing TDFAs in mixtures with organic solvents are normally used for non-absorbing surfaces. RAC agrees that the exposure scenario based on the application of the spray product to tiles in a bathroom is an appropriate model scenario presented for risk assessment. It cannot however be ruled out that some users could use organic solvent-based agents containing TDFAs for absorbing surfaces. However, based on the information available these products are not marketed for such applications and such use would constitute misuse.**

- **RAC agrees there are uncertainties with the applicability of the ConsExpo and SprayExpo models. Both ConsExpo and SprayExpo uses mass generation rates instead of applied amount. RAC agrees that SprayExpo is a more appropriate model to assess exposure for this use as ConsExpo assumes instantaneous evaporation of the solvent, instantaneous uniform dispersion of the spray throughout the whole room immediately upon its release independent of the actual dispersion conditions. SprayExpo contains a droplet impaction module for calculating the overspray during spraying onto a surface.**

- **RAC agrees that input parameters relating to the mass generation, airborne fraction and initial droplet/particle size distribution have a huge impact on the estimated mean event concentrations. While supporting data for input data on mass generation, airborne fraction and initial droplet/particle size distribution is limited, the other model input parameters used (room size, ventilation rate, spray/exposure duration) by the Dossier Submitter are considered appropriate and acceptable for the purpose of risk assessment.**

- **SprayExpo calculations for pump sprays using realistic case initial droplet/particle size distribution from Kawakami et al. (2015) identified RCR < 1 which supports that some pump sprays likely to be on the market do not pose a risk that is not adequately controlled. However, under worst case conditions calculations with SprayExpo indicates a potential risk from pump**

**spray exists under certain applications.**

- **RAC agrees that it is plausible, depending on the spray nozzle design of a pump or trigger spray that, immediately upon application, an inhalable fraction of aerosol may be generated that may reach the deep lung tissue.**
- **RAC agreed to derive exposure estimates based on the potential for particles to be <10 µm.**

***Key elements underpinning the RAC conclusion:***

Due to the intended use of these products (e.g. in bathrooms) it is likely and reasonably foreseeable that consumers will use the proofing and impregnating products in small enclosed spaces with poor ventilation and without respiratory protective equipment. This is supported by reported incidents showing consumers occasionally use impregnation sprays indoors in small rooms without opening windows or doors and without any personal protection.

The original dossier indicated that consumption of the mixtures for spray coating is indicated to be about 10 – 70 ml/$m^2$ depending on the application. RAC notes that the Norgaard (2009) publication reports an application of 10-40 g/$m^2$. These values are the ones used in the exposure estimates.

Spray products for consumers containing TDFAs in mixtures with organic solvents are marketed for use on non-absorbing surfaces. Volatile organic solvents like ethanol or 2-propanol are used for non-absorbing substrates as they enhance cross linking and make a good wetting of the substrate. Ethanol is able to penetrate and infiltrate the material (stone, wood). The hydrophobic and oleophobic TDFAs will go 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 is subject to abrasion on the surface.

Koch et al

RAC notes that Koch et al. (2009) released one aerosol spray can (approximately 200 g and not 120 g as indicated in the dossier) of "Magic Nano Glass & Ceramic" over a 5 minute period in a 60$m^3$ room. A peak concentration of approximately 11.5 mg/$m^3$ was able to reach the bronchioles and/or alveoli (< 10 µm) after 9 minutes and remained at a concentration above 4 mg/$m^3$ during the first 30 minutes of measurements. Koch also showed that when using pump sprays, less particles (peak concentration < 1.2 mg/$m^3$) are released. The use of pump sprays was associated with an approximately 20 fold lower risk of inhalation exposure to respirable aerosols than aerosol sprays.

Exposure Modelling

There is a substantial difference in how the two models handle droplet/particle distribution. SprayExpo takes shrinking of particles due to evaporation of the solvents into account whereas ConsExpo 4.1 does not. While ConsExpo can be used for non-volatile compounds released as an aerosol from a spray can or a trigger spray, sensitivity analysis undertaken during the development of SprayExpo[13] revealed that along with the substance release rate, the droplet spectrum is the process parameter that has a decisive impact on the exposure level. In contrast, the vapor pressure of the solvent only plays a secondary role for the exposure concentration of the active ingredient. SprayExpo was developed to estimate aerosol exposure during spray application of non-evaporating biocidal substances. This model takes into account turbulent diffusion, droplet evaporation and gravitational settling. In addition, it

[13] http://www.baua.de/en/Topics-from-A-to-Z/Hazardous-Substances/SprayExpo.html

includes a droplet impaction module for calculating the overspray during spraying onto a surface. For room spraying and spraying onto walls, comparisons between this model and experiments revealed that spray applications estimates from SprayExpo can generally be reproduced with an uncertainty of a factor of 4/5 or lower. Unlike SprayExpo, ConsExpo assumes instantaneous evaporation of the solvent, instantaneous uniform dispersion of the spray throughout the whole room immediately upon its release independent of the actual dispersion conditions which mean that it is more suitable to calculate exposure in small rooms rather than larger spaces. SprayExpo was considered by RAC as more suitable for modelling exposure for this use application (spray).

It is possible in SprayExpo to choose floor, ceiling or wall lining. When choosing floor treatment it is not possible to set the exposure duration different from the spray duration. The treated area is set through mass generation rate (same as ConsExpo) and spray duration.

It is noted that the Dossier Submitter initially used a mass generation rate for impregnation sprays of 4 g/s. While no default values are available for impregnation sprays this mass generation rate differs significantly from the default values used in ConsExpo for spray cans (0.8 and 2.2 g/sec). The Dossier Submitter subsequently revised the mass generation rate in the new exposure assessments. The mass generation rate for aerosols & trigger sprays was set to 0.3 g/s and 0.55 g/s, and for pumps to 0.1 g/s and 0.2 g/s.

The use of data on the number of particles generated from the Norgaard study is not appropriate for pump sprays and may not reflect exposure from pump or trigger sprays even under worst case conditions. The spray exposure estimates from the ConsExpo model for pump and trigger sprays have greater uncertainty than for aerosols and are likely to underestimate exposure as they do not take evaporation into account. However, when calculations using ConsExpo take evaporation into account similar exposures to those generated by SprayExpo are achieved. It is plausible that spray products that use pump and trigger sprays, depending on their spray nozzle design, will immediately upon application result in the generation of an inhalable fraction of aerosol, some of which may reach the deep lung tissue.

Particle size is an important factor as the size of the aerosol particle strongly influences the rate at which particles are removed from the air (no longer available for inhalation) as well as the degree of inhalability. Aerosol particles with aerodynamic diameters smaller than about 10 µm are of relevance to this exposure estimation. Data from Koch et al. suggest that the respirable fraction (<10 µm) is less in pump sprays. Based on studies from Yamashita et al. 1997, Saldo, 2011, Kawakami et al. 2015 and Losert et al. 2015, RAC agrees that 20% of the aerosol is <10 µm for aerosol cans, 3% for trigger sprays and 0.9% for pump sprays.

The exposure assessment in the dossier was refined and updated by the Dossier Submitter during the opinion development process for realistic and realistic worst case exposure using both ConsExpo 4.1 with and without a correction for evaporation, and SprayExpo. Even though NFP1 is for floor treatment, wall treatment was chosen for the models for scenario 1) and 2) so as to compare output from SprayExpo and ConsExpo.

The following four exposure scenarios were undertaken for NFP 1 (TDFAs & 2-propanol) for non-absorbing surfaces.

1) Bathroom of 10 $m^3$, 3.4 $m^2$ floor/wall tiles applying a high application of product per $m^2$ area (40 $g/m^2$).

2) Bathroom of 10 m³, 3.4 m² floor/wall tiles applying a lower application of product per m² area (10 g/m²).

3) Bathroom of 10 m³, 0.3 m² mirror (0.6 m x 0.48 m) applying a higher application of product per m² area (40 g/m²).

4) Bathroom of 10 m³, 0.3 m² mirror (0.6 m x 0.48 m) applying a lower application of product per m² area (10 g/m²).

At 40 g product per m² (RWC) a mass generation rate of 0.55 g product/sec is used for the aerosol dispenser and trigger sprays and 0.2 g product/sec for pump sprays.

At 10 g product per m² (RC) a mass generation rate of 0.3 g product/sec is used for the aerosol dispenser and trigger spray with 0.1 g product/sec for pump sprays.

The duration of application is compared to the actual physical process of spraying 1 m² that takes approximately 25 sec. While the mass generation rates impact on exposure the rates used are not considered conservative.

The most critical factor is the spray's ability to reach the deep lung tissue (<10 µm MMD).

The number of particles was estimated from chamber tests. The number of particles generated in the trigger spray chamber experiment was significantly less than the number of particles generated from high pressure nebulization in the animal experiment test chamber. No particle concentration measurements were available for NFP1 aerosol or pump sprays. The high pressure nebulizer generated significantly higher particle concentrations than trigger/pump sprays (1.4 x 105 – 4.6 x 106 particles/cm³) equating to a concentration of 0.5 mg/m³ – 42.4 mg/m³ (dry weight), i.e. the concentration mice were exposed to in the study. The droplet/particle size distribution of NFP1 from Norgaard (2009) was not used in updated exposure estimates as it was confirmed that the study did not measure the initial distribution of the spray.

The ratio of fine particles was examined in Kawakami et al 2015 and found that out of the three pump sprays used have two have less than 0.6% (0-0.4%)particles in the <9µm range and one has 0.8% of the particles in the <11 µm range. For five trigger sprays the ratio was >0.6% for the <9 µm range. However it is difficult to distinguish the initial droplet /particle size distributions from pump to trigger sprays.

The spray nozzle size of 0.5 mm was chosen at an angle of 30 degrees for all scenarios in SprayExpo.

