NORWEGIAN ENVIRONMENT AGENCY

M-759|2017

INVESTIGATION OF SOURCES TO PFBS IN THE ENVIRONMENT

REPORT OF 15 MAY 2017

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2017
NORWEGIAN ENVIRONMENT AGENCY

SOURCES OF PERFLUOROBUTANE SULFONIC ACID (PFBS) IN THE ENVIRONMENT

REPORT OF 15 MAY 2017

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PROJECT NO.	DOCUMENT NO.
A086083	02

VERSION	DATE OF ISSUE	DESCRIPTION	PREPARED	CHECKED	APPROVED
02	15 May 2017	Final report	AABH/CRL/AAJ	JEK/SIN	CRL

CONTENTS

APPENDICES

Preface

In 2016, the Norwegian Environment Agency collected information about the intrinsic properties, use and exposure of perfluorobutane sulfonic acid (PFBS) to assess the need for risk reduction measures (RMOA analysis) for this substance.

The overall aim of this project is to identify sources of PFBS in the environment by obtaining a better understanding of manufacture and use in the European Economic Area (EEA) and globally of PFBS, perfluorobutane sulfonyl fluoride PBSF and PFBS-related substances. PBSF is the starting material for the manufacture of PFBS and PFBS-related substances.

The project has been followed by a Steering Group consisting of:

- Ingunn Correll Myhre, Norwegian Environment Agency (Chair)
- Marit Kopangen, Norwegian Environment Agency
- Cecile Blom, Norwegian Environment Agency
- Audun Heggelund, Norwegian Environment Agency
- Carsten Lassen, COWI

The study was carried out from August to November 2016 by a working group consisting of Carsten Lassen (Project Manager), Anna Brinch, COWI A/S, Denmark and Allan Astrup Jensen, Nordic Institute for Product Sustainability, Environmental Chemistry and Toxicology, Denmark.

The survey was carried out by means of international market reports, direct contact with relevant companies, assessment of safety data sheets (SDS) and technical data sheets (TDS) for mixtures containing PFBS and related substances, consultation of selected peer-reviewed literature and previous surveys related to the substances.

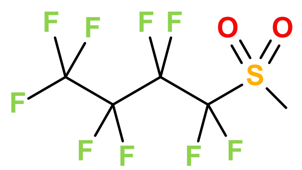
Dialogue with the main manufacturer of PFBS-related substances in the EEA, the 3M Company, was established and the company has provided some information on the application of PFBS-related substances in mixtures and articles. 3M has provided detailed confidential information for the RMOA analysis. The information in this report is aggregated and combined with information from other sources so as not to disclose market-sensitive information. The two other registrants under REACH, Miteni SpA. and SABIC Innovative Plastics BV, did not wish to provide information for the study.

Summary and conclusions

Perfluorobutane sulfonic acid (PFBS) and related substances are short-chain perfluoroalkyl substances used for a number of applications. The starting material for manufacture of the substances is perfluorobutane sulfonyl fluoride (PBSF); the global manufacture of PBSF indicates the total global consumption of PFBS-related substances. Total global manufacture of PBSF in 2015 is estimated at 317 tonnes, of which 299 tonnes are manufactured in China. Some of the PBSF is exported from China; however, some 216 tonnes were used within China for manufacture of products. The study has identified 16 PFBS-related substances with confirmed use. The total volume of PFBS-related substances registered under REACH was 22-210+ t/year, but some substances have confidential volume data; furthermore, registering of some of the substances may occur after the 31 May 2018 deadline. The total content of PFBS moieties of mixtures used in the EEA is estimated at 28-77 t/year. The main application area identified is water and stain repellent protection for leather, textiles and carpets and porous hard surfaces, representing 25-50 t/year of PFBS moieties in mixtures. Minor application areas include surfactants for inks, paints, waxes, etc.; flame retardants for polycarbonate; mist suppressants for metal plating, and surfactants for fluxes for production of electronics. On the basis of the knowledge available regarding applications, the potential for consumer and environmental exposure was assessed.

The substances concerned

This report investigates perfluorobutane sulfonic acid (PFBS) and its derivatives and precursors. These substances are short-chain or polymeric perfluoralkyl substances (PFAS) containing one or more perfluorobutane sulfonyl C_4-moieties:



Perfluorobutanesulfonyl moiety

In this report, the substances are collectively referred to as PFBS-related substances. Tonnages are generally expressed as tonnes PFBS moieties; however, data from REACH registrations and market reports represent tonnages of the substance in its entirety.

The basic substance is unbranched perfluorobutane sulfonyl fluoride (PBSF). Based on PBSF, PFBS, its salts and all other PFBS-related chemicals (functional derivatives, precursors) can be synthesized and produced.

Appendix B presents a gross list of more than 50 PFBS-related substances. Of these, 17 substances with identified CAS numbers or EC numbers and/or confirmed use are included in Table 1 overleaf. For all of the substances but one (with a confidential REACH Registration), the applications of the substances have been identified, but the application within the EEA has not been confirmed for all substances. The list is not considered to be exhaustive, but it is assumed to include the main applications. Full names of the substances are indicated in Appendix B.

Many of the substances have been notified by more than 100 companies in the EU in the Classification & Labelling Inventory under REACH (including all members of joint registrations and notifications), indicating that the substances are widely used in the EU.

Some of the PFBS derivatives are intermediates for the manufacture of side-chain-fluorinated urethane and acrylate polymers. The polymers are not listed in Table 1. The substances MeFBSA, MeFBSE and MeFBSAC are used as intermediates in the production of various fluorochemical acrylate and urethane polymers used as surfactants and in agents for repellent protection of textiles, leather, carpets and hard surfaces. In many of the mixtures, one or more of the three intermediates are present as residual constituents at low levels of <1%. Side chains of the polymer types may possess the ability to be released from the polymer chain to become PFBS precursors. The polymers are generally not pre-registered or registered under REACH, and CAS numbers and their exact composition are indicated as "confidential" in safety data sheets.

Table 1 PFBS-related substances with identified CAS numbers, applications and REACH registration status (exclude side-chain fluorinated polymers)

EC No	CAS No	Substance name	Abb.	Identified applications	C&L inventory number of notifications **	REACH registration status **
206-792-6	375-72-4	Perfluorobutane sulfonyl fluoride	PBSF	Raw material for manufacture of PFBS-related substances	103	Intermediate Use Only
206-793-1	375-73-5 and 59933-66-3	Perfluorobutanesulfonic acid	PFBS	Acid catalysts; Raw materials for photo acid generating agents; Synthetic raw materials	CAS no. 375-73-5: 29 CAS no: 59933-66-3: 1	CAS no. 375-73-5: Preregistered CAS no. 59933-66-3: indicated as "Name confidential or not available"
249-616-3	29420-49-3	Potassium perfluoro-butane-sulfonate	K-PFBS	Flame retardant for polycarbonate	123	Preregistered
252-043-1	34454-97-2	*N*-Methyl perfluoro-butane-sulfon-amidoethanol	MeF-BSE	Intermediate for PFBS-related polymers. Low levels in surfactants; repellent agents and tile grout additive	111	Registered volume: 10-100 t/y
253-270-9	36913-91-4	Perfluorobutanesulfonic anhydride		Laboratory chemicals; Intermediate [indicated in market report but application in the EEA not confirmed]	23	Preregistered
266-733-5	67584-55-8	*N*-Methyl perfluoro-butane-sulfon-amidoethyl acrylate	MeF-BSAC	Intermediate for PFBS-related polymers. Low levels in surfactant, repellent agents; Solder paste	222	Registered volume: 10-100 t/y
422-100-7	102061-82-5	Sodium perfluorobutane-sulfinate	Na-PFBSi	Not identified	Harmonised *	Registered; Confidential
442-960-7	332350-93-3	Triphenyl-(phenyl-methyl)-phosphonium *N*-methyl-perfluorobutanesulfonamide		Fluoroelastomers	Harmonised *	Registered; Confidential
444-440-5	220689-12-3	Tetrabutylphosphonium perfluorobutanesulfonate		Anti-static additive for plastics	Harmonised *	Registered volume: 1+ t/y
454-680-2	484024-67-1	Ammonium perfluorobutanesulfon-amidoethanolate		Electronic surfactants	EC no. 454-680-2: 1 CAS no. 484024-67-1: 3	Preregistered
468-070-9	-	Perfluorobutanesulfinic acid		Not identified	1	Registered; Confidential
609-746-7	39847-39-7	Bis(perfluorobutane-sulfonyl)imide		Surfactants, Acid catalyst, Raw material for ionic liquid	1	Preregistered

EC No	CAS No	Substance name	Abb.	Identified applications	C&L inventory number of notifications **	REACH registration status **
614-396-3	68298-12-4	*N*-Methyl perfluorobutane-sulfonamide	MeF-BSA	Intermediate used in the manufacture of monomers. Present at low level in surfactants and repellent agents	24	Preregistered
643-022-1	606967-06-0	1-Propanesulfonic acid, 3- [hexyl[(nonafluoro-butyl)-sulfonyl]amino]-2-hydroxy-, monoammonium salt		Surfactants	5	Preregistered
700-536-1	25628-08-4	Tetraethylammonium perfluorobutanesulfonate		Metal (chromium) plating	31	Registered volume: 1-10 t/y
-	1017237-78-3	Fluoroacrylate copolymer		Surfactants; Flux for the soldering of electronic components	48	Preregistered

* Harmonised classification according to the CLP Regulation (Regulation (EC) No 1272/2008).

** As reported by November 2016.

Global market for PBSF and PFBS

PBSF - According to a recent market report for PBSF, the global manufacture of PBSF increased from 287 tonnes in 2011 to 317 tonnes in 2015. As PBSF is the starting material for PFBS-related substances, this amount approximately indicates the total tonnage of the PFBS moieties of produced PFBS-related substances. According to the market report, manufacture in China in 2015 was 299 tonnes, accounting for 94% of the global manufacture of PBSF. Of this amount, 83 tonnes were exported. About 18 tonnes PBSF were produced in other parts of the world; therefore, approximately 100 tonnes were used as intermediate for synthesis of PFBS-related substances in other parts of the world. Of the 317 tonnes of PBSF produced globally in 2015, 173 tonnes were used for production of surfactants (probably including side-chain-fluorinated polymers, but this is not specified), 88 tonnes for pesticides, 46 tonnes for flame-retardants and 10 tonnes for other applications. The significant consumption for manufacture of pesticides has not been confirmed by other sources. The OECD surveys of use of the substances (together with other PFAS) from 2005 to 2009 do not mention production of pesticides, but these surveys do not include manufacture and use of the substances in China. In 2006, the reported manufacture of PBSF in the OECD countries was 40-60 tonnes. The data may indicate that a part of the former manufacture of PBSF outside China has now moved to China, from which it is exported for further processing. The market report does not provide specific information for regions outside China. Data from the US EPA CDR database indicate that PBSF is currently not imported into the USA, whereas recent production figures for PBSF are confidential. The 83 tonnes of PBSF exported from China may be used as intermediates for further manufacture of fluorinated chemicals in the EEA or in other countries, e.g. Japan.

