6:2 Fluorotelomer silanes and silicones: Environment tier II assessment

29 June 2018

CAS Registry Numbers: 51851-37-7, 73609-36-6, 85857-16-5, 85857-17-6, 94158-20-0, 78560-45-9, 104780-70-3, 115340-94-8, 115340-95-9, 115340-96-0, 115341-00-9

Preface

This assessment was carried out by staff of the National Industrial Chemicals Notification and Assessment Scheme (NICNAS) using the Inventory Multi-tiered Assessment and Prioritisation (IMAP) framework.

The IMAP framework addresses the human health and environmental impacts of previously unassessed industrial chemicals listed on the Australian Inventory of Chemical Substances (the Inventory).

The framework was developed with significant input from stakeholders and provides a more rapid, flexible and transparent approach for the assessment of chemicals listed on the Inventory.

Stage One of the implementation of this framework, which lasted four years from 1 July 2012, examined 3000 chemicals meeting characteristics identified by stakeholders as needing priority assessment. This included chemicals for which NICNAS already held exposure information, chemicals identified as a concern or for which regulatory action had been taken overseas, and chemicals detected in international studies analysing chemicals present in babies' umbilical cord blood.

Stage Two of IMAP began in July 2016. We are continuing to assess chemicals on the Inventory, including chemicals identified as a concern for which action has been taken overseas and chemicals that can be rapidly identified and assessed by using

Stage One information. We are also continuing to publish information for chemicals on the Inventory that pose a low risk to human health or the environment or both. This work provides efficiencies and enables us to identify higher risk chemicals requiring assessment.

The IMAP framework is a science and risk-based model designed to align the assessment effort with the human health and environmental impacts of chemicals. It has three tiers of assessment, with the assessment effort increasing with each tier. The Tier I assessment is a high throughput approach using tabulated electronic data. The Tier II assessment is an evaluation of risk on a substance-by-substance or chemical category-by-category basis. Tier III assessments are conducted to address specific concerns that could not be resolved during the Tier II assessment.

These assessments are carried out by staff employed by the Australian Government Department of Health and the Australian Government Department of the Environment and Energy. The human health and environment risk assessments are conducted and published separately, using information available at the time, and may be undertaken at different tiers.

This chemical or group of chemicals are being assessed at Tier II because the Tier I assessment indicated that it needed further investigation.

For more detail on this program please visit: www.nicnas.gov.au.

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Acronyms & Abbreviations

Grouping Rationale

This Tier II assessment considers the environmental risks associated with the industrial uses of 11 polyfluoroalkyl silanes and silicones. All of the chemicals in this group have a common 6:2 polyfluoroalkylsilane structural unit. This unit is composed of a terminal perfluorinated carbon chain segment containing six carbon atoms linked to a silicon atom through a non-fluorinated ethylene unit.

NICNAS has developed an action plan to assess and manage chemicals with a perfluorinated chain of four or more carbons which may degrade to perfluorinated carboxylic acids (PFCAs), perfluoroalkyl sulfonates and similar chemicals. Under the action plan, chemicals with a perfluorinated chain followed by an alkyl or aryl group are assumed to degrade to a mixture of PFCAs with both the original perfluorinated chain length, and with one fewer perfluorinated carbon atom (NICNAS, 2018).

Environmental biodegradation of polyfluoroalkyl chemicals is typically expected to result in the defluorination of at least one perfluorinated carbon atom in the parent chemical. However, these expectations are based on the biotransformation pathways established for fluorotelomer alcohols where the terminal group is an alcohol (Butt, et al., 2014). It is currently unclear whether the biotransformation of polyfluoroalkyl silanes will involve defluorination of one or more carbon atoms. Hence, for the purposes of this assessment, it is assumed that the terminal degradants include at least some perfluoroheptanoic acid (PFHpA; CAS RN 375-85-9), which retains the chain of six fully fluorinated carbon atoms that is common to all of the parent chemicals in this group.