NFP 1 is a floor treatment product. When treating a floor one would most likely not spend time in the room immediately after application until the floor is "dry". This means that the exposure time will be identical to the spray duration.

**TABLE 1. RWC EXPOSURE ESTIMATES USING CONSEXPO, CONSEXPO CORRECTING FOR EVAPORATION EFFECTS, AND SPRAYEXPO.**

| Scenarios | Model | Spray type | Mean event concentration [mg/m³] |
|---|---|---|---|
| 1) Impregnation of 3.4 m² tiles in a 10 m³ bathroom (approx. | ConsExpo | Aerosol | 1.9 |

| | | | |
|---|---|---|---|
| use 40 g/m²) | 4.1 | Trigger | 0.0043 |
| | | Pump | 0.0016 |
| | ConsExpo 4.1 With evaporation | Aerosol | 89.6 |
| | | Trigger | 20.7 |
| | | Pump | 7.5 |
| | SprayExpo | Aerosol | 97.1 |
| | | Trigger | 39.2 |
| | | Pump | 14 |
| 2) Impregnation of 3.4 m² tiles in a 10 m³ bathroom (use approx. 10 g/m²) | ConsExpo 4.1 | Aerosol | 0.56 |
| | | Trigger | 0.0013 |
| | | Pump | 0.00043 |
| | ConsExpo 4.1 With evaporation | Aerosol | 25.7 |
| | | Trigger | 6.1 |
| | | Pump | 2.0 |
| | SprayExpo | Aerosol | 27.3 |
| | | Trigger | 11.1 |
| | | Pump | 3.6 |
| 3) Spraying of a 0.3 m² mirror in a 10 m³ bathroom (use approx.40 g/m²) | ConsExpo 4.1 | Aerosol | 0.20 |
| | | Trigger | 0.00046 |
| | | Pump | 0.00017 |
| | ConsExpo 4.1 With evapouration | Aerosol | 9.3 |
| | | Trigger | 2.2 |
| | | Pump | 0.79 |
| | SprayExpo | Aerosol | 7.5 |
| | | Trigger | 2.9 |
| | | Pump | 1 |
| 4) Spraying of a 0.3 m² mirror in a 10 m³ bathroom (use 10 g/m²) | ConsExpo 4.1 | Aerosol | 0.0056 |
| | | Trigger | 0.0013 |
| | | Pump | 0.000043 |
| | ConsExpo 4.1 With evapouration | Aerosol | 2.5 |
| | | Trigger | 0.6 |
| | | Pump | 0.2 |
| | SprayExpo | Aerosol | 2.5 |
| | | Trigger | 1 |
| | | Pump | 0.34 |

When evaporation is taken into account, the ConsExpo estimations support the SprayExpo results.

Human Cases

There are many uncertainties in the evidence to support the proposal from the incident cases reported. With the exception to the incident cases reported for Magic Nano™ Glass & Ceramic

and Magic Nano™ Bath & WC, the EU incidents provide limited supporting evidence of the components in the sprays and whether an organic solvent was also present in the spray product. However most of the non EU incidents with impregnating proofing sprays did provide supporting evidence of the presence and use of organic solvents in the products. From an exposure perspective, the human incidents reported for Magic Nano appear to be the only incidents that a relationship has been established for exposure to TDFAs and organic solvents in the EU.

Worker exposure

The scope of the Dossier Submitter's proposal is focused on consumer exposure however the reported workplace incidents suggest that risks to workers can also arise from proofing sprays where occupational operational controls and risk management measures are not followed (the incidents reported was following a failure to use RPE and control emissions from a spray booth in Scotland).

Environmental exposure

Environmental exposure from consumer spray products is considered to be very limited as the use occurs indoors with limited release to the external environment. For professional uses the main application is via brushes, roller or high-volume-low-pressure (HVLP) guns. The latter could be the major source of direct release of the substances to the environment.

## Characterisation of risk

***Summary of proposal:***

Consumers

A quantitative risk assessment was carried out for the reaction product of TDFAs and 2-propanol applied by pump spray and in aerosolised form. The risk assessment is based on the product named NFP 1 in the articles by Nørgaard et al. The active substances in this product are hydrolysates and condensates of TDFAs in 2-propanol. Chemical analysis of NFP 1 using electrospray ionization mass spectrometry (ESI-MS) showed that it contained 1.1 ± 0.1 % active substances. The acute 4 hour DNEL was calculated to 0.017 mg/m$^3$.

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

Table 2 shows the measured and calculated exposure concentrations along with the characterisation ratios. A risk characterisation ratio above 1 shows that the risk is not adequately controlled.

**TABLE 2. EXPOSURE ESTIMATES AND RISK CHARACTERISATION RATIOS FOR NFP 1 IN DIFFERENT SCENARIOS**

| Scenarios | | | Mean event concentration (mg/m³) | RCR | |
|---|---|---|---|---|---|
| a1 | Spraying of 4 m² in a 10 m³ bathroom | Pump spray | 13 | 765 | ConsExpo |
| | | Aerosol dispenser | 41 | 2412 | |
| a2 | Spraying of 7 m² in a | Pump spray | 11 | 647 | ConsExpo |

| | | | | | |
|---|---|---|---|---|---|
| | 17.4 m³ bathroom | Aerosol dispenser | 42 | 2471 | |
| a2 | Spraying of 7 m² in a 17.4 m³ room | Pump spray | 1.4 | 82 | Measured values |
| | | Aerosol dispenser | 46 | 2718 | |
| b | Impregnation of a 6.2 m² sofa in a 58 m³ living room | Pump spray | 3.5 | 206 | ConsExpo |
| | | Aerosol dispenser | 11 | 647 | |
| c1 | Impregnation of a pair of shoes/boots in a 15 m³ kitchen | Pump spray | 1.6 | 94 | ConsExpo |
| | | Aerosol dispenser | 5.4 | 318 | |
| c2 | Impregnation of a pair of shoes/boots in a 10 m³ bathroom | Pump spray | 2.5 | 147 | ConsExpo |
| | | Aerosol dispenser | 8.1 | 476 | |

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

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

Table 2 should be interpreted very carefully, as the expected exposure values calculated by ConsExpo are based on a number of assumptions (see Background document B.8.3.2). Exposure concentrations are estimated for exposure durations from 5 minutes to 1 hour. The acute DNEL is based on a standard 4 hour $LC_{50}$. Thus, the RCR may be overestimated. The 4 hour $LC_{50}$ used for calculating the DNEL is based on TDFAs with 2-propanol as a solvent. As described in section 5.2.1 of the Background document, pulmonary toxicity also depends on the chain length/lipophilicity of the solvent. Mixtures of TDFAs and solvents that are less lipophilic then 2-propanol (e.g. methanol) are expected to have a higher $LC_{50}$ value and therefore a higher DNEL. Mixtures containing TDFAs and methanol are expected to have an $LC_{50}$ value that is only slightly higher than mixtures containing TDFAs and 2-propanol (see Background document 5.11). 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 solvent used in this product is a mixture of 2-propanol, 1-methoxy-2-propanol and ethylacrylate (see 5.2.1).

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

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

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

Koch et al. (2009) showed that release of approximately 120 g of the aerosol spray "Magic Nano Glass & Ceramic" in a model room with a volume of 60 m³ resulted in an exposure

concentration of non-volatile components of 11.5 mg/m$^3$ and with a particle size of <10 µm. From this RCRs of 88 and 48 can be derived, which shows that a risk exists, which is in line with the number of incidents that reported for Magic Nano Glass & Ceramic.

No human incidents are reported for the pump spray "Magic Nano Bath & WC". Koch et al. (2009) estimated that the risk of exposure is approximately 20-fold lower for the pump spray "Magic Nano bath & WC" than for the aerosol "Magic Nano Glass & Ceramic".

Taking also into account the fraction that is <10 µm, and the Dossier Submitter's proposal, this number should be adjusted to 20-45 times lower giving RCRs of approximately 2 and 1, indicating a risk, for the pump sprays. Pulmonary effects only occurred in rats exposed to the highest dose tested but 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.

Measured data

Vernez et al. (2004) and Nørgaard et al. (2010d) indicate 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$^3$ room.

Workers

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

***RAC conclusion:***

- **RAC agrees that the risks to consumers and the general public from the use of impregnating aerosol sprays containing TDFAs and 2-propanol are not adequately controlled when used under worst case conditions.**

- **RAC agrees that according to the derived RCR values the risk is higher for aerosols mixtures of TDFA and organic solvents than for trigger and pump sprays, an observation that corresponds with the human incidents reported for aerosol products.**

- **RAC concludes that the risks from trigger sprays are not adequately controlled under realistic worst case conditions and under realistic conditions where larger areas such as tiled areas may have to be treated.**

- **RAC also agrees that according to the derived RCR values the risk is higher for trigger sprays compared to pump sprays. However, exposure may occur, depending on the nozzle design, from the use of pump sprays immediately after application (when the product is applied under worst case conditions where larger areas such as tiled areas may have to be treated) and therefore the risk cannot be excluded.**

- **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 and how the ageing process (reducing the aerosol particle sizes) may affect the hazardous effects of the mixtures of TDFAs and organic solvents.**

***Key elements underpinning the RAC conclusion:***

Based on the RAC derived range of acute DNEL's of 0.068 mg/m$^3$ and 0.21 mg/m$^3$ RAC undertook a quantitative risk assessment for the reaction product of TDFAs and 2-propanol (NFP 1) in aerosols. The following table quantifies the risk based on an exposure assessment from SprayExpo where the concentration is calculated based on exposure to particles <10 µm for aerosol cans, trigger sprays and pump sprays following updated exposure calculations by the Dossier Submitter (Appendix 2 of the background document).