PFBS - According to a recent market report, the total global manufacture of PFBS increased from 23 tonnes in 2011 to 27 tonnes in 2015. Of the 27 tonnes manufactured in 2015, 17 tonnes were manufactured in China (of these, 7 tonnes were exported), 7 tonnes in Japan and 3 tonnes in the rest of the world (not further specified). According to the report, 19 tonnes were used globally as surfactants (or manufacture of surfactants; not specified), 4.4 tonnes were used as intermediates in the pharmaceutical industry, 1.4 tonnes as insecticides (or manufacture of insecticides; not specified) and 1.6 tonnes for other purposes.

Manufacture of PBSF and PFBS in the EEA[1]

PBSF is registered under REACH as an intermediate for the manufacture of MeFBSE, which is further used in part as an intermediate for manufacture of other substances. The registered volume for MeFBSE is 10-100 t/year. That amount may either be imported or produced from PBSF in the EEA. The data on global manufacture of PBSF makes it likely that a significant portion of the PBSF used in the EEA is imported from China.

PFBS - PFBS is not registered under REACH but may be imported or produced in volumes up to 100 t/year until 31 May 2018 without a registration. Based on the information in a global market report on PFBS regarding all manufacture outside China, manufacture in the EEA would likely be less than 3 t/year. No producers or importers of PFBS to the EEA have been identified.

Import and export of PFBS-related substances on their own, in mixtures and articles

Import of the substances on their own - No data on import of the substances on their own or in mixtures have been obtained from the three companies registering PFBS-related substances or from any other companies. Apart from the data indicating that 83 tonnes PBSF is exported from China, which potentially may be used for production in the EEA, no specific data on potential import to the EEA of the substances on their own are available.

Import of the substances in mixtures - The substances may be imported in two types of products: 1) surfactants and other mixtures used in manufacture of other mixtures or used as process chemicals; and 2) as surfactants in paints, adhesives, inks, and other final mixtures. No public data on import of the substances on their own or in mixtures have been obtained from the three companies registering PFBS-related substances or from any other companies.

Import of these substances in articles - Three main uses of these substances in articles have been identified:

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1 EEA: European Economic Area - consists of the EU Member States, Iceland, Liechtenstein and Norway. Volumes registered under REACH concerns the total manufacture/import of substances in the EEA.

1) Side-chain-fluorinated polymers are used in impregnating agents for leather (nubuck and suede), outdoor textiles and carpets,

2) PFBS salts are used as flame retardants in polycarbonate e.g. as used in electronics, and

3) Small quantities of PFBS-related substances in coatings of articles in which the substances have been used as surfactants (i.e. without a function in the final articles).

The available data do not allow for an exact estimate of the total quantities in imported articles. Outdoor textiles, leather and electronic articles used in the EEA are, to a large extent, imported from China; a significant portion of the PFBS-related substances and side-chain-fluorinated polymers produced in China may end up on the EEA market. With consumption of these substances in China of approximately 150 t/year for non-pesticide applications, it is considered likely that the amount of the PFBS-related substances is in the range of 5-50 t/year in terms of weight of PFBS moieties in articles imported to the EEA.

Application and consumption of the substances within the EEA

The majority of the PFBS-based substances is used as surfactants and in repellent protection. In this context, the term "surfactants" is used for agents mainly used to modify the surface tension of mixtures during formulation and/or application, whereas agents for "repellent protection" are used to modify the surface properties of solid materials.

Surfactants of paints, adhesives, etc. - PFBS-related substances are used in surfactants marketed for use as wetting, levelling and flow agents in various applications, including various paints and coatings, inks, polymers, adhesives, waxes, polishes and caulks. The use of the substances as surfactants is the major application globally. Based on the available information, it is estimated that the total quantity of PFBS-moieties in surfactants used for production of paints, adhesives, and waxes in the EU is on the order of 1-3 t/year.

Flame retardants - The use of K-PFBS as a flame retardant in polycarbonate for electrical and electronic articles is the third major application area for PFBS-based substances globally. Flame retardants based on K-PFBS are provided by many manufacturers in the EEA including Lanxess, Miteni SpA and 3M. One of the companies indicates on their website that the production capacity for K-PFBS is several tonnes. The substance is not yet registered but the manufacture and import may still reach 100 t/year in the EEA. The consumption of K-PFBS for production of polycarbonate in the EU is estimated to correspond to 1-10 t/year of PFBS moieties on the basis of the available information. Considering that the global consumption of PBSF for production of flame retardants is 46 t/year, and that much electronic equipment used in the EEA is imported from Asia, the total amount of PFBS moieties in polycarbonate placed on the market (e.g. in electrical and electronic equipment) is likely to be in the range of 2-20 t/year.

Agents for repellent protection of textiles, leather, furniture and carpets. - Various PFBS-related side-chain-fluorinated polymers are used as agents for oil, water and stain repellent protection for fabric, carpets, and leather (suede and nubuck). To the knowledge of the authors, the 3M Company is the only supplier of such products based on PFBS-chemistry, where the most well-known product line is Scotchgard™. The agents are used industrially for production of articles and are also available in consumer products such as aerosols for protective treatment of textiles, shoes and carpets. In the final articles, the majority of the PFBS moieties are attached to the polymers, and only a small fraction will be present as extractable PFBS or non-polymeric PFBS-related substances. Based on the information made available throughout the survey, the quantities of agents for repellent protection placed on the EEA market for industrial, professional and consumer applications correspond to 20-40 t/year PFBS moieties. This application is consequently the major application area in the EEA. It is assumed that import with articles is significant for this application area, as the majority of outdoor textiles and leather articles placed on the EEA market is imported from Asia. However, some export of articles, especially leather articles, manufactured within the EEA also takes place. Based on the available information, it is estimated that the total tonnage in terms of in articles placed on the EEA market and in mixtures for consumer applications (i.e. total end applications) is in the range of 20-60 t/year PFBS moieties.

Repellents for porous hard surfaces - PFBS-based substances and polymers are used for repellent protection of porous hard surfaces such as concrete, grout, unglazed tile, granite, clay, slate, limestone, marble and terracotta. The agents can be used either as penetrating sealers or as additives in various coating and sealer formulations. The agents are mainly used for professional and industrial applications but may be used by consumers to a limited extent. Based on the available information it is estimated that the total tonnage in terms of PFBS moieties in products placed on the EEA market and in mixtures for consumer applications is in the range of 5-10 t/year. Import and export with articles, e.g. treated stones, is assumed to be minor for this application area.

Metal plating - Tetraethylammonium perfluorobutanesulfonate is registered in volumes of 1-10 t/year for industrial use for metal (chromium) plating. One mixture with the substance used for this application has been identified. The mixture also contains a PFOS-related substance.

Surfactants and solder paste for electronics - A number of PFBS-related substances are included in surfactants and solder paste used in the electronic industry. In contrast to most of the surfactants mentioned above, these surfactants are used in industrial settings with limited risk of release to the environment and of consumer exposure. Based on the available information, it is roughly estimated that the total consumption in the EEA is very small and likely in the range of 0.1-1 t/year.

Pesticides - According to a global market report, the second largest application of PBSF globally was the production of pesticides. No PFBS-related pesticides are approved for use in the EU. It cannot be excluded that PFBS-related substances are used as auxiliaries in some pesticides.

Other applications - PFBS-related substances are used for a number of other applications: In curatives for fluoroelastomer formulations, as surfactants in the manufacture of synthetic leather and extrusion of synthetic fibre, acid catalysts and photoacid generations for lithography, anti-static additive for plastics and laboratory agents. The total consumption for other applications is roughly estimated at <3 tonnes.

Summary - The available information on PFBS-related substances in mixtures and articles placed on the EU market is summarised in Table 2. The middle column represents the quantities of mixtures used in the EEA either for production of other mixtures and articles (e.g. surfactants used for production of paint or repellent agents for production of leather) or for end-applications (e.g. in metal plating). The right column represents the end-applications (i.e. the PFBS moieties in paint, textile and leather articles placed on the market) and takes import and export of mixtures and articles into account.

Table 2 Estimated quantities of PFBS moieties of mixtures and end-application in the EEA

Application area	Mixtures used in the EEA (t/year PFBS moieties)	End applications of mixtures and articles in the EEA (t/year PFBS moieties)
Surfactants in paints, inks, etc.	1-3	1-3
Flame retardants for polycarbonate	1-10	2-20
Repellent agents for textiles, leather, carpets, etc.	20-40	20-60
Repellent agents for hard surfaces	5-10 *	5-10
Metal plating	1-10 *	1-10
Solder paste	0.1-1 *	0.1-1
Other applications	0.1-3	0.1-3
Total	28-77	29-107

* The applications are mainly end-applications and included in the right column as well

Potential for exposure of consumers and the environment

Releases to the environment - The applied substances and their degradation products may be released to the environment by formulation and application of mixtures, during service life of treated articles and materials, and by disposal of treated articles and materials.

The major application of the PFBS-related substances are as polymers used as surfactants and as agents for repellent protection of textiles, leather, carpets, stone and tile. The applied polymer mixtures may contain starting constituents, intermediates and impurities at low concentrations. According to safety data sheets, some of the mixtures contain <1% of the volatile intermediates MeFBSE, MeFBSA and MeFBSAC, which likely are released from the mixtures or treated materials during the service life.

A major release pathway is weathering of the treated materials (where the polymers may be released together with the substrate) and releases from degradation of the polymers during the service life. Degradation experiments on polymers used for repellent protection indicate that the main degradation product is perfluorobutane sulfonamide (FBSA). This was coincident with the detection of the major fabric protector components that contain side-chains with the N-methyl-perfluorobutane sulfonyl moiety. Studies indicate that up to 75% of the polymer used for carpet protection may be extracted from the carpet and disposed of to the sewer during the service life. For other applications, releases during the service life are likely to be significant as well. In situations where the agents are released as polymers, the polymers may later be degraded during wastewater treatment or within the environment. Former use of PFAS-based fire-fighting foams with longer-chain homologues have resulted in serious ground- and surface water contamination of firefighting training fields. Firefighting foams placed on the EEA market today, however, do not appear to be based on PFBS chemistry.

Consumer exposure - An assessment of direct consumer exposure routes has been undertaken, whereas the exposure of humans via the environments is beyond the scope of the study. Relatively few studies on consumer exposure to PFBS-based substances are available as most studies have focused on longer chain homologues.

Consumers' impregnation of outdoor clothes, shoes, carpets, etc. with Scotchgard™ or similar repellent protection products in spray cans may, if carried out without sufficient ventilation and protection equipment, result in significant consumer inhalation exposure to PFBS-related substances. This may also be the case with spray application of agents for protection of stone and tile or spray application of paints containing PFBS-based surfactants. The two latter product groups are, however, not specifically marketed for spray application.