The IMAP Environment Tier II assessment of PFHpA concluded that this PFCA is extremely persistent in the environment and has uncertain bioaccumulation potential and toxicity (NICNAS, 2015a). No data were available to demonstrate that PFHpA is less hazardous to the environment than the hazardous homologue, perfluorooctanoic acid (PFOA; CAS RN 335-67-1), which is

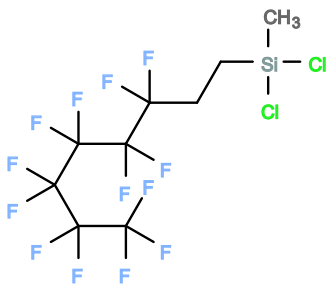
a Persistent (P), Bioaccumulative (B) and Toxic (T) chemical (NICNAS, 2015b). Therefore, under the action plan, PFHpA is considered to be of equivalent concern to PFOA.

The degradation of PFHpA is very slow compared with the rate of formation from degradation of its precursor chemicals. It will therefore be assumed for the purposes of this assessment that the primary risk posed by the chemicals in this group is their contribution to the cumulative concentration of PFHpA in the environment. The IMAP Environment Tier II assessment for perfluoroheptanoic acid (PFHpA) and its direct precursors (NICNAS, 2015a) has been used as a reference assessment.

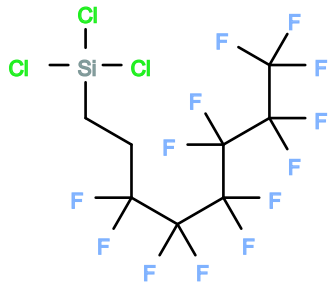
Chemical Identity

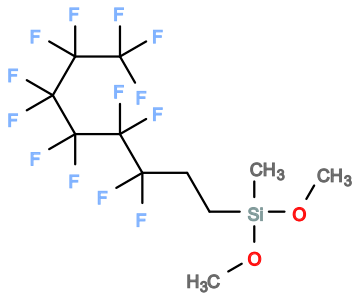
6:2 fluorotelomer silanes

All of the silanes in this group are derived from the linear fluorotelomer olefin, 1*H*,1*H*,2*H*-perfluoro-1-octene (6:2 FTO; CAS RN 25291-17-2) (Buck, et al., 2011). They are all reactive chemicals and some are precursors to the 6:2 fluorotelomer silicones in this group or other related fluorosilicone polymers.

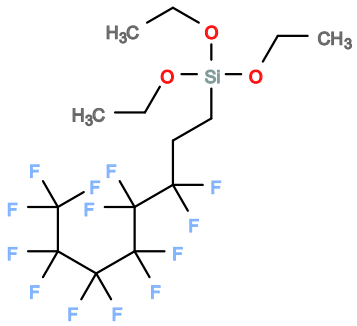
CAS RN	73609-36-6
Chemical Name	Silane, dichloromethyl(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)-
Synonyms	1*H*,1*H*,2*H*,2*H*-perfluorooctylmethyldichlorosilane
Structural Formula	
Molecular Formula	$C_9H_7Cl_2F_{13}Si$
Molecular Weight (g/mol)	461.14
SMILES	[Cl][Si](Cl)(C)CCC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F

CAS RN	78560-45-9

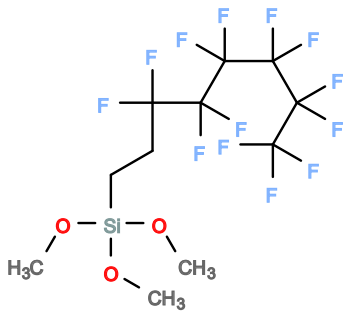
Chemical Name	Silane, trichloro(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)-
Synonyms	1*H*,1*H*,2*H*,2*H*-perfluorooctyltrichlorosilane
Structural Formula	
Molecular Formula	$C_8H_4Cl_3F_{13}Si$
Molecular Weight (g/mol)	481.55
SMILES	FC(F)(CC[Si](Cl)(Cl)Cl)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F