**TABLE 3. SUMMARY OF RISK CHARACTERISATION**

| Scenarios | Model | Spray type | Mean event concentration [mg/m³] | RCR (with DNEL 0.068 mg/m³) | RCR (with DNEL 0.21 mg/m³) |
|---|---|---|---|---|---|
| 1) RWC Impregnation of 3.4 m² tiles in a 10 m³ bathroom (approx. use 40 g/m²) | SprayExpo | **Aerosol** | 97.1 | 1428 | 462 |
| | | **Trigger** | 39.2 | 576 | 187 |
| | | **Pump** | 14 | 206 | 67 |
| 2) RC Impregnation of 3.4 m² tiles in a 10 m³ bathroom (use approx. 10 g/m²) | SprayExpo | **Aerosol** | 27.3 | 401 | 130 |
| | | **Trigger** | 11.1 | 163 | 53 |
| | | **Pump** | 3.8 | 55 | 18 |
| 3) RWC Spraying of a 0.3 m² mirror in a 10 m³ bathroom (use approx.40 g/m²) | SprayExpo | **Aerosol** | 7.5 | 110 | 36 |
| | | **Trigger** | 2.9 | 43 | 14 |
| | | **Pump** | 1.0 | 15 | 5 |
| 4) RC Spraying of a 0.3 m² mirror in a 10 m³ bathroom (use 10 g/m²) | SprayExpo | **Aerosol** | 2.5 | 37 | 12 |
| | | **Trigger** | 1 | 15 | 5 |
| | | **Pump** | 0.35 | 5 | 1.6 |

Table 3 shows that for exposure estimates using SprayExpo all RCR's are greater than 1 for aerosols for both DNELs and therefore the risk is not adequately controlled for consumers and the general public under realistic and worst case conditions.

For trigger sprays the RCRs are greater than 1 under RWC conditions for both DNELs. Trigger spray use in RC conditions for larger areas such as tiled areas is also above 1 for both DNELs.

For pump sprays the RCR is also greater than 1 for RWC scenario where the area to be treated is large. RCRs for pump sprays are lower than trigger and aerosol sprays which supports the very low number of incidents involving pump sprays.

**Uncertainties in the risk characterisation**

Uncertainties relating to the use of models will have an impact on the RCRs. However, they are likely to be less with SprayExpo than ConsExpo (Spray application). Koch et al (2012) found that on average the exposure concentrations are slightly overestimated by SprayExpo

the geometric standard deviation (GSD) of 2.3 means that in about 70% of cases the model is in agreement with the measured values within a factor of 4-5.

When considering the magnitude of the RCR values it is important to note that pulmonary toxicity depends on the ability of the reaction products and solvent to reach the lungs and the lipophilicity of the solvent used as the solvent facilitates contact between the hydrolysates and condensates of TDFAs and the SP-B proteins in the lung. Solvents that are less lipophilic than 2-propanol, are expected to have a slightly lower toxicity whereas mixtures of TDFAs and more lipophilic solvents are expected to have a higher toxicity (in terms of the earlier onset of lung injury in comparison to less lipophilic solvents). However, lack of information on the impact of lipophilicity of different solvents on toxicity does not allow RAC to determine whether any organic solvents would have no toxicity concerns.

While the mass generation rate for trigger sprays used in the model was higher based on information from Delmaar than the mass generation measured by Norgaard it is still in the lower end of the table values from the Delmaar & Feilberg studies which could mean there is still a possibility for higher exposures from aerosol and trigger sprays.

## Evidence if the risk management measures and operational conditions implemented and recommended by the manufactures and/or importers are not sufficient to control the risk

***Summary of proposal:***

The toxic substances in the Magic Nano Glass & Ceramic™ and the Magic Nano Bath & WC™ were likely to be fluorosilane with unknown length of the per/poly-fluoroalkyl chain. The Dossier Submitter assumed that these could be TDFAs, but could not prove its similarity. It is argued by the Dossier Submitter that the observed cases were linked to these specific products.

Toxicity of hydrolysates is dependent on the ability of the hydrolysates to reach the deep lung tissue (<10 µm) and the presence of an organic solvent to facilitate contact with SP-B protein.

Classification and labelling by the manufacturer or importer based only on the individual parent ingredients of the product will not reflect the actual hazard from the reaction products to users following exposure. No evidence has been provided to show that information on this specific hazard has been included in the "other hazards" section of safety data sheets for TDFAs.

Workers exposure

Only very few incidents of occupational exposure to impregnation sprays in aerosol dispensers resulting in respiratory illness are reported.

**RAC conclusion:**

- **Existing risk management measures and operational conditions implemented and recommended by the manufactures and/or importers are not sufficient to reflect the particular hazards associated with consumer exposure to mixtures containing TDFAs and 2-propanol.**
- **Occupational risk management measures for workers which prevent inhalation of the mixture are considered sufficient. The few incidents reported of occupational exposure relate to misuse of occupational controls.**

- **RAC agrees that mixtures of TDFAs and solvent mixtures should be labelled "Fatal if inhaled" to ensure that professionals using the products are aware of the specific hazard associated with the use of TDFAs and organic solvents.**

***Key elements underpinning the RAC conclusion:***

Evidence from the animal study, reported incidents involving magic nano and the exposure modelling support that the risk is not properly controlled. Incidents among workers appear to only relate to the misuse of the substance or failure to comply with occupational risk management measures and controls. As the toxicity hazards are not related to the individual substances on their own but to the mixture of TDFAs and organic solvents, it is important that the inhalation hazards associated with formulated TDFAs and organic solvents is communicated in the supply chain. No evidence has been provided to support that this was happening. Therefore it is important that the "Other Hazards" sections of TDFAs safety data sheet include the inhalation hazards "Fatal if inhaled" that result when TDFAs are formulated with organic solvents in an aerosol form where MMAD particels <10 µm have the potential to be generated. This is to ensure downstream formulators and users take appropriate risk management measures and communicate these hazards further in the supply chain.

## Evidence if the existing regulatory risk management instruments are not sufficient

***Summary of proposal:***

**Product Safety Directive (PSD)** - 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 therefore it is not suitably appropriate to use PSD as the risk management measure to address the risks from other brands of impregnation proofing sprays or other aerosol products containing organic solvents and TDFAs. 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.

**Harmonised C&L** – The parent substances do not fulfil the criteria in CLP, Article 36(1) for proposing a harmonised classification therefore it is not relevant to consider this risk management option for the mixture.

**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. Since it appears that none of the products affiliated with the incidents reported were labelled as acute toxic to humans introduction of an amendment to CLP is not considered a relevant RMO in the context of this proposal.

**Inclusion in the Candidate List with the aim of inclusion in Annex XIV -** 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.

**Voluntary measures**

As 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 it is considered not possible to achieve a comprehensive and effective results through a voluntary agreement.

**Information campaigns**

The Dossier Submitter considers that information campaigns directed to the consumers would have very limited effect, if any, on this problem as only very few consumers are in a position to choose other products than those offered by the retailers and many of the products for bathrooms are used indoors not outdoors. The Dossier Submitter notes that incidents are reported for impregnation product with contents different than mixtures containing TDFAs and organic solvents and an information campaign directed at formulators, producers and distributors on how to classify and label impregnation spray products correctly according to CLP could be suggested but the effect of such a campaign is considered to be uncertain.

***RAC conclusion:***

- ***RAC considers that for issues relating to individual specific products the existing legislation under PSD could be effective in urgent cases (for a limited duration) in having these products removed from the market once the concern is identified. However, PSD is not an appropriate measure as a long-term instrument in preventing the specific issue relating to the hazards associated with the reaction products of TDFAs combined with organic solvents.***
- ***RAC agrees that a restriction under REACH would send a clear message that TDFAs should not be used in conjunction with 2-propanol or any other organic solvent and as such would be appropriate was to prevent future incidents. As the hazard is associated with the use of formulations of TDFAs and organic solvents along with the generation of particles in the respirable range <10 µm. RAC considers there is merit considering a requirement for impregnation/waterproofing pump and trigger sprays to be tested prior to being placed on the market.***

***Key elements underpinning the RAC conclusion:***

**PSD**

PSD is applicable and requires that only safe products are placed on the market. It also contains a requirement that producers must inform consumers of the risks associated with the products they supply. The Directive provides for an alert system (Rapid Alert System for non-food dangerous products - RAPEX) between the EU Member States, Norway, Iceland and Liechtenstein, and the Commission to rapidly inform of dangerous products. The directive applies in the absence of specific European regulations on safety of certain product categories and complements the provisions of sector legislation, which do not cover certain matters. The PSD addressed the safety concern for Magic Nano Glass & Ceramic and the Magic Nano Bath & WC as both were withdrawn from the market in 2006. However, as the general knowledge, of importers and producers, about the risk when combining polyfluoro octyl silanes with organic solvents in spray products is limited each occurance of an incident could only be addressed on an individual product case-by-case basis and therefore it is not suitably appropriate to use PSD as the risk management measure to address the risks from other brands of impregnating/proofing sprays or other aerosol products containing organic solvents and TDFAs.

**CLP**

Classification

The objective of the CLP Regulation is to determine which properties of substances and mixtures requires classification and labelling, such that any hazards from the substance or mixture is identified and communicated to the user. Based on the evidence from the studies on NFP1, mixtures 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 spray products containing TDFAs and organic solvents should classify and label the containers appropriately in accordance with this.

Introducing a harmonised classification is only applicable to substances and it is not applicable as the acute toxicity effect is not known for the individual parent substance but only known to occur from the reaction products when TDFAs arepresent with organic solvents.

The classification (and labelling) on harmonised dangerous properties alone is not an appropriate risk management instrument that prevents the use of (dangerous) ingredients in a product.

Labelling for other hazards

The dossier does not provide evidence as to whether the "Other Hazards" section of safety data sheets (SDS's) for TDFAs substances contains any information that the product should be labelled fatal if inhaled when combined with organic solvents. It appears that in none of the incidents reported, the products were labelled as acute toxic to humans which could be deduced that the "Other Hazards" section of SDS for TDFAs did not contain information on the specific concern with the use of TDFAs with organic solvents.