Consumers' use of PFBS-impregnated clothing items may also result in direct skin exposure to of PFBS-related substances from weathering and releases of impurities. Infants and toddlers may be exposed by sucking on the impregnated fabrics. Storage of newly impregnated clothes and shoes in shops and at home may generate PFBS and related substances in indoor air and dust with potential human exposure. Repellent agents used on tile and stone floors indoors may result in dermal exposure.

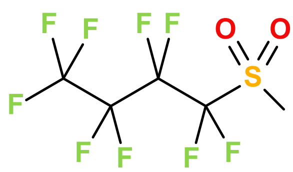
The use of PFBS-related substances as surfactants in low concentrations in paints and inks is considered to result only in insignificant direct consumer exposure but these many "insignificant" sources may prove to constitute a long-term problem as regards contamination of the environment.

Sammendrag og konklusjon

Perfluorbutansulfonsyre (PFBS) og relaterte stoffer er kortkjedede perfluoralkylforbindelser som brukes i en rekke applikasjoner. Utgangsmaterialet ifm. framstillingen av stoffene er perfluorbutansulfonylfluorid (PBSF), og den globale framstillingen av PBSF angir det samlede globale forbruket av PFBS-relaterte stoffer. Den samlede globale framstilling av PBSF i 2015 er anslått til 317 tonn og av denne mengden fremstilles 299 tonn i Kina. Noe PBSF eksporteres fra Kina, men omkring 216 tonn blir anvendt i Kina for produktfremstilling. Denne undersøkelsen har identifisert 16 PFBS-relaterte stoffer med bekreftet bruk. Den samlede mengden av PFBS-relaterte stoffer registrert i REACH var 22-210+ t/år, men noen stoffer har konfidensielle mengdedata, og derfor må registrering av noen av stoffene vente til deadline for 3. runde av registreringen den 31. mai 2018. Det totale innholdet av PFBS-enheter (moieties) i blandinger brukt i EØS er estimert til 28-77 t/år. De viktigste applikasjonsområdene identifisert er vann- og flekkavvisende midler for lær, tekstiler, tepper og porøse harde overflater som representerer 25-50 t/år av PFBS-enheter i blandinger. Mindre bruksområder er overflateaktive stoffer til trykkfarger, maling, voks, osv., flammehemmere til polykarbonat, midler for olje, antiduggmidler til forkromming, og overflateaktive stoffer til flussmidler i produksjon av elektronikk. Basert på kunnskap om de forskjellige bruksområdene, har potensialet for eksponering av forbrukerne og miljøet blitt vurdert.

De aktuelle stoffene

Denne rapporten undersøker perfluorobutansulfonsyre (PFBS) samt dets derivater og forstadier. Disse stoffene er kortkjedede eller polymere perfluoralkylforbindelser (PFAS) som inneholder en eller flere perfluorobutan sulfonyl C_4-enheter:



Perfluorobutansulfonyl-enhet

Slike stoffer vil i denne rapporten bli referert til som PFBS-relaterte stoffer. Tonnasjer er generelt uttrykt som tonn PFBS-enheter, men data fra REACH-registreringer og markedsrapporter representerer tonnasjen av hele stoffet.

Utgangsmaterialet er lineær perfluorbutansulfonylfluorid (PBSF). PFBS, dets salter og alle andre PFBS-relaterte stoffer (funksjonelle derivater, kjemiske forstadier) kan syntetiseres og fremstilles fra PBSF.

Vedlegg B inneholder en samlet oversikt over mer enn 50 PFBS-relaterte stoffer. Av disse er 17 stoffer identifisert med CAS-numre eller EC numre og/eller bekreftet bruk er inkludert i tabell 1 på neste side. For alle disse stoffene unntatt et (med konfidensielt REACH registreringsnummer), er bruken av stoffene blitt identifisert, men bruken innen EØS har ikke blitt endelig bekreftet for alle stoffene. Listen kan ikke betraktes som fullstendig, men inkluderer sannsynligvis de viktigste bruksområdene. Fullt navn på stoffene er oppgitt i vedlegg B.

Mange av stoffene er deklarert av mer enn 100 selskaper i EUs klassifiserings- og merkingsfortegnelsen under REACH (inkl. alle medlemmer av fellesregistreringer og -notifikasjoner), noe som indikerer at stoffene er mye brukt i EU.

Noen av PFBS-derivatene er mellomprodukter i framstilling av sidekjede-fluorerte uretan- og acrylatpolymerer. Polymerene er ikke oppført i tabell 1. Stoffene MeFBSA, MeFBSE og MeFBSAC brukes som mellomprodukter ved fremstilling av forskjellige fluorkjemiske akrylat- og uretanpolymerer som brukes i overflateaktive midler og i midler for beskyttelse av tekstiler, lær, tepper og harde overflater. I mange av blandingene er en eller flere av de tre mellomproduktene tilstede i lave nivåer på <1%. Sidekjedene fra disse polymertypene kan spaltes av fra polymerkjeden og bli forstadier til PFBS. Polymerene er generelt ikke preregistrerte eller registrerte under REACH, og deres CAS numre og nøyaktige sammensetninger er oppgitt som "konfidensiell" i sikkerhetsdatabladene.

Tabell 1. PFBS-relaterte stoffer med identifiserte CAS-numre, bruksområder og REACH registreringsstatus (sidekjede-fluorerte polymerer er ikke inkludert)

EC nr.	CAS nr.	Stoffnavn	For-kor-telse	Identifisert bruks-område	C&L behold-ning, antall notifikasjoner **	REACH regis-teringsstatus **
206-792-6	375-72-4	Perfluorobutansulfo-nylfluorid	PBSF	Råvarer til framstilling av PFBS-relaterte stof-fer	103	Kun som mel-lomprodukt
206-793-1	375-73-5 og 59933-66-3	Perfluorbutansulfon-syre	PFBS	Syrekatalysatorer; Rå-varer til fotosyre-gene-rerende midler; Synte-tiske råstoffer	CAS nr. 375-73-5: 29 CAS nr. 59933-66-3:1	CAS nr. 375-73-5: Preregistrert CAS nr. 59933-66-3: oppgitt som "Navn er fortrolig eller ikke tilgjengelig"
249-616-3	29420-49-3	Kalium perfluor-butansulfonat	K-PFBS	Flammehemmer til po-lykarbonat	123	Preregistrert
252-043-1	34454-97-2	*N*-Methylperfluor-butan sulfonamidoethanol	MeF-BSE	Mellomprodukt for PFBS-relaterte polyme-rer. Lave nivåer i over-flateaktive stoffer; im-pregneringsmiddel ; flisefugemasse additiv	111	Registrert mengde: 10-100 t/år
253-270-9	36913-91-4	Perfluorsulfonsyre-anhydrid		Laboratoriekjemikalier; mellomprodukt [indi-kert i markedsrapport, men bruken i EØS er ikke bekreftet]	23	Preregistrert
266-733-5	67584-55-8	*N*-Methyl perfluor-butansulfonamido-ethyl acrylat	MeF-BSAC	Mellomprodukt i PFBS-relaterte polymerer; lave nivåer i overflate-aktive stoffer; impreg-nering; loddepasta	222	Registrert mengde: 10-100 t/år
422-100-7	102061-82-5	Natrium perfluor-butansulfinat	Na-PFBSi	Ikke identifisert	Harmonisert*	Registrert mengde: Konfi-densielt
442-960-7	332350-93-3	Trifenyl-(fenyletyl)–fosfonium *N*-metyl-perfluoroktan sulfon-amid		Fluoroelastomerer	Harmonisert*	Registrert mengde: Konfi-densielt
444-440-5	220689-12-3	Tetrabutylfosfo-nium perfluorbutansul-fonat		Antistatisk additiv til plast	Harmonisert*	Registrert mengde: 1+ t/år
454-680-2	484024-67-1	Ammonium perfluor-sulfonamido etanolat		Overflateaktive stoffer til elektronikk	EC nr. 454-680-2: 1 CAS nr. 484024-67-1: 3	Preregistrert
468-070-9	-	Perfluorbutansulfin-syre		Ikke identifisert	1	Registrert mengde: Konfi-densielt

EC nr.	CAS nr.	Stoffnavn	For-kor-telse	Identifisert bruks-område	C&L behold-ning, antall notifikasjoner **	REACH regis-teringsstatus **
609-746-7	39847-39-7	Bis(perfluorbutan-sulfonyl)imid		Overflateaktive stoffer; syrekatalysatorer; Rå-varer til ionisk væske	1	Preregistrert
614-396-3	68298-12-4	*N*-Metyl perfluor-butansulfonamid	MeF-BSA	Mellomprodukt brukt i produksjon av mono-mere. Tilsteder i lave nivåer i overflateaktive stoffer; impregnerings-midler	24	Preregistrert
643-022-1	606967-06-0	1-propansulfonsyre-Propansulfonsyre, 3-[heksyl [(nonafluor-obutyl) sulfonyl] amino] -2-hydroksy-, mono-ammoniums-alt		Overflateaktive stoffer	5	Preregistrert
700-536-1	25628-08-4	Tetraetylammonium perfluorbutansulfo-nat		Metalbelegging (krom)	31	Registrert mengde: 1-10 t/år
-	1017237-78-3	Fluoracrylat kopoly-mer		Overflateaktive stoffer; flussmiddel til lodding av elektroniske kom-ponenter	48	Preregistrert

* Harmonisert klassifisering iht. CLP-regelverket (Regulation (EC) No 1272/2008).

** Som rapportert i november 2016.

Globale markeder for PBSF og PFBS

PBSF - Ifølge en fersk markedsrapport for PBSF har den globale framstillingen av PBSF økt fra 287 tonn i 2011 til 317 tonn i 2015. Da PBSF er utgangsmateriale for PFBS-relaterte stoffer, indikerer denne mengden omtrent den samlede tonnasjen av PFBS-enheter av de produserte PFBS-relaterte stoffene. Ifølge markedsrapporten var framstillingen i Kina i 2015 299 tonn, noe som utgjør 94% av den globale framstilling av PBSF. Av denne mengden ble 83 tonn eksportert. Omtrent 18 tonn PBSF ble produsert i andre deler av verden, og dermed ble ca. 100 tonn anvendt i andre deler av verden som mellomprodukt til syntese av PFBS-relaterte stoffer. Av de 317 tonn av PBSF som ble produsert globalt i 2015, ble 173 tonn brukt til framstilling av overflateaktive stoffer (antageligvis inkludert sidekjede-fluorerte polymerer, men dette er ikke spesifisert), 88 tonn ble brukt til framstilling av plantevernmidler, 46 tonn til framstilling av flammehemmere og 10 tonn til andre applikasjoner. Det store forbruket i framstilling av plantevernmidler har ikke blitt bekreftet av andre kilder. Framstillingen av plantevernmidler nevnes heller ikke i OECDs undersøkelser om bruken av stoffet (sammen med andre PFAS) fra 2005 til 2009, men disse undersøkelsene inkluderer ikke framstilling og bruken av stoffene i Kina. I 2006 var den rapporterte framstillingen av PBSF i OECD-land 40-60 tonn. Disse tallene indikerer at andelen av PBSF som tidligere ble fremstilt utenfor Kina, nå er flyttet til Kina, og at det eksporteres til videre prosessering.