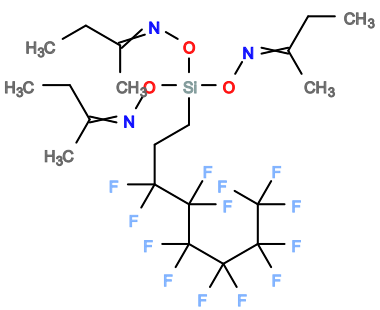
CAS RN	85857-17-6
Chemical Name	Silane, dimethoxymethyl(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)-
Synonyms	1*H*,1*H*,2*H*,2*H*-perfluorooctylmethyldimethoxysilane
Structural Formula	

Molecular Formula	$C_{11}H_{13}F_{13}O_2Si$
Molecular Weight (g/mol)	452.30
SMILES	CO[Si](OC)(C)CCC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F

CAS RN	51851-37-7
Chemical Name	Silane, triethoxy(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)-
Synonyms	1*H*,1*H*,2*H*,2*H*-perfluorooctyltriethoxysilane
Structural Formula	
Molecular Formula	$C_{14}H_{19}F_{13}O_3Si$
Molecular Weight (g/mol)	510.38
SMILES	CCO[Si](CCC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F)(OCC)OCC

CAS RN	85857-16-5
Chemical Name	Silane, trimethoxy(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)-

Synonyms	1*H*,1*H*,2*H*,2*H*-perfluorooctyltrimethoxysilane
Structural Formula	
Molecular Formula	$C_{11}H_{13}F_{13}O_3Si$
Molecular Weight (g/mol)	468.30
SMILES	FC(F)(CC[Si](OC)(OC)(OC))C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F

CAS RN	94158-20-0
Chemical Name	2-Butanone, O,O',O''-[(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silylidyne]oxime
Structural Formula	
Molecular Formula	$C_{20}H_{28}F_{13}N_3O_3Si$
Molecular Weight (g/mol)	633.54

SMILES	CCC(C)=NO[Si](CCC(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)C(F)(F)F)(ON=C(C)CC)ON=C(C)CC

6:2 fluorotelomer silicones

The following chemicals are fluorosilicone polymers that are composed of repeating organosiloxane moieties wherein the silicon atoms of the 6:2 polyfluoroalkylsilane units are connected to adjacent silicon atoms in the polymer backbone through shared oxygen atoms (Moretto, et al., 2012).

CAS RN	104780-70-3
Chemical Name	Siloxanes and silicones, dimethyl, methyl 3-(1,1,2,2-tetrafluoroethoxy)propyl, methyl 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-

CAS RN	115340-94-8
Chemical Name	Siloxanes and silicones, dimethyl, methyl 3-(1,1,2,2-tetrafluoroethoxy)propyl, methyl 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl, hydroxy terminated

CAS RN	115340-95-9
Chemical Name	Siloxanes and silicones, dimethyl, methyl 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl

CAS RN	115340-96-0
Chemical Name	Siloxanes and silicones, dimethyl, methyl 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl, hydroxy terminated

CAS RN	115341-00-9
Chemical Name	Siloxanes and silicones, methyl 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl, hydroxy terminated

Physical and Chemical Properties

Limited experimental physical or chemical property data are available for the chemicals in this group.

According to information in dossiers submitted under the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) legislation in the European Union (EU), the trimethoxy silane derivative (CAS RN 85857-16-5) and the dichloromethyl silane derivative (CAS RN 73609-36-6) in this group are both liquids under ambient conditions (REACH, 2018a; 2018b).

The silanes are expected to hydrolyse in water and release 6:2 polyfluoroalkylsilanols which can undergo self-condensation reactions to form fluoro-organic polysiloxanes (Nielsen, 2014).

Import, Manufacture and Use

Australia

Information collected by NICNAS in 2006 indicated that the chemicals in this group were not manufactured, imported or used in Australia at that time (NICNAS, 2016).