Packaging

Annex II Part 3 "Special rules on packaging" has no provisions that restrict the use of aerosol packaging on substances and mixtures intended for supply to the general public that are classified as "Fatal if inhaled".

**REACH**

REACH Article 129 Safeguard clause.

RAC considers that the outbreak of incidents involving impregnation sprays, such as the case of Magic nano, are justifiable grounds for considering national action under the REACH safeguard clause. However, Article 129 still contains a provision for the preparation of an Annex XIV dossier where the measure is to restrict the placing on the market.

Guidance

Guidance on waterproofing aerosols has been developed by some national authorities[14] which recommended the characterisation of the particle size distribution of the spray product, and inhalation testing on the formulation (active ingredient and solvent) to be tested in a modified OECD TG 403 test at a MMAD between 0.7 and 1.5 µm. In this document it is referred to the US Silicones Environmental, Health and Safety Council (SEHSC) mentioning that particle size

[14] Guidance for Industry. Recommendations on waterproofing Aerosols in order to Minimisze Consumer Inhalation Toxicity Risks. Authors: Federal Office of Public Health, Switzerland. Food and consumer Product Safety Authority, The Netherlands. Federal Institute for Risk Assessment, Germany, December 2008

MMAD should be at least 30 µm with no more than 1% of particles < 10 µm. The Japanese guideline[15] recommends the ratio of MMAD particles <10 µm should not exceeds 0.6%.

Guidance on Safety Assessment of impregnation sprays is also published by industry[16] refers to the above mentioned guidance document[17] and recommends that the concentration of respirable particles should be outside the critical range. However no information on the thresholds for critical fraction of respirable particles were given neither in this document nor in the linked document of the European Aerosol Federation[18].

Technical solutions may exist in theory assuming that hazardous effects could be prevented e.g. if no relevant fraction of particle sizes < 10 µm were produced during the spray application. However no information is available to estimate which fraction of <10 µm particles could be considered as safe. Whether 1% as recommended by SEHSC is safe, remains open regarding the observations of Yamashita et al. (1997) who observed lung damage in mice at 1.6 ±0.03 % of <10 µm partiles of fluorocarbon resins with n-heptane as solvent.

# JUSTIFICATION IF ACTION IS REQUIRED ON AN UNION WIDE BASIS

## Justification for the opinion of RAC

***Summary of proposal:***

The Dossier Submitters justification for acting on a Union-wide basis originates from the EU-wide distribution of incidents of lung injuries due to use of spray products by consumers in order to avoid different legislative requirements in Member States creating unequal market conditions. The proposed restriction addresses the risk for consumers arising from use of spray products containing mixtures containing (3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanetriol and its TDFA derivatives 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. In order to adequately protect consumers, the dossier submitted considers that a restriction should target imported as well as EU produced spray products intended for use by consumers and the general public.

***RAC conclusion:***

**Based on the key principles of ensuring a consistent level of protection across the EU and of maintaining the free movement of goods, RAC support the view that any necessary action to address risks associated with (3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanetriol and its TDFA derivatives, (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 in all Member States.**

***Key elements underpinning the RAC conclusion:***

RAC notes that while the parent substances in proofing and impregnating sprays implicated

[15] https://www.ncbi.nlm.nih.gov/labs/articles/26821469/ Particle Size Distribution of Aerosols Sprayed From Household Hand-Pump Sprays Containing Fluorine-Based and Silicone-Based Compounds T Kawakami et al. Kokuritsu Iyakuhin Shokuhin Eisei Kenkyusho Hokoku (133), 37-41. 2015.

[16] http://www.ikw.org/fileadmin/content/downloads/Haushaltspflege/HP_Example-impregnation-spray.pdf

[17] Guidance for Industry. Recommendations on waterproofing Aerosols in order to Minimisze Consumer Inhalation Toxicity Risks. Authors: Federal Office of Public Health, Switzerland. Food and consumer Product Safety Authority, The Netherlands. Federal Institute for Risk Assessment, Germany, December 2008

[18] http://www.aerosol.org/publications/7/36/Guide-on-Particle-Size-Measurement-From-Aerosol-Products

in human incidents could not be identified there is some evidence linking the presence of (3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanetriol and its TDFA derivatives and solvents in Magic Nano Glass & Ceramic and Magic Nano Bath & WC.

While information has been made available during the public consultation for products containing TDFA's & organic solvents this has only been with respect to professional uses.

RAC also notes that while the PSP Directive is applicable and resulted in the withdrawal of the market of Magic Nano Glass & Ceramic and Magic Nano Bath & WC http://ec.europa.eu/consumers/consumers_safety/safety_products/rapex/alerts/main/?event=main.weeklyReport.Print&web_report_id=165 this was a specific product measure. There is currently no restriction under REACH on the placing on the market of mixtures of TDFAs 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.

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".

This proposal only targets mixtures of TDFAs and solvents. While evidence of the parent substance is not available for all incidents reported involving proofing or impregnation sprays, there is evidence that many of the proofing sprays contained solvents. As the hypothesis for the toxic effect is that the solvent, depending on its lipophilicity, facilitates contact between the "proofing reaction products" and the SP-B proteins in the lung thus inhibiting the pulmonary surfactant. This hypothesis may also be relevant to other impregnating sprays. Therefore, importers and formulators of proofing sprays should consider this information when classifying mixtures that use organic solvents with other proofing parent substances in aerosol packaging to establish if those mixtures might have similar effects when packaged for use as aerosols or sprays. There is also merit based on cases with other impregnating/proofing aerosol products to consider a requirement to test the toxicity of such products prior to being placed on the market.

## Justification for the opinion of SEAC

***Summary of the proposal:***

The main objective of the proposal is to reduce or prevent consumers' exposure to mixtures containing TDFAs used in a combination with organic solvents in spray products intended for consumers across all EU Member States. The risk is not related to TDFAs as substances on their own but to the hydrolysis and condensation products of TDFAs when they are used together with organic solvents. The proposed scope of the restriction proposal is targeted to spray products for supply to the general public.

The Dossier Submitter, reported several cases involving respiratory disorders were observed in a number of Member States following the application of proofing/impregnation spray products on the surface of absorbing or non-absorbing materials since 1979, as evidence that the targeted spray products pose an unacceptable risk. The Dossier Submitter also reported on scientific studies showing that aerosolised mixtures of TDFAs and organic solvents can

cause serious acute lung injury in mice. Spray products based on those mixtures for proofing/impregnation surfaces are commercially available for professional users and could also be available for the general public. Therefore, risks to human health caused by such products, specifically among the general public, are according to the Dossier Submitter the justification for the proposed restriction.

To support that action is required on an EU wide basis, the Dossier Submitter argues that proofing/impregnation spray products may be produced, imported and used in all Member States. The proposed restriction targets both products used for absorbing surfaces (textile and leather) and non-absorbing surfaces (tile and ceramics). According to the assumptions made by the Dossier Submitter about 20-200 kg TDFAs in approximately 6 800 – 100 000 spray product units (in combination with solvents) are sold yearly to the general public. Incidents to consumers from the use of impregnation sprays have been documented in seven EU Member States, namely Denmark, France, Germany, the Netherlands, Spain, Sweden and the United Kingdom. It is not known if these sprays contained TDFAs or not. The Dossier Submitter has therefore assessed that an EU wide restriction is necessary to minimise the risks. It is also highlighted that an EU wide restriction would remove any potential distorting effects that national restrictions might have on the free circulation of goods on the common market, and thereby ensuring equal market conditions and a level playing field for all the actors on the internal market.

***SEAC conclusions***

See opinion of SEAC.

***Key elements underpinning the SEAC conclusions***

See opinion of SEAC.

## JUSTIFICATION WHETHER THE SUGGESTED RESTRICTION IS THE MOST APPROPRIATE EU WIDE MEASURE

### Justification for the opinion of RAC

***Summary of proposal:***

The dossier provides a short overview of possible EU wide legislative measures as well as 2 RMOs that are further assessed in addition to the proposed restriction. These EU wide legislative measures are the following:

**RMO1 (proposed restriction):**

A ban of mixtures containing (3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanetriol and its TDFA derivatives and organic solvents in spray products for consumer use with a concentration of TDFAs equal to or greater than 2 ppb by weight.

The proposed restriction was considered by the Dossier Submitter to be the most appropriate EU wide measure due to its higher effectiveness, proportionality and practicality, compared to the other RMOs. Alternatives to (3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanetriol and its TDFA derivatives in combination with organic solvents are available at the same price according to the Dossier Submitter.

**RMO2:**

A ban of mixtures containing (3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanetriol and its TDFA derivatives and organic solvents in spray products for consumer use with a concentration of (3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanetriol and its TDFA derivatives equal to or greater than 0.00008% (800 ppb).

Compared to the proposed restriction, the Dossier Submitter foresees that for the same capacity of risk reduction, RMO2 would bring significantly higher costs for monitoring and enforcement. However, the costs for industry might be lower when compared to RMO 1.

RMO 1 & 2 could actually allow the use of polyfluoralkyl trialkoxysilanes with polyfluoralkyl chain lengths different from octyl as a drop in alternative.

**RMO3:**

A ban of mixtures containing (3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanetriol and its TDFA derivatives and organic solvent in aerosol dispensers for consumer use with a concentration of TDFAs equal to or greater than 2 ppb by weight.

This RMO is considered by the Dossier Submitter to have lower risk reduction capacity than RMO 1 and 2 as the risk from spray products other than aerosol dispensers are not addressed. However it is expected that the cost from this RMO is also lower as it would impact fewer actors on the market than RMO1. The Dossier Submitter considers that this restriction have a higher average cost-effectiveness than RMO1, it is easier to implement as other application methods are available at about the same price and lower costs for the enforcement.