Markedsrapporten gir ikke spesifikk informasjon for regioner utenfor Kina.

Data fra US EPA CDR-databasen viser at PBSF for øyeblikket ikke importeres til USA, men de siste tallene for framstillingen av PBSF er konfidensielle. De 83 tonn PBSF som eksporteres fra Kina, kan anvendes som mellomprodukter til ytterligere framstilling av fluorerte kjemikalier i EØS eller i andre land, f.eks. Japan.

PFBS – Ifølge en fersk markedsrapport for PFBS, er den totale globale framstillingen av PFBS økt fra 23 tonn i 2011 til 27 tonn i 2015. Av de 27 tonn i 2015 ble 17 tonn fremstilt i Kina (av disse ble 7 tonn eksportert), 7 tonn ble fremstilt i Japan og 3 tonn i resten av verden (ikke ytterligere spesifisert). Ifølge rapporten ble det globalt sett brukt 19 tonn som overflateaktive stoffer (eller til framstillingen av overflateaktive stoffer, ikke spesifisert), 4,4 tonn som mellomprodukt i den farmasøytiske industri, 1,4 tonn som insektmiddel (eller til framstillingen av insektmiddel, ikke spesifisert) og 1,6 tonn til andre formål.

Framstilling av PBSF og PFBS i EØS[2]

PBSF er registeret under REACH som et mellomprodukt i framstillingen av MeFBSE som delvis benyttes som mellomprodukt i framstillingen av andre stoffer. Den registrerte mengden av MeFBSE er 10-100 t/år. Denne mengden er enten importert til eller fremstillet fra PBSF i EØS. Data for den globale framstillingen av PBSF tyder på at en betydelig andel av den PBSF som brukes i EØS, er importert fra Kina.

PFBS er ikke registeret under REACH, men kan frem til 31 mai 2018 importers eller fremstilles i mengder på opptil 100 t/år uten å være registrert. På bakgrunn av opplysninger fra den globale markedsrapporten for PFBS vedrørende den samlede framstillingen utenfor Kina, vil framstillingen i EØS sannsynligvis være mindre enn 3 t/år. Det har ikke blitt identifisert fremstillere eller importører av PFBS i EØS.

Import og eksport av PFBS-relaterte stoffer alene, i blandinger og produkter

Import av stoffene alene – Det har ikke vært mulig å fremskaffe data for import av stoffene alene eller i blandinger fra noen av de tre registranter av PFBS-relaterte stoffer eller fra andre virksomheter. Ut over data for de 83 tonn PBSF som eksporteres fra Kina og som potensielt kan anvendes i produksjon i EØS, er det ikke tilgjengelig spesifikke data om mulig import til EØS av stoffene.

Import av stoffene i blandinger – Stoffene kan importeres i to typer produkter: 1) som overflateaktive stoffer og andre blandinger som benyttes i framstillingen av andre blandinger eller som prosesskjemikalier og 2) som overflateaktive midler i malinger, lim, trykkfarger og andre blandinger. Det har ikke vært mulig å fremskaffe offentlige data for import av stoffene alene eller i blandinger fra noen av de tre registrantene av PFBS-relaterte stoffer eller fra andre virksomheter.

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[2] EØS: Forkortelse for det Europeiske Økonomiske Samarbeidsområde – består av EU medlemslandene, Island, Liechtenstein og Norge. Mengder registeret under REACH gjelder den totale framstilling/import av stoffene i EØS.

Import av stoffene i produkter – Tre hovedbruksområder for stoffene i produkter har blitt identifisert:

1 Sidekjede-fluorerte polymerer benyttes i impregneringsmidler til lær (nubuck og semsket skinn), utendørstekstiler og tepper,

2 PFBS-salter benyttes som flammehemmere i polykarbonat som f.eks. brukes i elektronikk, og

3 Små mengder PFBS-relaterte stoffer i beleggene på produkter der stoffene har blitt anvendt som overflateaktivt middel (det vil si, uten en funksjon i det ferdige produktet).

De tilgjengelige data gir ikke mulighet for et nøyaktig estimat av de samlede mengdene i importerte produkter. Utendørstekstiler, lær og elektroniske produkter som anvendes i EØS, er i stor grad importert fra Kina, og en betydelig andel av de PFBS-relaterte stoffene og sidekjede-fluorerte polymerene som er produsert i Kina, ender muligens på EØS-markedet. Med et forbruk av disse stoffene i Kina på ca. 150 t/år for bruk utenom plantevernmidler, er det antatt sannsynlig at mengden av de PFBS-relaterte stoffene i form av vekten av PFBS-enheter i importerte produkter, er i området 5-50 t/år.

Bruk og forbruk av stoffene innen EØS

Størstedelen av de PFBS-baserte stoffene benyttes som overflateaktive midler og impregneringsmidler. I denne sammenhengen benyttes utrykket "overflateaktive midler" på midler som hovedsakelig benyttes til å modifisere overflatespenningen på blandinger under formulering og/eller applikasjon, mens "impregneringsmidler" benyttes til å modifisere overflateegenskapene til faste materialer.

Overflateaktive midler i maling, lim osv. - PFBS-relaterte stoffer brukes i overflateaktive stoffer som markedsføres til fuktings-, utjevnings- og flowmidler i forskjellige malinger og overflatebelegg (coating), blekk, polymerer, lim, voks samt pusse- og tettemidler. Bruken av stoffene som overflateaktive midler, er den viktigste bruken globalt. Basert på tilgjengelig informasjon anslås det at den totale mengden av PFBS-enheter i overflateaktive stoffer som brukes i produksjonen av maling, lim og voks, sannsynligvis vil være i størrelsesordenen 1-35 t/år i EU. Det foreligger ingen offentlige data som kan peke på den viktigste sluttbruken av de overflateaktive stoffene.

Flammehemmere – Bruken av K-PFBS som flammehemmer i polykarbonat til elektriske og elektroniske produkter, er globalt sett det tredje største bruksområdet for PFBS-baserte stoffer. Flammehemmere basert på K-PFBS leveres av mange produsenter i EØS bl.a. Lanxess, Miteni SpA og 3M. Et av firmaene oppgir på sin hjemmeside at kapasiteten for framstilling av K-PFBS er flere tonn. Stoffet er ennå ikke registrert, men framstillingen og importen kan være opptil 100 t/år i EØS. Forbruket av K-PFBS til produksjon av polykarbonat i EU er på basis av den tilgjengelige informasjon, antatt å tilsvare 1-10 t/år av PFBS-enheter. Hvis man tar den globale produksjonen av flammehemmere på 46 t/år i betraktning, samt at mye elektronikk i EØS importeres fra Asia, er den totale mengde av PFBS-enheter i polykarbonat som markedsføres (f.eks. i elektrisk og elektronisk utstyr) sannsynligvis i størrelsesordenen 2-20 t/år.

Impregneringsmidler til tekstiler, lær, møbler og tepper. - Forskjellige PFBS-relaterte sidekjede-fluorerte polymere anvendes som olje-, vann- og flekkmidler til stoff, tepper og lær (semsket skinn og nubuck). 3M er etter forfatternes kjennskap, den eneste leverandøren av slike produkter basert på PFBS-kjemi, og den mest kjente produktlinjen er Scotchgard™. Midlene brukes industrielt til framstilling av produkter og er også tilgjengelige i forbrukerprodukter som aerosoler til beskyttende behandling av tekstiler, sko og tepper. I de endelige produktene vil hovedparten av PFBS-enheter være bundet til polymerer, og kun en liten fraksjon vil være til stede som ekstraherbar PFBS eller ikke-polymer PFBS. Basert på tilgjengelig informasjon i denne undersøkelsen, er mengdene av impregneringsmidler for disse formålene i EØS-markedet for industrielle, profesjonelle og private aktører tilsvarende 20-40 t/år PFBS-enheter. Dette anvendelsesområdet er dermed viktig i EØS. Det er antatt at import er viktig da de fleste av utendørstekstiler og lærprodukter på EØS-markedet er importert fra Asia, men noen eksport av produkter, spesielt lærprodukter, produsert innenfor EØS finner også sted. På bakgrunn av de tilgjengelige opplysningene vurderes det at den samlede tonnasje i form av produkter på EØS-markedet og i blandinger til forbrukerprodukter (dvs. totalt sluttbruk) ligger i området 20-60 t/år PFBS-enheter.

Impregneringsmidler til porøse harde overflater - PFBS-baserte stoffer og polymerer benyttes i impregneringsmidler til porøse harde overflater som betong, mørtel, uglasserte fliser, granitt, leire, skifer, kalkstein, marmor og terrakotta. Midlene kan anvendes enten som gjennomtrengende tetningsmidler eller som tilsetningsstoffer i forskjellige belegnings- og tetningsblandinger. Midlene brukes hovedsakelig til profesjonell og industriell bruk, men kan i begrenset omfang anvendes av forbrukerne. På grunnlag av de tilgjengelige opplysningene, vurderes det at den samlede tonnasjen i form av PFBS-enheter i produkter på EØS-markedet og i blandinger til forbrukeranvendelser er i området 5-10 t/år. Import og eksport av produkter som f.eks. behandlet stein, antas å være liten for dette bruksområdet.

Metalbelegg- Tetraetylammonium perfluorbutansulfonat er registrert i mengder på 1-10 t/år til industrielt bruk til metalbelegg (krom). Én stoffblanding med dette stoffet er blitt identifisert. Stoffblandingen inneholder også et PFOS-relatert stoff.

Overflateaktive stoffer og loddepasta til elektronikk - En rekke PFBS-relaterte stoffer er å finne i overflateaktive stoffer og loddepasta som benyttes i den elektroniske industrien. I motsetning til de fleste av de ovennevnte overflateaktive stoffene, brukes disse overflateaktive stoffene i industrielle miljøer med begrenset risiko for utslipp til miljøet og forbrukereksponering. På bakgrunn av de tilgjengelige opplysningene, anslås det grovt at det samlede forbruket i EØS er meget liten og ligger trolig i området 0,1-1 t/år.

Pesticider – Ifølge en global markedsrapport er den nest største anvendelse av PBSF globalt sett, framstillingen av plantevernmidler. Ingen PFBS-relaterte plantevernmidler er godkjent til bruk i EU. Det kan ikke utelukkes at PFBS-relaterte stoffer brukes som hjelpestoffer i enkelte plantevernmidler.