Some of the chemicals in this group may be present in the environment due to historic use or release from pre-treated articles. However, release from these uses is beyond the scope of this assessment.

International

The silanes in this group have identified uses in cosmetics, spray-on nanofilm surface coatings, paints and lacquers, adhesion promoters between inorganic and fluoropolymer materials, and as industrial intermediates in the production of fluorosilicone polymers (Danish EPA, 2015; REACH, 2018a; 2018b; 2018c).

The fluorosilicone polymers represented by CAS RNs 115340-95-9 and 104780-70-3 were reported to have uses in paints, lacquers and varnishes. The polymer represented by CAS RN 115340-95-9 also had reported use in surface-active agents (Nordic Council of Ministers, 2016).

Environmental Regulatory Status

Australia

The use of the chemicals in this group is not subject to specific national environmental regulations.

United Nations

The chemicals in this group are not currently identified as Persistent Organic Pollutants (UNEP, 2001), ozone depleting substances (UNEP, 1987), or hazardous substances for the purpose of international trade (UNEP & FAO, 1998).

OECD

The chemicals in this group have been identified as fluorinated chemicals that potentially degrade to perfluoroalkyl acids (OECD, 2018).

The chemicals in this group have not been sponsored for assessment under the Cooperative Chemicals Assessment Program (CoCAP) (OECD, 2017).

Canada

The chemicals in this group are not listed on the Domestic Substances List (DSL).

There is a Significant New Activity (SNAc) notice in place for the triethoxysilane derivative in this group (CAS RN 51851-37-7) (Government of Canada, 2013). This Notice applies to uses of this chemical in Canada other than as an industrial or commercial surface modification agent, or as an industrial or commercial adhesion promoter between inorganic materials and fluoropolymers.

European Union

The dichloromethyl- and trimethoxy silane derivatives (CAS RNs 73609-36-6 and 85857-16-5, respectively) are registered, and the dimethoxymethyl-, triethoxy-, trichloro- and trioximino-silane derivatives (CAS RNs 85857-17-6, 51851-37-7, 78560-45-9 and 94158-20-0, respectively) are preregistered under REACH.

An Annex XV restriction proposal has been submitted for (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, 2018). The proposal specifically identifies the trimethoxy- and the triethoxy-silanes (CAS RNs 85857-16-5 and 51851-37-7) as examples of derivatives of the 6:2 polyfluoroalkylsilanetriol that are included within the restriction. Under the restriction, these chemicals could not be used at greater than 2 parts per billion in spray product formulations with organic solvents for non-professional use. This restriction proposal is largely based on the inhalation toxicity of some consumer spray products containing these chemicals.

United States of America

A final Significant New Use Rule (SNUR) has been issued for the triethoxy silane derivative (CAS RN 51851-37-7) based on inhalation toxicity (US EPA, 2003). Under the Rule, the United States Environmental Protection Agency (US EPA) must be notified before manufacture, importation, or processing of this chemical for use in the United States.

Environmental Exposure

Based on international use pattern information, the chemicals in this group may have industrial uses in Australia. Release to the environment may occur during the use and disposal of formulations and products containing these chemicals.

For this assessment, it has been assumed that all of the chemicals in this group will ultimately degrade to PFHpA, at least in part. This conservative assumption has been made because there is no information currently available regarding the environmental biotransformation of polyfluoroalkyl silanes. The available information on the environmental fate and behaviour of PFHpA is presented in the IMAP Environment Tier II assessment for perfluoroheptanoic acid and its direct precursors (NICNAS, 2015a).

Studies have identified PFCAs, including PFHpA, in various locations worldwide including in 100 % of samples taken from the Parramatta River (main tributary to Sydney Harbour) and in other locations such as Antarctica and the European Alps (Cai, et al., 2012; Kirchgeorg, et al., 2013; Thompson, et al., 2011; Zhao, et al., 2012). Perfluorocarboxylic acids are extremely persistent in the environment and they are globally distributed pollutants (NICNAS, 2015b; 2015c; 2015d).