**RAC conclusion:**

**While RAC agrees that a restriction is an appropriate EU wide measure to prevent the hazard and associated risks to consumers with the use of sprays containing TDFAs and organic solvents. While there is evidence confirming the previous presence of TDFA's & organic solvents in spray products on the market for consumer use, there is currently (since 2014) no evidence confirming the presence of such spray products on the EU market for consumers. However, as professional products still exist on the market without the proposed restriction in place, there is a potential that these could be replaced on the market for consumer use.**

***Key elements underpinning the RAC conclusion:***

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.

In the case of the use of TDFAs with organic solvents RAC agrees that a restriction on the use of TDFAs with organic solvents is the most appropriate for the following reasons

- Animal tests have shown that when TDFAs is used in combination with organic solvent in impregnating proofing sprays the resulting hydrolysates are acute toxicby inhalation when the product is respirable.
- based on the 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 them 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.

- the acute toxic effect is not evident from data on the individual parent substances so in the absence of test data on proofing sprays these products are likely to be incorrectly classified under CLP.
- While an amendment to CLP Annex II Part 3 would address the packaging of all substances or mixtures classified as acute toxic by inhalation. CLP has no provision to harmonise effects relating to a mixture which is only applicable when two or more substances are used together.
- In general, test data for the purpose of classification and labelling or REACH is applicable to the individual substances rather than testing of the final mixtures. In the case of proofing sprays, as the health effect is not observed following exposure in the individual substances but following exposure to the mixture it is not possible to determine that such an effect exists without there being a requirement to test all proofing sprays mixtures containing organic solvents prior to them being placed on the market. Such a legal provision in not currently in place in the EU.
- 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).
- While a requirement for the testing of the final impregnating/proofing before it is placed on the market would be appropriate in identifying those products which do not comply with the PSD. There is no defined set of appropriate test procedures to test formulated impregnation/proofing spray products.
- There is limited information to support that TDFAs & organic solvent products are currently on the market in the EU for consumers. While RAC consider a restriction would be effective
- RAC cannot conclude, from the reported poisoning incidents whether the proposal warrants an EU wide measure as the Dossier Submitter nor RAC could confirm the presence of TDFAs and organic solvents in the reported accidents involving impregnation, proofing sprays. However RAC consider an EU wide restriction would be effective measure to address the risks (identified in animal studies) associated with the use of mixtures of TDFA and organic solvents in spray products.
- The 725 EU incidents involving these products types have been reported in 8 of the EU Member States (UK, DK, NL, SE, FR, ES, IE & DE) see BD Table 6. RAC do acknowledge that impregnation, proofing sprays are used and available for sale to consumers and the general public across the EU and that a restriction would be appropriate in preventing respiratiory incidents resulting from exposure to TDFAs & organic solvents.

Professional users covered by occupational health regulation are assumed to be provided with 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 and in cases are associated with the misuse of occupational controls to protect workers from exposure.

A restriction under REACH is considered an appropriate risk management measure to control the risks from the use of impregnating proofingsprays of TDFAs and organic solvents.

As the effect has been related to proofing sprays RAC suggests that COM and Member States should perhaps consider whether there is a need to require proofing spray mixtures containing organic solvents to be tested to ensure they are correctly classified, labelled and packaged. Industry would then be able to determine whether proofing products classified as acute toxic by inhalation are suitably safe for use by consumers when placed on the market in aerosol, pump or trigger spray packaging.

## Justification for the opinion of SEAC

## Scope including derogations

***Summary of proposal:***

The dossier provides a short overview of possible EU wide legislative measures as well as two RMOs that are further assessed in addition to the proposed restriction. These EU wide legislative measures are the following:

A Restriction options

RMO1 (proposed restriction)

A ban of mixtures containing TDFAs and organic solvents in spray products for consumer use with a concentration of TDFAs equal to or greater than 2ppb by weight.

The proposed restriction was considered by the Dossier Submitter to be the most appropriate EU wide measure due to its higher effectiveness, proportionality and practicality, compared to the other RMOs. Alternatives to TDFAs in a combination with organic solvents are available at the same price according to the Dossier Submitter. RMO 1 could allow the use of polyfluoralkyl trialkoxysilanes with polyfluoralkyl chain lengths different from octyl as a drop-in alternative, provided that these drop-in raw materials do not contain TDFAs as residues.

RMO2

A ban of mixtures containing TDFAs and organic solvents in spray products for consumer use with a concentration of TDFAs equal to or greater than 800 ppb by weight.

Compared to the proposed restriction, the Dossier Submitter foresees that for the same capacity of risk reduction, RMO2 would bring significantly higher costs for monitoring and enforcement because of the quantitative tests that are significantly more expensive. However, the costs for industry might be lower when compared to RMO 1 if the presence of TDFAs as impurities were below 800 ppb. As RMO2 would allow the use of polyfluoralkyl trialkoxysilanes with polyfluoralkyl chain lengths different from octyl as drop-in alternatives.

RMO3

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

This RMO is considered by the Dossier Submitter to have lower risk reduction capacity than RMO 1 and 2 as the risk from spray products other than aerosol dispensers is not addressed. However, it is expected that the cost from this RMO is also lower as it would impact fewer actors on the market than RMO1. The Dossier Submitter considers that this restriction has a higher average cost-effectiveness than RMO1, it is easier to implement as other application methods are available at about the same price, and enforcement costs are lower.

B Non-restriction options

Harmonised C&L

The Dossier submitter concludes that this risk management option has no potential to reduce or control the risks as the parent substances do not fulfil the criteria in CLP, Article 36(1) for proposing a harmonised classification. Mixtures of TDFAs and organic solvents could fulfil the criteria for classification with Acute Toxicity, Category 1 or 2, but only classification of substances can be harmonised under the CLP Regulation.

Inclusion on the candidate list and eventual inclusion in Annex XIV

This RMO is irrelevant because according to the available information the substances targeted by this proposal do not fulfil the criteria of Article 57 of the REACH Regulation.

Amendment to CLP Annex II part 3

The Dossier Submitter notes that if the Commission introduces 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" this could result in a removal of the most dangerous impregnation products from the market if they are classified correctly. However, it seems that none of the products related to the reported incidents were labelled as acute toxic to humans, and so, this RMO is considered not relevant in the context of this restriction proposal by the Dossier Submitter.

Establishment of an IOEL for the workers environment under Workers Legislation

This RMO is irrelevant as workers are out of the scope of this restriction proposal.

Product Safety Directive

The Dossier Submitter has rejected the Product Safety Directive (PSD) for a number of reasons. The first reason is that the knowledge of importers/producers about the risk combining TDFAs with organic solvents in spray products is limited. The second reason is the periodic revisions foreseen and the fact that this directive imposes a case-by-case evaluation. The third argument presented by the Dossier Submitter is that the directive should be linked to the relevant products specific legislation, which in this case is according to the Dossier Submitter the REACH regulation.

Voluntary agreements

It is claimed by the industry that 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. Therefore, there is a risk that a number of companies will be out of the voluntary agreement between some parties. Therefore, this RMO is considered likely

by the Dossier Submitter to be ineffective in order to control the risks. Furthermore, the manufacturers sell TDFAs to distributors and not directly to the producers of proofing/impregnation products.

Information campaigns including labelling

The Dossier Submitter claims that information campaigns directed to consumers have very limited effect. The ground for this claim is based on experience that shows that private consumers have used the products indoors even if it is stated on the label of the spray products that the product should only be used outdoors. Additionally, for such product types to be used on furniture or in bathrooms, it is reasonable to expect that these products will always be used indoors.

***SEAC conclusion***

See opinion of SEAC.

***Key elements underpinning the SEAC conclusion***

See opinion of SEAC.

## Effectiveness in reducing the identified risks

### Justification for the opinion of RAC

***Summary of proposal:***

The restriction is considered effective in reducing the risks for consumers when applying mixtures based on TDFAs and organic solvents. 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 the lack of convincing animal toxicity data and 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 potentially harmful mixtures (e.g. causing lung injury) of other mixtures of fluorinated substances and organic solvents.

Introduction of a risk-based limit value of e.g. 0.00008% (0.8 mg/kg, 800 ppb, based on the risk calculation for an aerosolised NFP 1-like product (see BD B.9.1.1.2.) and an extra assessment factor of 10 for combinations of TDFAs and organic solvent) for spray products containing TDFAs and organic solvents has been considered by the Dossier Submitter (the analytical detection limit is 2 ppb). This limit would avoid that other mixtures containing other substances where TDFAs could be found as an impurity would be effected.

***RAC conclusion:***

- **RAC considers that in the absence of appropriate provision for the testing of of the final impregnating/proofing before it is placed on the market, a REACH restriction is an appropriate risk management measure addressed at consumers as it will specifically reflect the particular concerns of the use of TDFAs and solvents in mixtures placed on the market in spray products. However, as the incidents and the risk assessment have related to proofing impregnation/sealing sprays the ECHA guidance on restrictions should reflect this.**
- **The proposal does not restrict uses of TDFAs and organic solvent mixtures by industrial and professionals. However, RAC notes that there is a need to ensure mixtures of TDFAs and organic solvents are correctly labelled as fatal if inhaled to ensure that professional and industrial users are properly informed about the hazards.**

***Key elements underpinning the RAC conclusion:***

While PSD may be effective in the case of removing individual products on a case by case basis from the market there is no risk management measure currently in place that prevents the risk or specifically reflects the particular reaction product hazard when the general public use TDFAs and solvents in spray products.

The current proposed measure will address not only the placing on the market of proofing and impregnating sprays but all spray products placed on the market for sale to the general public and consumers.

As professional and industrial uses are not proposed for restriction there is a need to ensure communication of information in the supply chain and that all mixtures of TDFAs and organic solvents are appropriately labelled "Fatal if inhaled".