Andre bruksområder - PFBS-relaterte stoffer brukes på en rekke andre områder: I herdemidler for fluoroelastimerformuleringer, som overflateaktivt middel i produksjonen av syntetisk lær og ekstrudering av syntetiske fibre, som syrekatalysator og fotosyregenerering til litografi, antistatisk additiv til plast og som laboratoriepreparater. Det totale forbruket for andre applikasjoner er grovt anslått til <3 tonn.

Sammendrag - Den tilgjengelige informasjonen om PFBS-relaterte stoffer i blandinger og produkter på EU-markedet er oppsummert i tabell 2. Den venstre kolonnen representerer mengder av blandinger som brukes i EØS enten i produksjon av andre blandinger og produkter (f.eks. overflateaktive stoffer som brukes i produksjon av maling eller impregneringsmidler i produksjon av lær) eller brukt i sluttapplikasjoner (f.eks. metallbelegg). Den høyre kolonnen representerer sluttapplikasjonene (dvs. PFBS-enheter i maling, tekstil og lærvarer på markedet) og tar hensyn til import og eksport av blandinger og produkter.

Tabell 3 Estimerte mengder av PFBS-enheter i blandinger brukt i EØS.

Bruksområde	Blandinger som brukes I EØS (t/år PFBS-enheter)	Sluttbruk av blandinger og produkter i EØS (t/år PFBS-enheter)
Overflateaktive stoffer I maling, blekk etc.	1-3	1-3
Flammehemmere for poly-karbonat	1-10	2-20
Impregneringsmidler for tekstiler, lær, tepper etc.	20-40	20-60
Impregneringsmidler for harde overflater	5-10 *	5-10
Metallbelegg	1-10 *	1-10
Loddemasse	0,1-1 *	0,1-1
Andre bruksområder	0,1-3	0,1-3
Totalt	28-77	29-107

* Bruksområdene er hovedsakelig sluttapplikasjoner og inngår også i høyre kolonne

Potensiale for eksponering av forbrukere og miljøet

Utslipp til miljøet - De anvendte stoffene og deres nedbrytningsprodukter kan ende opp i miljøet fra blandinger og anvendelse av blandinger, under levetiden til de behandlede produktene / materialene eller ved avhending av disse.

Hovedanvendelsen til PFBS-relaterte stoffer er polymerer som brukes som overflateaktive stoffer og som impregnerings- og overflatemidler til tekstiler, lær, tepper, stein og fliser. De anvendte polymerblandingene kan inneholde utgangsstoffer, mellomprodukter og urenheter i lave konsentrasjoner. Ifølge sikkerhetsdatabladene inneholder noen av blandingene <1% av de flyktige mellomproduktene MeFBSE, MeFBSA, MeFBSAC. Disse vil sannsynligvis frigis fra blandingene eller de behandlede materialene i løpet av deres levetid.

En viktig utslippskilde er fra forvitring av de behandlede materialene (hvor polymerene kan slippes ut sammen med substratet) samt utslipp fra nedbrytning av polymerene i løpet av polymerens levetid. Nedbrytningseksperimenter av polymerer som brukes til impregnering viser at hovednedbrytningsproduktet er perfluorobutansulfonamid (FBSA). Dette var sammenfallende med påvising av de viktigste stoffbeskyttelseskomponentene som inneholder sidekjeder med N-metylperflorobutansulfonyl-enheter. Studier viser at opptil 75% av polymerene brukt til impregnering av tepper, kan frigjøres fra teppene i løpet av bruksperioden og ende opp i kloakken. Utslippene i løpet av levetiden er trolig også svært viktige for andre bruksområder. I de tilfellene der stoffene frigjøres som polymerer, kan polymerene senere brytes ned under behandling av avløpsvannet eller etter utslipp til miljøet. Tidligere bruk av PFAS-baserte brannskum, basert på PFBS og lengre kjedehomologer, har resultert i alvorlig grunn- og overflatevannforurensing av brannøvingsfelt. Brannskum som finnes på EØS-markedet i dag, er imidlertid ikke basert på PFBS-kjemi.

Forbrukereksponering - En vurdering av kilder for direkte forbrukereksponering har blitt gjennomført, selv om eksponeringen av mennesker via miljøet ligger utenfor omfanget av denne studien.

Relativt få studier av forbrukereksponering av PFBS-baserte stoffer er tilgjengelige, ettersom de fleste studier har fokusert på homogenene med lengre kjede.

Forbrukeres impregnering av utendørstøy, sko, tepper osv. med Scotchgard™ eller liknende impregneringsmidler i spraybokser kan, hvis det skjer uten tilstrekkelig ventilasjon og beskyttelsesutstyr, resultere i innånding av høye konsentrasjoner av PFBS-relaterte stoffer. Det samme kan være tilfellet med sprøyteapplikasjon av midler for beskyttelse av stein og flis eller spraypåføring av malinger med PFBS-baserte overflateaktive stoffer. De to sistnevnte produktgruppene er imidlertid ikke spesielt markedsført for sprøyteapplikasjon.

Forbrukernes bruk av PFBS-impregnerte klær kan også resultere i hudeksponering av PFBS-relaterte stoffer fra nedbrytning og frigjøring av urenheter. Spedbarn og småbarn kan bli eksponert ved å suge på de impregnerte stoffene. Oppbevaring av ny-impregnert tøy og sko i butikker og i hjemmet kan medføre PFBS i inneluft og støv med potensiell human eksponering. Impregneringsmidler som brukes for fliser og steingulv innendørs kan føre til hudeksponering.

Bruk av PFBS-derivater som overflateaktive midler i lave konsentrasjoner i maling og blekk, kan resultere i ubetydelig direkte forbrukereksponering, men de mange små kildene kan være et langsiktig problem knyttet til miljøforurensing.

1 Introduction

1.1 Background and aim of the project

PFBS is the acronym for perfluorobutane sulfonic acid and its salts. PFBS is a short-chain (C_4) perfluoroalkanesulfonate (PFAS). It was introduced by the 3M Company in 2000 as a substitute for the later banned long-chain (C_8) perfluorooctanesulfonic acid (PFOS). Until 2003, the 3M Company was the major global manufacturer of PFOS and related substances from perfluorooctanesulfonyl fluoride (POSF) as the starting material. The company manufactured approximately 3,665 t POSF/y, or 78% of the estimated global manufacture of 4,650 t POSF/y, when manufacture peaked in 2000.

There are many PFBS-related substances in use produced from PBSF as the starting material. The basic PFBS is not registered under REACH and has limited applications. An understanding of the market and the application of PFBS-related substances would therefore require understanding of the use and application of PBSF and PBSF-derived substances.

Limited information on the actual use of the PFBS-related substances is available. PBSF is registered as an intermediate under REACH, and quantitative information about consumption is deficient in the registrations. Detailed data on the trade of PBSF-derived substances is not available, but data on the global and European manufacture of PBSF and the consumption of the substance for the manufacture of various derivatives might provide an indication of the market for these substances.

PFBS-related substances are substances that contain the PFBS-fragment and they may degrade to PFBS in the environment. PFBS is highly persistent and some data indicate that PFBS (and some of the PFBS-related substances) also have other hazardous intrinsic properties. PFBS and some of the PFBS-related substances have been detected in the environment and in human blood.

In 2016, the Norwegian Environment Agency was collecting information about the intrinsic properties, use and exposure of PFBS to assess the need for risk reduction measures (RMOA analysis) for PFBS. The Norwegian Institute for Public Health and the Norwegian Institute for Water Research (NIVA) are investigating the health and environmental effects of PFBS and PFBS-related substances, on behalf of the Norwegian Environment Agency. These effects are consequently not subjects of the current project.

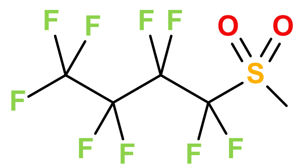
1.1.1 Aim of the project

The overall aim of this project is to identify sources of perfluorobutane sulfonic acid (PFBS) in the environment. More specifically the objectives of the project are to obtain a better understanding of:

- manufacture of PFBS and PFBS-related substances in EEA and globally;
- import and use of these substances in the EEA including the amounts of the substances imported in articles;
- the global manufacture of perfluorobutane sulfonyl fluoride (PBSF) and the import and export of the substances into/from EEA;
- the possible exposure of the environment and consumers to these substances.

1.2 The substances concerned

This report investigates perfluorobutane sulfonic acid (PFBS) and its derivatives and precursors. These substances are short-chain perfluoroalkyl substances (PFAS) containing one or more perfluorobutane sulfonyl C_4-moieties[3]:



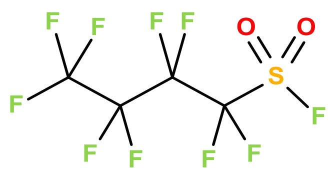
Perfluorobutanesulfonyl moiety

The perfluorobutyl-moiety is highly stable and neither hydrophilic nor lipophilic.

Appendix B lists PBSF, PFBS and various salts and functional derivatives with formulas and some properties. The substances are collectively referred to as PFBS-related substances in this report.

1.2.1 PBSF

For manufacture, the starting material is unbranched perfluorobutane sulfonyl fluoride (PBSF). It is a chemical intermediate, which in fact is a functional derivative (acid fluoride) of PFBS.

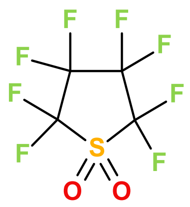


Perfluorobutanesulfonyl fluoride (PBSF)

PBSF is a clear, colourless and moisture sensitive liquid. It is heavier than water and not water-soluble but reacts (hydrolyses) slowly with water, though faster at higher pH. PBSF has a lower boiling point than water and is rather volatile.

3 C_4 = the moiety contains a four-carbon perfluorinated chain

Commercial PBSF is from the production process contaminated with the cyclic perfluorosulfolane:



Perfluorosulfolane

Based on PBSF ($C_4F_9SO_2F$), PFBS ($C_4F_9SO_3H$), its salts and all other PFBS-related chemicals (functional derivatives, precursors) can be synthesized and produced, e.g. perfluorobutanesulfonamides, by reaction with amines. PBSF itself is manufactured from the unhalogenated butane sulfonyl fluoride ($C_4H_9SO_2F$) by electrochemical fluorination (ECF). A reaction scheme is shown in Figure .

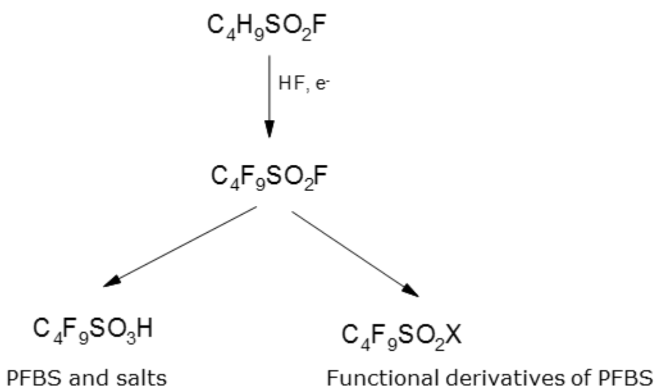
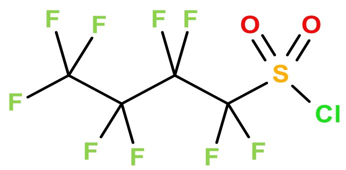
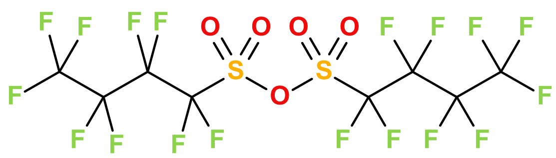


Figure 1 Formation of either PFBS and salts or functional derivative (for example "X" may be an amino group).