Environmental Effects

The chemicals in this group are expected to be degraded to the extremely persistent perfluorocarboxylic acid, PFHpA, in the environment. The currently available environmental hazard data for this PFCA are presented in the IMAP Environment Tier II assessment for PFHpA and its direct precursors (NICNAS, 2015a). The primary toxicity concern for PFCAs is chronic toxicity, especially intergenerational toxicity. There is currently insufficient information to conclude whether the long-term toxicity of PFHpA is comparable to toxic long-chain homologues or to less toxic short-chain perfluorocarboxylic acids. Under the NICNAS action plan, PFHpA is assumed to be of equivalent concern to PFOA which is an extremely persistent and bioaccumulative chemical with high chronic toxicity.

Human health effects of the chemicals in this group are discussed in the IMAP Tier II Health assessment (NICNAS, 2016).

Categorisation of Environmental Hazard

Insufficient data are presented in this assessment to categorise the parent chemicals in this group according to domestic environmental hazard thresholds (EPHC, 2009). The potential terminal degradant, PFHpA, is categorised as being persistent (P), and as having uncertain bioaccumulation potential (uncertain B) and uncertain toxicity (uncertain T) (NICNAS, 2015a).

Risk Characterisation

Risk quotients (RQs) have not been calculated for these chemicals.

PFHpA formed by degradation of the parent chemicals in this group may occur in the environment from multiple sources. Due to their extreme persistence in the environment, levels of PFCAs including PFHpA may continue to increase over time due to indirect release pathways. The scale and time frame of such an increase, and its relevance to characterising the long term environmental risk profile of PFCAs, currently remain unknown.

Key Findings

The chemicals in this group have been identified as indirect precursors to PFHpA with possible industrial uses in Australia. The principal environmental risk posed by these chemicals is assumed to result from their contribution to cumulative environmental emissions of this extremely persistent perfluorocarboxylic acid. The IMAP environment assessment of PFHpA has previously established that this PFCA is of equivalent concern to PFOA. Hence, under the NICNAS action plan, industrial uses of the chemicals in this group in Australia should be restricted to only essential uses and less hazardous alternatives should be used for all non-essential uses.

The findings in this assessment are subject to the assumption that environmental biotransformation of polyfluoroalkyl silanes does not result in defluorination of the perfluorinated carbon chain segment. NICNAS may reconsider whether the chemicals in this group are indirect precursors to PFHpA if sufficient information is made available to demonstrate that polyfluoroalkyl silanes are defluorinated during biotransformation, or that the dominant degradation product from 6:2 polyfluoroalkylsilanes is the short-chain perfluorocarboxylic acid, perfluorohexanoic acid (PFHxA; CAS RN 307-24-4), or shorter-chain homologues.

Recommendations

The common degradation product of the chemicals in this group has been assessed as having the potential to give rise to adverse outcomes for the environment. These chemicals are currently listed on the Australian Inventory of Chemical Substances (the Inventory), and are available to be introduced into Australia without the requirement for assessment by NICNAS. Other chemicals with reduced potential for adverse outcomes are becoming available but, given the properties of these chemicals, their assessment as new chemicals under the Industrial Chemicals (Notification and Assessment) Act 1989 (the ICNA Act) is still required to fully characterise the human health and the environmental risks associated with their use.

It is recommended that NICNAS consult with industry and other stakeholders to consider strategies, including regulatory mechanisms available under the ICNA Act, to encourage the use of safer chemistry.

Environmental Hazard Classification

Insufficient data are available to classify the aquatic hazards of the parent chemicals in this group according to the third edition of the United Nations' Globally Harmonized System of Classification and Labelling of Chemicals (GHS) (UNECE, 2009).

It is noted that PFHpA is classified as Chronic Aquatic Category 4 (H413: May cause long lasting harmful effects to aquatic life) under the GHS (NICNAS, 2015a).

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