## Socio-economic impact

### Justification for the opinion of SEAC

#### Costs

***Summary of proposal:***

The Dossier Submitter submitted a qualitative assessment of the proportionality of the restriction proposal and also some quantitative information on the assessment of costs such as:

- prices of some alternative substances;
- estimated cost of the laboratory tests to ensure compliance;
- a rough estimation of the annual number of units of spray proofing/impregnation products containing TDFAs used with organic solvents on the market and an estimation the consumer price per can an assessment of reformulation costs per formula using the estimation presented for D4/D5 substitution as a benchmark.

No information on reformulation costs for mixtures of TDFAs and organic solvents used in spray products for consumers is available because there is no information about the number of formulas that need to be reformulated. However, it is identified that costs are expected

only for substitution to other substances than polyfluoroalkyl trialkoxysilanes, which might be more complicated and therefore would imply an increase of reformulation costs. All the quantitative information was used by the Dossier Submitter to substantiate the assessment.

Production and compliance costs

No significant impacts have been identified by the Dossier Submitter for any of the actors manufacturing, formulating, importing, or supplying TDFAs or mixtures based on TDFAs or any other polyfluoroalkyl trialkoxysilanes.

For consumers using the spray products with TDFAs and organic solvents, no significant impacts have been identified by the Dossier Submitter as the substitution to other mixtures (polyfluoroalkyl trialkoxysilanes with different polyfluoroalkyl chain than the octyl chain), or alternative application methods, have not previously influenced the price of the final impregnation product. For all niche applications, it is not known whether any loss of functionality would occur.

The conclusion of the Dossier Submitter is that the compliance costs, in general, would be quite limited for the concerned actors.

Distribution of costs and impacts on sales

The Dossier Submitter has not identified any impacts on sales or distribution of costs for any of the concerned actors in the supply chain. For the TDFAs manufacturers in the EU (<4 manufacturers), it is estimated that less than 10 % of TDFAs annual production is used in proofing/impregnation spray products. From these assumptions, DS estimates that only 1% is used in the products targeted by this restriction proposal. The estimated yearly volumes sold in spray products in combination with solvents to the general public are 20-200 kg. SEAC presumes that these figures include imported TDFAs with polyfluorooctyl trimethoxysilane which, according to the available information, is not manufactured in the EU. The number of cans sold yearly to the general public is estimated at 6 800-100 000 cans. With an estimated turnover of €8-12 per can, these cans represent a total annual turnover between €54 000 and €1 200 000.

According to the Dossier Submitter, the number of formulators and producers of aerosol dispensers containing TDFAs is not known. But based on information from industry, the number of producers, including producers for professional uses of TDFAs, may likely be in the range of tens to several hundred companies.

Costs for ensuring compliance

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.

For other alternatives substances, as insufficient information is given about their use in the spray products in the Safety Data Sheets, importers, distributors and retailers may need to request further information from the producers of the spray products. The additional costs for such compliance documentation are considered to be very small by the Dossier Submitter without making any quantitative estimations of these costs.

Additional compliance checks may have to be carried out by various actors in the supply chain. It is expected by the Dossier Submitter that downstream users and dealers would rely on information from manufacturers while the costs for verification by laboratory tests would probably be relatively small. The costs for testing may be limited to around €300 per test, for a qualitative analysis aiming to indicate whether the product contains one or more substances

meeting the target group formula. If a qualitative analysis is conducted aiming to identify all substances that meet the targeted group formula used in the product, the cost would be around €1 000. Actors in the supply chains for the concerned sector are used to exchange information on hazardous substances used in products.

The Dossier Submitter foresees that importers are likely to require documentation about the compliance of the imported products with the restriction. The foreign producers are expected to bear the costs for documenting compliance for imported products. The administrative costs for importers to collect and verify the documentation are considered insignificant according to the assessment by the Dossier Submitter.

Reformulation costs

Polyfluoroalkyl trialkoxysilanes with polyfluoralkyl chains different from the TDFAs were considered as drop-in alternatives which could easily substitute TDFAs in proofing/impregnation spray products, without including any extra costs. The Dossier Submitter does not foresee the need for any changes to process and the prices of raw materials of the alternatives are at the same level or cheaper than TDFAs. There is no information if the substitutes will be used in the same amounts as TDFAs, but a lower performance could be expected for these substances with polyfluoralkyl chains length shorter than TDFAs. No significant reformulation costs are expected for these alternatives. However, the substitution of TDFAs in proofing/impregnation spray products by other substances than polyfluoroalkyl trialkoxysilanes might not be so easy. In the absence of other information, the Dossier Submitter has used the estimation of the reformulation costs to substitute D4 and D5 in wash-off personal care products as a benchmark for the reformulation costs of TDFAs. The Dossier Submitter concludes that the annualised costs of reformulation per formula should be 30% of the estimated value for D4/D5 substitution, which is €8 000-12 000.

***SEAC conclusion***

See opinion of SEAC.

***Key elements underpinning the SEAC conclusion***

See opinion of SEAC.

**Benefits**

***Summary of proposal:***

According to the Dossier submitter, the yearly average number of EU28 consumer incidents related to spray products containing TDFAs and organic solvents are estimated to 330-660 cases. This estimated number of incidents due to sprays containing TDFAs and organic solvents is based on an extrapolation of the numbers of calls to the Danish Poison Control Hotline (2200 calls, central value) regarding impregnation spray products in general (Table 6 of the Background Document). The ratio of the Danish population to the total EU population was used together with the assumption that 20% to 40% are related to exposure of TDFAs in organic solvents, to derive the number of reported incidents related to impregnation sprays containing TDFAs in Europe. The benefits of the proposed restriction would avoid incidents of respiratory illness. The avoided costs related to respiratory diseases are monetised at €160 000- €460 000. That is the estimated total annual health benefits for the EU from the implementation of the proposed restriction.

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

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

The Dossier Submitter considers the environmental benefits of the proposed restriction to be small as the substances concerned are expected to be substituted with other application methods of the same substances or substances with a similar environmental profile. For alternative mixtures based on polyfluoroalkyl trialkoxysilanes with shorter polyfluoroalkyl chains, the data on environmental effects are limited.

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 conclusion***

See opinion of SEAC.

***Key elements underpinning the SEAC conclusion***

See opinion of SEAC.

**Other impacts**

***Summary of proposal:***

The other impacts assessed by the Dossier Submitter regards the social impacts and wider economic impacts such as loss of export revenue and distributional impacts. None of the other impacts assessed are considered by the Dossier Submitter to be significant for the actors of concern.

*Social impacts*

The Dossier Submitter considers the potential loss of employment to be marginal. The Dossier Submitter has identified that the proposed restriction could 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. This implies a situation where a substitution is made for other application methods. If a substitution leads to the use of mixtures based on polyfluoroalkyl trialkoxysilanes with other polyfluoroalkyl chain lengths than TDFAs, it is estimated by the Dossier Submitter that this would have very limited effect on the employment in the EU for the manufacturers of the substances due to the very low volumes used.

The possible changes in price for the end users are not considered to be significant by the Dossier Submitter as the alternatives are not more expensive.

*Wider economic impacts*

Loss of export revenue

According to the Dossier Submitter the proposal will not influence the export of the substance or the use of the same in mixtures in spray products.

The main producers of the affected products are small companies carrying their own brands supplying for a regional or local market. No impacts have therefore been identified by the Dossier Submitter for producers of spray products organised in the trade associations. The consultation with industry conducted by the Dossier Submitter, assisted by ECHA, during the development of this restriction proposal also confirms this. The exportation to non EU countries as well as the loss of revenue due to the implementation of the proposed restriction is estimated to be marginal by the Dossier Submitter.

Distributional impacts

The Dossier Submitter has indicated that the proposed restriction could result in small distributional effects due to a change from companies specialised in the production of spray products to companies filling the mixtures on trigger sprays.

***SEAC conclusion***

See opinion of SEAC.

***Key elements underpinning the SEAC conclusion***

See opinion of SEAC.

**Overall proportionality**

***Summary of proposal:***

The Dossier Submitter concludes that the proposed restriction is proportionate to the risk as alternative application methods and other spray products without TDFAs are already available. Furthermore, the negative effects on the market are estimated by the Dossier Submitter to be marginal while potential health effects of the application of the targeted mixture in aerosol dispensers are expected to bring positive effects.

The following elements were mentioned by the Dossier Submitter to support that the proposed restriction is proportional to the risks:

- It has been demonstrated in animal studies that the reaction products of the targeted mixtures applied as aerosol cause adverse effects of the same type as reported from many incidents of a syndrome of acute lung injury. The 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 manufacturers 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 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

***SEAC conclusion***

See opinion of SEAC.

***Key elements underpinning the SEAC conclusion***

See opinion of SEAC.

## Practicality, incl. enforceability

### Justification for the opinion of RAC

***Summary of proposal:***

The proposed restriction is considered effective in reducing the risks for these mixtures in particular although other impregnation agents are not addressed by this proposal. This proposal avoids the issue that at the present, there is a lack of standardised test methods to quantify 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanetriol and its TDFA derivatives.

The restriction requires that 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanetriol and its TDFA derivatives is prohibited from being formulated along with organic solvents in the production of spray products intended for supply to the general public in the EU. This message is easy to communicate down the supply chain and the restriction can be enforced.

A standardised method would ensure reproducible enforcement. A combination of two methods for analysing the targeted substances were suggested, the technical devices can be purchased. The detection limit of these methods is 1-2 ppb.

***RAC conclusion:***

- **RAC agrees the message that 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanetriol and its TDFA derivatives must not be used in mixtures along with organic solvents in spray products intended for supply to the general public is clear message that can be communicated in Annex XVII REACH**.