In the same family as PBSF is the analogue perfluorobutanesulfonyl chloride (PBSCl), a reagent for fluorotagging of nucleophiles, and perfluorosulfonic anhydride, both of which are clear, colourless and highly reactive substances that readily hydrolyse in water:



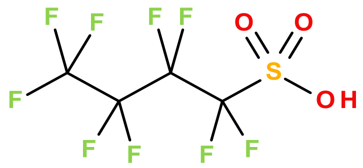
Perfluorobutanesulfonyl chloride



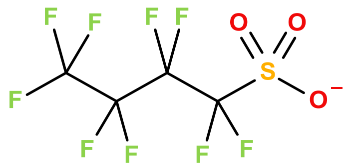
Perfluorobutanesulfonic anhydride

1.2.2 PFBS and salts

The acronym PFBS is used both for the acid itself and for the sulfonate anion as part of the salts of sulfonic acid, and can be considered as direct precursors:



Perfluorobutane sulfonic acid (PFBS)



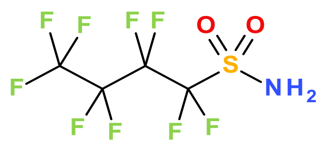
Perfluorobutanesulfonate (PFBS)

PFBS is a heavy colourless liquid with a very high boiling point and low surface tension. It is readily soluble, dissociates in water and is a strong acid. The salts are crystalline, non-volatile solids, highly soluble in water and with high melting points. The salts are direct precursors of PFBS. The most important salt is potassium perfluorobutanesulfonate (K-PFBS), used as flame retardant, but the tetrabutylphosphonium (antistatic agent) and the tetraethylammonium salts (used for metal plating) are also important. Furthermore, the bis(2-hydroxyethyl) ammonium salt and other bulky salts are also in use, but their use in the EEA has not been demonstrated in this study.

Because of their relatively high water solubilities, these salts can be transported over long distances in the environment by sea currents.

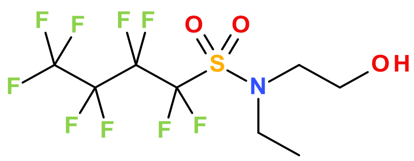
1.2.3 PFBS-related substances (functional derivatives, indirect precursors)

The most important functional derivatives in use as surfactants and impregnation agents are various substituted perfluorobutanesulfonamides, –perfluorobutanesulfonamidoalkanols and -perfluorobutanesulfonamidoalkyl acrylates/methacrylates. The most simple of these substances is perfluorobutanesulfonamide (FBSA):

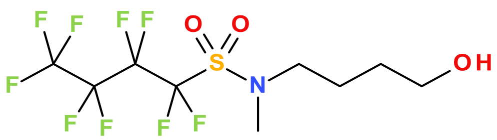


Perfluorobutanesulfonamide (FBSA)

Some more complex sulfonamides do have functional groups, which are more lipophilic and make the substance more volatile and capable of being transported long distances by air as vapour (and less with water):

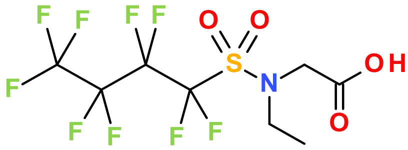


N-Ethyl perfluorobutanesulfonamidoethanol (EtBSE)



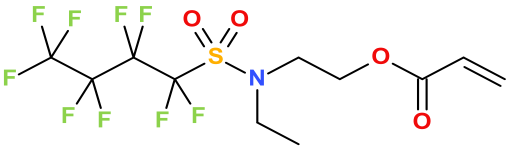
N-(4-Hydroxybutyl) N-methyl perfluorobutanesulfonamide

The alcohol group can be oxidized or metabolized into more hydrophilic carboxylic acids such as *N*-ethyl perfluorobutanesulfonamidoacetic acid (actual use not demonstrated):

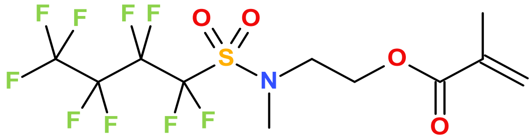


N-Ethyl perfluorobutanesulfonamidoacetic acid (EtFBSAA)

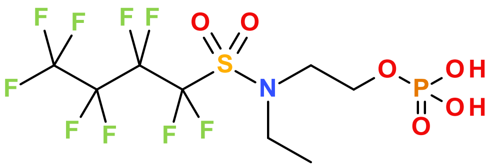
The alcohol group can also be esterified with acrylic-, methacrylic or phosphoric acid:



N-Ethyl perfluorobutanesulfonamidoethyl acrylate (EtFBSAC)



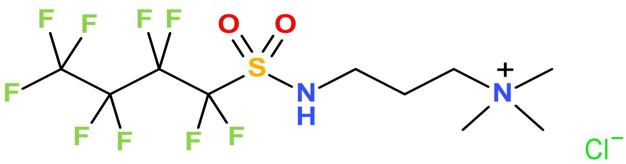
N-Methyl perfluorobutanesulfonamidoethyl methacrylate (MeFBSAC)



N-Ethyl perfluorobutanesulfonamidoethyl phosphate (mono-PAP)

These chemicals are widely used as intermediates and in surfactants and agents for repellent protection.

Some quaternary ammonium compounds related to PFBS have been reported as used in the photo industry and in fire-fighting foams (but not identified in this study). An example is perfluorobutanesulfonamide, *N*-(*N′*,*N′*,*N′*-trimethyl-propanaminium) chloride:



Perfluorobutanesulfonamide N-(N′,N′,N′-trimethyl-propanaminium) chloride

Contradictory to the non-degradable perfluorobutyl chain, the various functional groups attached to the chain are degradable. In the environment and in organisms, the derivatives discussed in this subchapter are transformed into the basic PFBS over time; these derivatives are therefore called PFBS precursors.

Perfluorobutanesulfonamidoethanol and its acrylate/methacrylate derivatives are basic materials for side-chain-fluorinated urethane and acrylate polymers widely used in agents for repellent protection e.g. within the Scotchgard™ products line. Side chains of each of these polymer types may possess the ability to sever from the polymer chain to become PFBS precursors. A likely release process is illustrated in Figure 2:

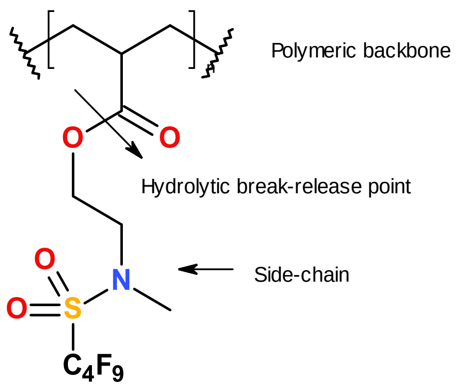


Figure 2 *Illustration of potential release of N-methyl perfluorobutanesulfon-amidoethanol from the acrylate side-chain of the polymeric material.*

This transformation/release process depends on circumstances, may occur over longer time periods and be incomplete.

1.3 Data collection methodology

The survey on the manufacture and use of PFBS and PFBS-related substances was carried out by means of the following:

- Acquisition of international market reports on PFBS and PBSF.
- Enquiries to companies that have registered the substances under REACH or are otherwise identified as manufacturers of mixtures containing the substances.
- Assessment of safety data sheets (SDS) and technical data sheets (TDS) for mixtures containing PFBS and related substances, identified based on CAS numbers. The SDSs were identified from the websites of companies known to manufacture and supply the substances and mixtures with PFBS-related substances. Furthermore, searches on relevant CAS numbers in combination with either "safety data sheet", "SDS" or "technical data sheet" were conducted using Google in order to identify other relevant mixtures.
- Enquiries to relevant Norwegian and European industry associations. The trade organisations were encouraged to forward the specific enquiry to relevant members.

  Consultation of selected peer-reviewed literature and previous surveys related to the substances.

2 Global manufacture and use of PFBS and PBSF

Data on the actual global manufacture and use of PFBS and PBSF have been obtained by combining information from market reports with information obtained from major global producers of the substances.

2.1 Production and use of PFBS

According to a recent market report for PFBS, the total global manufacture of PFBS increased from 23 tonnes in 2011 to 27 tonnes in 2015 (Prof Research Global, 2016b). Of the 27 tonnes manufactured in 2015, 17 tonnes were manufactured in China, 7 tonnes in Japan and 3 tonnes in the rest of the world (not further specified). According to the report, 19 tonnes were used globally as surfactants (or for manufacture of surfactants; not specified), 4.4 tonnes as intermediates in the pharmaceutical industry (specific application not indicated), 1.4 tonnes as insecticides (or manufacture of insecticides; not specified) and 1.6 tonnes for other purposes. The actual end-applications are not specified and it is unclear as to what extent the substance is used as an intermediate for manufacture of surfactants and insecticides or used on its own in these applications. Whereas the data for the Chinese manufacture and consumption appears to be based on actual data from companies (actual data for some years and modelled for other years), the consumption estimates for the "rest of the world" should be interpreted with care, but are used here as the best available data. The data could indicate that the consumption data for the "rest of the world" are extrapolated from Chinese consumption figures without specific data for the rest of the world.

As indicated in Section 2.3, no manufacture or consumption of PFBS on its own was reported in the 2005 and 2006 OECD surveys. The surveys were, however, not comprehensive as data from China were not included. PFBS is not registered under REACH as produced in or imported into the EEA.

Table 4 Global and Chinese PFBS manufacture and consumption by application area (Prof Research Global, 2016b). The uncertainties on the figures are not reported but are probably significant for the "rest of the world".

	2011, t/year				2015, t/year			
	China	Japan	Rest of the world	Total	China	Japan	Rest of the world	Total
Production	15.2	5.7	2.4	23.3	17.4	6.5	2.7	26.6
Export	6.6				8.0			
Import							6.6	
Consumption: *								
- surfactants	6.1		10.8	16.9	6.7		12.5	19.2
- intermediate in pharmaceutical industry	1.5		2.4	3.9	1.6		2.8	4.4
- insecticide	0.4		0.8	1.2	0.4		1.0	1.4
- other	0.6		0.8	1.4	0.7		0.9	1.6
Total consumption	**8.6**		**14.8**	**23.4**	**9.4**		**17.2**	**26.6**

* Consumption figures for the "Rest of the world" include consumption in Japan.