- **RAC agrees that the proposed legal text by the Dossier Submitter is not exclusive to cover proofing impregnating products but would also apply to any spray product supplied to the general public and consumers containing an organic solvent and TDFAs.**

- **RAC has suggested some rewording to try and make it clear that the restriction only applies to sprays products when 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanetriol and its TDFA derivatives and organic solvents are used together in the one mixture.**

- **Enforcement of the 2 ppb requirement would require confirmation from formulators and importers of spray products that 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanetriol and its TDFA derivatives in combination with organic solvents are not present in consumer spray products.**

- **The limit of 2 ppb allows industry and enforcement authorities to determine that no relevant concentration of 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanetriol and its TDFA derivatives is present in the spray product and thus the product is in compliance with the requirement for the absence of TDFAs and organic solvents in the mixture.**

- **For products containing (water-based) 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanetriol and its TDFA derivatives above 2 ppb information on the lack of organic solvents must be generated. In addition standard methods on residual solvents are established (Headspace method**

**USP 467[19]) and can be conducted by enforcement authorities.**

- **RAC agrees with Forum's advice that formulation of mixtures containing organic solvents and** 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanetriol and its TDFA derivatives **alone shall not be included in the restriction based on the lack of evidence on the risk related to formulation as such.**

- **RAC agrees that manufacture of spray products containing organic solvents and** 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanetriol and its TDFA derivatives **that will be used in the EU (and their imports) should be restricted. However it is to note that manufacture of products to be exported are not covered by a restriction measure under REACH.**

- **RAC notes that further validation through COM on standardisation of analytical methods is needed.**

***Key elements underpinning the RAC and SEAC conclusion:***

The incidents of concern identified is in proofing sprays and the risk assessment has been based on proofing sprays. Information from poison centres continues to be reported for impregnation products however there is still no evidence available that these products contain mixtures of TDFAs and organic solvents. The dossier highlights that those formulating and importing these products are not aware of the risk so by focusing the restriction on these products it may be better at raising awareness in the sector. The current wording would mean that all consumer sprays containing organic solvents would have to be checked that they do not contain 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanetriol and its TDFA derivatives .

Forum raised the question whether the sampling of liquids and pressurised fluids fit with the proposed methods which were not yet tested for TDFAs analysis. The Dossier Submitter clarifies that TDFAs are to analysed in the released spray.Spray products generating a single peak of TDFAs in the spray mist that exceeds 2 ppb are within the scope of this restriction.

As the TOP Assay which was initialy proposed as a commercially available test method has not been tested for suitability to detect TDFAs, the Dossier Submitter considers to replace the TOP Assay method with the combination of direct infusion ESI-MS and APCI-MS for the analysis (Norgaard et al., 2010b and 2010c) which is also commercially available. The low temperature plasma (LTP) ionisation has been recommended to detect 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanetriol and its TDFA derivatives in their unreacted state. However, this method is not commercially available. Both methods (with a LOD of 1-2 ppb) will be able to detect 2 ppb.

Forum recommends to use the limit of quantification which according to good science practice should be 10 times greater, however the Dossier Submitter insists on a limit value based on a non-detectable content of TDFAs. RAC understands that 2 ppb is not a risk based value, rather the restriction proposal intends to ban TDFAs in the organic solvent mixture.

In principle, other spray products containing polyfluorinatied trialkoxysilanies may be affected when TDFAs occur in trace levels. The Dossier Submitter indicates that the existence of TDFAs as impurities is unknown to the Dossier Submitter, in such cases the spray products will also be covered by the restriction.

A ban on the formulation of mixtures containing TDFAs is a not necessary condition from the Forum's view. A ban on the formulation of TDFAs and organic solvents was included by the

[19] USP 467 Residual Solvents https://hmc.usp.org/sites/default/files/documents/HMC/GCs-Pdfs/c467.pdf

Dossier submitter to ease the enforcement. The Dossier Submitter explained that this relates to manufacture of impregnating sprays in the EU which is something that can be checked by inspectors through inspection of practices and documentation on sites where such spray products are manufactured in the EU without the need to undertake any chemical analysis.

A previous producer of the formulation for spray products for the supply to the general public and for professional applications can still use the formulation for the professional products. FORUM and the Dossier Submitter agreed that the labelling of mixtures for professional use only may be helpful.

FORUM considered that the proposed restriction wording would require modification and an appropriately available test method to be enforceable. The Dossier Submitter clarified the following following Forum advice.

- The proposed test method is a combination of direct infusion ESI-MS and APCI-MS for the analysis of the parent substances which has a LOD of 1-2 ppb.

- The proposed limit of 2 ppb applies to any individual TDFAs or related intermediate TDFAs detected in the spray and does not require quantification of TDFAs in a chemical mixture (i.e. no LOQ is required for enforcement) as the quantification is complex and an expensive task.

- Mixtures that contain other polyfluoroalkyl trialkoxysilanes with TDFAs in trace levels above the limit value exist should be considered as coming within the scope of the restriction.

- The scope of the restriction is intended to apply to individual substances and not to the cumulative level of all TDFAs substances. The justification is that an impregnation mixture should contain between 0.5 and 2 % TDFAs. If a mixture contains more than one substance belonging to the group of TDFAs they will react with the solvent to create the same intermediate TDFAs if the solvent is an alcohol. In this case it is the sum that is actually measured.

- The intention behind prohibiting the formulation of TDFAs and organic solvents in spray products on the EU market intended for sale to the general public is to assist enforcement (enforcement can be done upon site inspection by checking inputs to production).

- It is not intended to prohibit the formulation of such products for export outside the EU. The restriction should apply to all consumer spray products for the purpose of impregnation or sealing of the surfaces/materials of concern.

- According to the background document the detection limit (LOD) for ESI-MS and APCI-MS depends on the Mass Spectrometry (MS) equipment and that for modern equipment a LOD of 1-2 ppb can be achieved for the parent silanes. The limit proposed is 2 ppb.

- According to Nørgaard et al. 2010: *Characterisation of nanofilm spray products by mass spectrometry* it is possible to distinguish between polyfluorooctyl trimethoxysilane and polyfluorooctyl triethoxysilane. Some peaks in the MS will, tough, overlap (be the same). However, if the mixture contains an alcohol (e.g. 2-propanol) that can react with the alkoxy part of TDFAs it is the MS-spectrum of this new intermediate TDFAs (e.g. polyfluorooctyl triisopropoxysilane) that will be seen.

- Information from the public consultation has not identified any spray products

containing TDFAs and organic solvents for consumers since 2014. It did yield information relating to 8 products for professional use containing TDFAs, 4 of which are water-based and for absorbing surfaces with the other 4 products being organic solvent based.

## Justification for the opinion of SEAC

***Summary of the proposal:***

As the proposed restriction includes a ban on the use of TDFAs in mixtures used in spray products it is considered effective in reducing the risks for these mixtures in particular because other impregnation agents are not addressed by this proposal. This proposal also avoids the issue that there is a lack of test methods to quantify TDFAs.

For the proposed restriction, the drop-in alternatives available for TDFAs might not be allowed to be used as alternatives, mainly because it is not known if there are no polyfluoroalkyl trialkoxysilanes exclusively with polyfluoroalkyl chain different from octyl polyfluoroalkyl silanes available on the market. The content of TDFAs in these substances as impurity seems likely to occur. However, the Dossier Submitter notes that there are alternatives such as silicones and other alkyl siloxanes available that could provide the same protection however with inferior quality. Also, different application methods of mixtures of TDFAs and organic solvents as well water based mixtures could be used as an alternative instead of the organic solvents. But it is not clear if the water based mixtures would be applicable for non-absorbing surfaces. The Dossier Submitter, therefore concludes that substitution is both technically and economically feasible for these products. The Dossier Submitter also concluded that the proposal is implementable and manageable.

Formulators of products that currently contain TDFAs need to reformulate their products 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. The retailers of aerosol and spray producers may request a declaration from their suppliers that none of their products contains TDFAs. The authorities may as the main instrument for enforcement request information about the content of product composition from the suppliers of the consumer products.

Compliance tests are expected to be undertaken as spot test campaigns and even to assess the level of compliance. The Dosser Submitter claims that at present there are no EU standards neither adequate nor analytic standard method available. The Dossier submitter has proposed to use a combination of direct infusion ESI-MS and APCI-MS in their proposal. In addition, the TOP Assay method, is currently being implemented by a commercial laboratory for analysing PFOA and PFOA precursors, could be adapted to analyse the targeted substances with a limit of detection of 2 ppb. However further information provided after the submission indicates that the TOP assay method might not be applicable to use for running TDFAs analysis as it has not been tested for such a use.

***SEAC conclusion***

See opinion of SEAC.

***Key elements underpinning the SEAC conclusion***

See opinion of SEAC.

## Monitorability

### Justification for the opinion of RAC

***Summary of proposal:***

The Dossier Submitter has proposed that the restriction can be monitored at two levels:
The restriction may be monitored by use of information from national systems for monitoring of poisonings and the EU Rapid Alert System for Non-Food Products (RAPEX).

***RAC conclusion:***

**RAC consider that, unless dedicated inspections are undertaken at the manufacturers of impregnation, proofing etc. sprays or testing is conducted on the final or imported products, determining compliance using RAPEX may not be effective since RAPEX alerts are not an instrument to systematically monitor the presence of new series of incidents and are unlikely to be able confirm the presence of TDFAs in the product.**

***Key elements underpinning the RAC conclusion:***

Enforcement can be undertaken at the production sites or when imported. At the formulation site the ingredients can be checked on-site. The label can be checked for "professional use only" and the SDS can be checked for the presence of 'Fatal if inhaled'. In addition the formulation can be tested for the lack or presence of 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanetriol and its TDFA derivatives and organic solvents.

A comprehensive monitoring system covering all poisoning incidents does not exist in most Member States. Even if such a system were to exist it would be impeded as the active substances of the spray products are usually not indicated on the packaging. The chemical identification of the active substances would therefore not be recorded. In addition RAPEX notification do not reflect the availability of spray products containing TDFAs and organic solvents in a systematic or representative approach on a national or EU level.