Global manufacture of other substances

Market research reports are available for two other PFBS-related substances: Potassium nonafluorobutane sulfonate (CAS No. 29420-49-3) and nonafluorobutane-1-sulfonic anhydride (CAS No. 36913-91-4). The two reports have not been obtained. The former substance is used as flame retardant and the consumption of PBSF for production of flame retardants indicated in Section 2.2 can be used as an indication of the extent of Chinese and global manufacture of this substance. The latter substance is reported to be used as a laboratory chemical for manufacture of substances and in scientific research and development. This usage is further described in Section 3.2.7.

2.2 Production and use of PBSF

According to a recent market report for PBSF, the global manufacture of PBSF increased from 287 tonnes in 2011 to 317 tonnes in 2015 as shown in Table 5. The data are based on analysis of data from 10 Chinese manufacturers of PBSF and an estimate for the "rest of the world". The "rest of the world" is not divided into continents or regions and no manufacturer-specific data are provided. Whereas the data for Chinese manufacture and consumption appears to be based on actual data from companies (actual data for some years and modelled for other years), the data for the "rest of the world" should be interpreted with care but are used here as the best available data.

According to the report, the manufacture of PBSF in China in 2015 was 299 tonnes, accounting for 94% of the global manufacture of PBSF. The percentage likewise was 94% in 2011. The data may indicate that global manufacture is modelled on the basis of a relatively limited database. It is not indicated as to how the data in the reports are generated. Of the 299 tonnes manufactured in 2015, 83 tonnes (28%) were exported. According to the report, the majority of the PBSF used for further processing in the "rest of the world" is imported from China. Based on data from other sources, the "rest of the world" most likely consists of Europe and the USA, where production facilities for PFBS-related substances exist.

As indicated in Section 2.3, a manufacture of 40-60 tonnes PBSF was reported in the 2006 OECD survey (OECD, 2006). The survey is not comprehensive and the actual production volumes may have been higher as data from China was not included. The same survey reported that up to 160 tonnes of PFBS-related substances were used as intermediates for the production of catalysts and for manufacture of other PFBS-related substances. This amount may refer to the use of PBSF but may also include other PFBS-related intermediates. The production data from the market report is not contradictory to the data from the OECD surveys if some of the former manufacture in the "rest of the world" is currently imported from China.

Table 5 Global and Chinese PBSF manufacturing and consumption by application area (Prof Research Global, 2016a). The uncertainties on the figures are not reported but are probably quite large for the "rest of the world".

	China, t/year		Rest of the world, t/year		Globally, t/year	
	2011	2015	2011	2015	2011	2015
Production	**270**	**299**	**17**	**18**	**287**	**317**
Export	72	83				
Import			72	83		
Consumption, production of:						
- surfactants	109	119	48	54	158	173
- pesticides	54	59	25	29	79	88
- flame retardants	28	32	12	14	41	46
- other	6	7	2	3	9	10
Total consumption	**189**	**216**	**89**	**100**	**287**	**317**

According to the report, the major application area was for production of surfactants, which accounted for 55% of global consumption in 2015. The market researcher was asked if this amount includes PBSF used for production of side-chain-fluorinated polymers for repellence, but they have not yet provided an answer.

Surprisingly, production of pesticides is indicated as the second largest application area, accounting for 28% of consumption while production of flame retardants accounted for 14%. The use of PBSF for the production of pesticides has not been reported in the OECD surveys. Websites of Chinese manufacturers of PBSF do mention production of pesticides as one of the application areas for the substance, e.g. Xiaochang Xiangshun Chemical Co. (2016) indicating "*Main use: used to synthesize fluorin surface active agent, pesticide and pigment intermediates and used to synthesize many fluorin special surface active agent*." [editor's note: spelling as indicated at the website]

The third largest use area is flame retardants. PFBS potassium salt, K-PFBS, is the only PFBS-related substance used as a flame retardant. The global manufacture in 2015 is indicated to be 46 tonnes.

2.3 Historic consumption figures

Data on the production volumes of PFBS and PBSF were collected from OECD Member Countries and companies by the OECD in 2005 and 2006 as part of the surveys of perfluoroalkyl substances (PFAS). The data obtained by the OECD cannot be considered comprehensive, in particular as regards manufacture and use in non-OECD countries, but they do give an indication of the production volumes and main applications of the substances. The last survey from 2009 focused on longer chain PFASs and did not include data on PFBS-related substances.

According to OECD (2006), analysis of the complete responses to the 2006 survey of perfluorinated substances indicated that three countries manufactured/imported three PFAS-related substances in 2005; all three chemicals were perfluorobutane sulfonate (PFBS)-related substances. The chemicals were:

- Potassium perfluorobutanesulfonate, K-PFBS (CAS No. 29420-49-3): 50 to 160 tonnes
- PBSF (CAS No. 375-72-4) – 40 to 60 tonnes
- Bis[2-(*N*-methyl perfluorobutanesulfonamido)ethoxy] phosphoric acid (CAS No. 120945-47-3) – 20 to 50 kg (see note below).

In addition, seven countries provided incomplete responses to the 2006 survey on PFAS related substances. Only one compound, PFBS potassium salt, was identified, while another four substances were indicated as "probably PFBS based substances". The total volume was 1.0 to 2.4 tonnes in 2005 (OECD, 2006).

The OECD surveys do not include data on the manufacture and use of PFBS on its own.

The uses of PFBS-related substances in 2005 were as follows:

- Up to 160 tonnes of PFBS-related substances were used as manufacturing intermediates for the production of catalysts, and for other PFAS related substances [note: if some of the substances are used to produce other substances within the group, the 160 tonnes may be greater than the total of the final substances]

- About 30-50 tonnes of PFBS-related compounds were used as flame retardants [note: reported by company in Germany for a previous survey (OECD, 2005) to be PFBS potassium salt, K-PFBS, CAS No. 29420-49-3]

- About 10 tonnes were used as an additive in plastics [note: not further described, but may represent another application, as flame retardants were reported separately]

- Other uses with low concentrations of PFBS chemicals included: an additive in industrial coating products (less than 500 kg), in acid mist suppression formulations (about 50 kg), in rubber moulding and as a defoamer in the electroplating industry.

- A minimal amount of PFBS-related substances were used as analytical reagents in laboratories (OECD, 2006).

The survey of PFAS-related substances showed that more PFBS-related chemicals were replacing PFOS/PFOA-related substances. The production volume of PFBS-related compounds had increased markedly since the 2004 survey.

Regarding bis[2-(*N*-methyl perfluorbutanesulfonamido)ethoxy] phosphoric acid ester, CAS No. 120945-47-3, for the 2005 OECD survey, a company in Germany reported that in 2003 some 20-50 tonnes were used as a defoamer in the electroplating industry (OECD, 2005). [authors' note: the 2005 survey indicated 20-50 tonnes while the 2006 survey indicated the consumption as 20-50 kg]. The CAS number is indicated in ECHA's database of preregistered substances as "Name confidential or not available". No current uses of this substance have been identified.

Production/import to the USA. Based on figures from the US EPA's CDR database, the annual manufacture of PBSF in the USA in 2006 was in the range of 227-454 t/year (Wang *et al.*, 2014a). This figure may indicate that the figures from the OECD surveys do not include all consumption in the OECD countries. The manufacture of K-PFBS was reported to be <227 t/year while it in the previous years were reported to be in the range 4.54-227 t/year (standard ranges converted from US units). A search in the database indicated that recent production figures for PBSF and K-PFBS are confidential, whereas it is indicated in the database that these substances are not currently imported into the USA.

3 Production, import and use of PFBS, PBSF and PFBS-related substances in the EEA

3.1 Production, import and use of PFBS, PBSF, and PFBS-related substances on their own

Data on the use of the substances in the EEA have been obtained from the registration database at ECHA's website, market research reports and contact with major manufacturers.

3.1.1 Registration data

Eight substances are registered under the REACH legislation, see Table 6. For three of the registered substances, data on the registered volume per year is confidential, and the volume for PBSF is indicated as "Intermediate Use Only". For tetrabutylphosphonium perfluorobutanesulfonate the registered volume is set at 1+ t/year. As described below, PBSF is solely used for manufacture of one of the other registered substances.

As the deadline to register substances manufactured or imported at 1-100 t/year is 31 May 2018, PFBS and a number of PFBS-related substances manufactured or imported in these volumes may be registered within the next couple of years. However, the current registration information for these substances may still indicate a fraction of the total volume.

Five of the substances have been registered by 3M Belgium BVBA/SPRL while one substance is registered by Miteni SpA and SABIC Innovative Plastics BV. The registrants for the remaining substances were indicated as "confidential".

Polymeric substances, such as PFBS-related polyurethane used in impregnation agents, are exempt from registration requirements and consequently no data on these substances are available from the registration database at ECHA's website.

***N*-Methyl perfluorobutanesulfonamidoethanol** (MeFBSE, CAS no. 34454-97-2) is registered for industrial use as an intermediate for manufacture of other substances and it is indicated that no subsequent service life is relevant. The substance is present at low levels in several of the identified mixtures used as fluorosurfactants for various applications (Section 3.2.1) and tile grout additives (Section 3.2.4). The application of the mixtures may include industrial, professional and possibly consumer uses.

Tetraethylammonium perfluorobutanesulfonate (CAS No. 25628-08-4) is registered for use in metal plating and further described in Section 3.2.5.

***N*-Methyl perfluorobutanesulfonamidoethyl acrylate** (MeFBSAC, CAS No. 67584-55-8) is registered for use as a laboratory agent and industrial polymerization of C_4-acrylate. It is indicated that no subsequent service life is relevant. The substance is, however, included in several of the identified mixtures used as fluorosurfactants for various applications (Section 3.2.1). The application of the mixtures may include industrial, professional and possibly consumer use.

Perfluorobutane sulfonyl fluoride (PBSF, CAS No. 375-72-4) is registered as an intermediate for the manufacture of MeFBSE, which is further used as an intermediate for manufacture of other substances. The registered volume for MeFBSE is 10-100 t/year, as shown in Table 6. The molecular weight of PBSF is 302, whereas for MeFBSE it is 357. The 10-100 t/year represents total manufacture and import and indicates that the maximum manufactured volume is 8.4-84 t/year.

Two registrations exist for **Tetrabutylphosphonium perfluoro-butanesulfonate** (CAS No. 220689-12-3), one full registration by Miteni SpA and SABIC Innovative Plastics BV, and one NONS (Notification of New Substances) registration, containing only confidential information regarding registrants, uses, volumes and so on. In the full registration, the substance is registered for use as an additive, while its use in plastic articles is indicated as a subsequent service life. The registered volume is 1+ t/year without further specification.

Sodium perfluorobutanesulfinate (CAS No. 102061-82-5) and **triphenyl(phenylmethyl)phosphonium *N*-methyl perfluorobutanesulfonamide (1:1)** (CAS No. 332350-93-3) and **perfluorobutanesulfinic acid** (EC No. 468-070-9, no CAS No. indicated) are all registered as CBI (confidential business information), and all information in the registrations are confidential.