Poisoning incident monitoring information would potentially only provide statistics of the number of incidents involving the use of proofing/impregnation products. The data may also provide information on the presence or absence of organic solvent-based spray products, but up to date will in most case not be able to inform about the active ingredients.

The current proposed wording by the Dossier Submitter covers all spray products sold to the general public and not just impregnating proofing sprays it may be difficult for Member States to identify what other products contain TDFA's and organic solvents.

RAC consider unless market surveillance is undertaken or testing is conducted, determining compliance using RAPEX will likely only be based on reported incidents to the national poison centres. Such notifications are unlikely to be able to confirm the presence of TDFAs in the product.

## Justification for the opinion of SEAC

***Summary of the proposal:***

The Dossier Submitter states that the proposed restriction could be monitored either by monitoring of the number of poisoning incidents or the monitoring of non-compliance. To monitor the non-compliance, the Dossier Submitter identifies that the RAPEX system can be used to monitor the compliance with the restriction at an EU level. In addition, national control campaigns could be coordinated by Forum to further monitor the compliance.

***SEAC conclusion***

See opinion of SEAC.

***Key elements underpinning the RAC and SEAC conclusions***

See opinion of SEAC.

# UNCERTAINTIES IN THE EVALUATION OF RAC AND SEAC

**RAC**

***Summary of proposal:***

Several of the uncertainties are related to lack of information and lack of knowledge on downstream uses in the industry. The proposal is based primarily on on the basis of effects seen in experiments with mice exposed to aerosolised mixtures containing TDFAs and organic solvent. The results are compared to incidents reported to poison centres using certain proofing impregnation spray products.

While it is not possible to confirm the human incidents with the actual composition of the spray products, as data on the products composition does not exist. 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. There were 154 incidents in 2006 in Germany involving two aerosol products Magic Nano Glass & Ceramic" and "Magic Nano Bath & WC" which 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.
It is also not possible to confirm if as a result of the poisoning incidents and the requirements of the PSD whether the market has already changed.Following the incidents with Magic Nano consumer products were still available on the market in Sweden until 2014.
It is also not clear to what extent the propsed restriction proposed would affect mixtures based on other polyfluorinated trialkoxysilanes due to trace levels of TDFAs in the mixtures. The present scope is rather narrow and limited to TDFAs while additional incidents exist from uses of products containing less defined fluorinated polymers or other ingredients will not be covered by the restriction proposal. Uncertainties about the effectiveness in reduction of incidents remain.

*RAC conclusion:*

- **RAC agrees that the toxic substances in the Magic Nano Glass & Ceramic and the Magic Nano Bath & WC were likely to be fluorosilanes with unknown length of the per/poly-fluoroalkyl chain.**

- **RAC agrees that parameters such as the application pressure, type of nozzle and volatility of the mixture influence the droplet/particle size. In spray products with a higher percentage of particles less than 10 µm increase the ability and likeliness of the substances to reach the alveoli and thus the toxicity of the product.**

- **RAC agrees that sprays generated from organic solvents may result in particle sizes becoming smaller over time by the evaporation of organic solvents, such that these particles can easily penetrate the alveolus. While no assessment of the variation in volatility of solvents used in aerosols was undertaken in the dossier even if the solvent is replaced with a less toxic solvent that is more volatile, the inhalation exposure will be increased.**

- **RAC agrees similar effects as seen for the Magic Nano aerosol products are to be expected in aerosol products containing TDFAs & organic solvents. Spray products containing TDFAs in mixtures with organic solvents are normally used for non-absorbing surfaces. While it cannot be ruled out that some users could use organic solvent-based agents for absorbing surfaces these products are not marketed for such applications and such use would constitute a foreseeable misuse.**

- **RAC cannot confirm if the risks are properly controlled from all pump and triggers sprays. However, theer is evidence to support that pump and particularly trigger sprays produce aerosols in the range < 10 µm**.

- **In the absence of Forum review on updated information on testing RAC agrees that the proposed test method of using** a **combination of direct infusion ESI-MS and APCI-MS may be a suitabile test method to determine compliance.**

- **Inhalation toxicity testing of each individual compound is not sufficient to assess the hazard of formulated products of TDFAs and organic solvents.**

- **At present no specific (TDFAs-related) consumer incident information on pump and trigger sprays is available. Taking the recent information from commercially available impregnation pump sprays into account that identified particle sizes <11 µm or in the nanometer sizes in pump sprays (Kawakami et al. 2015, Losert et al., 2015), the generation of respirable particles <10 µm can not be excluded. As no firm information exist on the threshold concentration that does not cause harm, there is a potential risk for pump and trigger spray applications.**

- **The Dossier Submitter assumed in the original exposure assessment that all generated aerosols have relevant fractions of MMAD < 10 µm but data from the Koch study (2009) does support this for aerosol products (with more than**

**20% of particles < 10 µm) and a lower particle concentration of respirable fraction for pump sprays (less than 0.9%). Therefore the Dossier Submitters original exposure assessment may have over estimated the risk.**

- **RAC agrees there are greater uncertainties with the applicability of the ConsExpo model compared to SprayExpo. RAC considers that the input parameters for the exposure modelling for pump and trigger spray have greater uncertainty.**
- Key elements underpinning the RAC conclusion(s):

RAC in noting that the Dossier Submitter could not prove the similarity of the products on the market responsible for human incidents considers that the toxic substances in the Magic Nano Glass & Ceramic and the Magic Nano Bath & WC were likely to be fluorosilane with unknown length of the per/poly-fluoroalkyl chain.

While it could be argued there is no need for further action because the PSD was effective in addressing the issue, as the Magic nano specific products were withdrawn from the market PSD is a product specific piece of legislation and will not address the use of TDFAs and organic solvents under other product brand names**.**

The test data on aerosolised mixtures of perfluorinated silanes and 2-propanol confirmed lung toxicity in a mouse model. A study by Yamashita et al[20] which tested 4 identical waterproofing sprays with different mist particle sizes supports that the toxicity of waterproofing sprays is influenced by mist particle size generated. RAC agrees if a similar aerosol product containing a mixture of these substances were on the market, similar effects as seen for the Magic Nano aerosol products are to be expected.

There are no human cases involving pump and trigger sprays containing 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanetriol and its TDFA derivatives and organic solvents. The Norgaard particle size distribution provides information on nebulised TDFAs and organic solvents where concentrations of 16.1 mg/m$^3$ (particles <10 µm) resulted in no lung effects in mice. Therefore considering a theoretical concentration of particles less than <10 µm (after correction for this fraction of 3% in trigger sprays and 0.9% in pump sprays) then it is unlikely that human cases would appear for exposures using pump sprays. This raises some uncertainties regarding the risks from pump and trigger sprays.

It is questionable how effective the monitorability of the restriction will be from national poison centre data due to existing difficulties confirming the presence of TDFA's in the product or from notifications to RAPEX because a comprehensive monitoring system covering all poisoning incidents does not exist in most (if any) Member States.

The Dossier Submitter has indicated that the detection limit (LOD) for ESI-MS and APCI-MS depends on the Mass Spectrometry (MS) equipment and that for modern equipment a LOD of 1-2 ppb can be achieved for the parent silanes. The limit proposed in the dossier is 2 ppb.

The Dossier Submitter does not suggest quantification of TDFAs in a chemical mixture (i.e. no LOQ is required for enforcement) as this is complex and expensive task. Mixtures based on other polyfluoroalkyl trialkoxysilanes that contain TDFAs in trace levels above the limit value exist they will be covered by the restriction.

According to Nørgaard et al. 2010: *Characterisation of nanofilm spray products by mass*

[20] Yamashita M., Yamashita M., Tanaka J., et al. (1997b) Toxicity of waterproofing spray is influenced by the mist particle size.VetHum Toxicol39, 332-33

*spectrometry* is possible to distinguish between polyfluorooctyl trimethoxysilane and polyfluorooctyl triethoxysilane. Some peaks in the MS will, tough, overlap (be the same). However, if the mixture contains an alcohol (e.g. 2-propanol) that can react with the alkoxy part of TDFAs it is the MS-spectrum of this new intermediate TDFAs (e.g. polyfluorooctyl triisopropoxysilane) that will be seen.

**SEAC**

***Summary of proposal:***

The major uncertainties of importance for the socio-economic assessment identified by the Dossier Submitter are the following:

- The number of the reported poisoning incidents for which the targeted mixtures have been the cause.
- 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 effect of the substances.
- The total number of spray products with targeted mixtures sold annually within the EU.
- To what extent the active substances and mixtures for impregnation products that are not based on TDFAs are manufactured within the EU or imported into the EU, respectively.
- The estimation of the reformulation costs using D4/D5 case as a benchmark.
- 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 yet been applied for fluorinated silanes, silanols and siloxanes.
- The risks for spray products based on other polyfluoralkyl trialkoxysilanes different from TDFAs.
- Test costs to ensure compliance.

***SEAC conclusions***

See opinion of SEAC.

***Key elements underpinning the SEAC conclusions***

See opinion of SEAC.

## Appendix 1

**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** | Facric | 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 initial 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% (the critical % <10 µm that corresponds to a DNEL of 0.068 mg/m$^3$ 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 A1 with a droplet/particle size distribution estimated to MMD of 81.5 µm and a GSD of approximately 2.1 reasonably well represents these three trigger spray and will be used for the exposure concentration calculations. 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%.

## REFERENCES

Koch W., Behnke W., Berger-Preiß E., Kock H., Gerling S., Hahn S., Schröder K. (2012) Validation of an EDP assisted model for assessing inhalation exposure and dermal exposure during spraying processes, available from: http://www.baua.de/en/Publications/Expert-Papers/F2137.pdf?__blob=publicationFile&v=9