Table 6 Registration data for registered PFBS-related substances

EC No.	CAS No.	Chemical name Abbreviation	Registered volume, t/year	Registrant	Manufactured in the EEA*	Indicated uses and Environmental Release Categories (ERC) for use of the substance
252-043-1	34454-97-2	*N*-Methyl perfluorobutanesulfonamidoethanol MeFBSE	10-100	3M Belgium BVBA/SPRL	Yes	**Use as intermediate or monomer in form of flakes or liquid substance** ERC 6a: Industrial use resulting in manufacture of another substance (use of intermediates) ERC 6c: Industrial use of monomers for manufacture of thermoplastics No subsequent service life relevant

EC No.	CAS No.	Chemical name Abbreviation	Registered volume, t/year	Registrant	Manufactured in the EEA*	Indicated uses and Environmental Release Categories (ERC) for use of the substance
700-536-1	25628-08-4	Tetraethylammonium perfluorobutanesulfonate	1-10	Confidential	Yes	**Industrial use of the substance for metal (chromium) plating** ERC 4: Industrial use of processing aids in processes and products, not becoming part of articles No. subsequent service life relevant
266-733-5	67584-55-8	*N*-Methyl perfluorobutanesulfonamidoethyl acrylate MeFBSAC	10-100	3M Belgium BVBA/SPRL	Yes	**Use as laboratory agent** ERC 6c: Industrial use of monomers for manufacture of thermoplastics No. subsequent service life relevant **Industrial polymerization of C_4-acrylate** ERC 6c: Industrial use of monomers for manufacture of thermoplastics No. subsequent service life relevant
206-792-6	375-72-4	Perfluorobutane sulfonyl fluoride PBSF	Intermediate Use Only	3M Belgium BVBA/SPRL	Yes	**Use as Intermediate in the manufacture e.g. of the alcohol MeFBSE** ERC 6a: Industrial use resulting in manufacture of another substance (use of intermediates) No. subsequent service life relevant

EC No.	CAS No.	Chemical name Abbreviation	Registered volume, t/year	Registrant	Manufactured in the EEA*	Indicated uses and Environmental Release Categories (ERC) for use of the substance
444-440-5	220689-12-3	Tetrabutyl-phosphonium perfluorobutanesulfonate	1+	Miteni SpA	Yes	**Use as additive** ERC 5: Industrial use resulting in inclusion into or onto a matrix SU 12: Manufacture of plastics products, including compounding and conversion Subsequent service life relevant for that use: AC 13: Plastic articles ERC 10a: Wide dispersive outdoor use of long-life articles and materials with low release ERC 11a: Wide dispersive indoor use of long-life articles and materials with low release ERC 12a: Industrial processing of articles with abrasive techniques (low release)
			Confidential	Confidential	Confidential	Confidential
422-100-7	102061-82-5	Sodium perfluorobutanesulfinate	Confidential	3M Belgium BVBA/SPRL	Confidential	Confidential
442-960-7	332350-93-3	Triphenyl(phenylmethyl)phosphonium *N*-methylperfluorobutanesulfon-amide (1:1)	Confidential	3M Belgium BVBA/SPRL	Confidential	Confidential
468-070-9	not indicated	Perfluorobutanesulfinic acid	Confidential	Confidential	Confidential	Confidential

* It is assumed that the substance is produced to some extent within the EEA if manufacture in included in the lifecycle description of the registration dossier. The Environmental Release Categories for this life-cycle step are ERC 1: Manufacture of substances for all substances.

3.1.2 Data on import and export from market reports and contact with industry

No data on export of the substances on their own or in mixtures have been obtained from the three companies registering PFBS-related substances or from any other companies. Apart from the data regarding the 83 tonnes PBSF exported from China, which may potentially be used for production in the EEA, no specific data on potential import to the EEA of the substances on their own are available.

3.2 Use of PFBS and PFBS-related substances in mixtures and articles

3.2.1 Surfactants for inks, paints, waxes, etc.

PFBS-related substances may be used in surfactants for use as wetting, levelling and flow agents in various applications, including architectural coatings, paints, inks, polymers, adhesives, waxes, polishes, caulks, high solids coatings, water reducible coatings, radiation curable coatings and resins, as well as other industrial coatings. The substances provide low dynamic surface tension in aqueous formulations and low interfacial surface tensions.

Life cycle stages

The following life cycle stages exist for this application:

- Manufacture of the substances
- Production of surfactants
- Production of paints, adhesives, etc.
- Applications of paints, adhesives, etc.
- Use of articles and surfaces with paints, adhesives, etc.
- Disposal of articles and surfaces with paints, adhesives, etc.

Substances used

Identified substances used for these applications are:

- Fluoroacrylate copolymer (CAS No. 1017237-78-3)
- *N*-Methyl perfluorobutanesulfonamidoethanol (MeFBSE) (CAS No. 34454-97-2)
- *N*-Methyl perfluorobutanesulfonamide (MeFBSA) (CAS No. 68298-12-4)
- *N*-Methyl perfluorobutanesulfonamidoethyl acrylate (MeFBSAC) (CAS No. 67584-55-8)
- 1-Propanesulfonic acid, 3- [hexyl[(nonafluoro-butyl)-sulfonyl]amino]-2-hydroxy-, monoammonium salt (CAS No. 606967-06-0).

In many of the mixtures, the fluoroacrylate copolymer is the main constituent, whereas MeFBSE, MeFBSA, and MeFBSAC are present at low levels of <1%. In a notification for one of the surfactants, FC-4420, for the Australian NICNAS programme, these other constituents are indicated as "*residual polyfluoroalkyl starting constituents and/or impurities of the notified polymer*" (NICNAS, 2015).

Mixtures containing the substances

Surfactant mixtures - A number of surfactant mixtures have been identified:

The 3M™ Novec™ fluorosurfactants are examples of specific surfactant products containing PFBS-related substances. It is a family of advanced wetting and levelling agents, used in a broad range of aqueous and solvent-borne coatings and some products (but not all) in this product line are based on PFBS-related chemistry. This is the case for the 3M™ Fluorosurfactants FC-4430, FC-4432 and FC-4434, for example, which are intended to be used only in non-emissive permanent coatings.

According to the notification of fluorosurfactant FC-4430 for the Australian NICNAS programme, the surfactant can be used in powder coating products and a variety of waterborne, solvent-borne and high-solids organic polymer coatings for electronic components in the computer and telecommunications industry, office furniture and pipes in chemical plants (NICNAS, 2015). Other industrial applications for the notified polymer are in pre-formulated inks and in the manufacture of insulation foam. (NICNAS, 2015).

Recommended use levels of FC-4430 and FC-4432 for these products are 0.05 - 0.3% active surfactant. The PFBS-related substances account for approximately 90% of the surfactants, and the concentration of the substances in the final mixtures (paint, adhesive, etc.) is consequently slightly less than 0.05-0.3%. 3M™ Fluorosurfactant FC-4434 is a diluted solution of 25% active fluorochemical surfactant in a water miscible solvent. The recommended use level is 0.05-0.3% active surfactant.

Final mixtures - Contact with potential users of the surfactants (e.g. via the European trade association CEPE and the Norwegian Paint Makers Association) has not revealed specific information regarding end uses. Only a few products with the CAS numbers listed above are registered in the Spin Database of the Nordic product registers and they are all registered as "surfactants", i.e. the database does not hold any data on the final mixtures. Likely the surfactants are used in some highly specific products which are difficult to identify; the manufacturers of the surfactants have not provided information on downstream uses of the surfactants, other than that there are no food-contact end-uses for the adhesives, resins and inks.

Paints – The data sheets for the surfactants indicate that the surfactants may also be used for "architectural coatings", similar to decorative paints. A pamphlet for the Novec™ fluorosurfactants for paints and coatings shows a consumer painting a wall (3M, 2009). The fluorosurfactant FC-4430 in Australia indicates that applications include domestic decorative paints that would be available to consumers. The 3M Company has confirmed that the abovementioned fluorosurfactant products may be used in both industrial and consumer paints. It is not indicated as to whether the paints are used for indoor or outdoor applications. According to a major actor within the Danish paint industry, there is no usage of mixtures with PFBS-related substances in regular decorative paints manufactured and sold in Denmark.

Data collecting activities have only identified the use of PFBS and related substances in one type of epoxy coating:

- CHO-SHIELD® 4997 Part A, containing <0.8% fluoroacrylate copolymer (CAS No. 1017237-78-3). This mixture is a part of a four-part conductive coating system.

Based on the information on recommended use levels, it is expected that the concentrations of the PFBS-related substances in the final mixtures are in the range of 0.01-0.3%.

Articles containing the substances

The final mixtures are used to form coatings or adhesives which form part of various articles or are used in building and construction. No specific information on the presence of PFBS-related substances in articles has been identified.

Quantities used

As mentioned, only a few products with the CAS numbers listed above are registered in the Spin database of the Nordic product registers and the total registered volume is indicated as 0 tonnes.

According to the notification of Fluorosurfactant FC-4430 in Australia, the surfactant is intended to be imported into Australia in quantities of up to 29.1 t/year primarily in, or for, production of paints and coatings (NICNAS, 2015).

Based on the available information, it is estimated that the total content of PFBS-moieties in surfactants for paints, adhesives, waxes, etc. in the EEA is on the order of 1-3 t/year. The relatively small quantities indicate that the use of these surfactants in the mixtures is not widespread and the surfactants may in fact be used by relatively few formulators of these mixtures across the EEA. A portion of the final mixtures may be exported and some final mixtures with PFBS-related surfactants may be imported, but it is roughly estimated that the end-applications in the EEA correspond to 1-3 t/year.

3.2.2 Flame retardants for polycarbonate

Potassium perfluorobutane sulfonate (K-PFBS) is used in flame retardants for polycarbonate, used mainly in electrical and electronic equipment. The use of PFBS-related substances as flame retardants for other types of materials has not been identified, but product data sheets indicate that K-PFBS may be suitable for other plastics.

Life cycle stages

The following life cycle stages exist for this application:

- Manufacture of the substances
- Production of the flame retardants
- Production of polycarbonate
- Use of polycarbonate for production of articles
- Use of articles with polycarbonate
- Disposal of articles with polycarbonate

Substances used

The identified substance used for these applications is:

- Potassium perfluorobutane sulfonate (K-PFBS) (CAS No. 29420-49-3).

Mixtures containing the substances

Many different flame retardant products with K-PFBS are marketed. The following flame retardant mixtures have been identified:

- RM65 from the Italian company Miteni SpA. According to a brochure from Miteni SpA (Miteni, no year indicated), RM65 has only a minor influence on the chemical and physical characteristics of the polycarbonate, such as visual aspect and optical brightness, and is therefore particularly suitable for use in transparent and pigmented polycarbonate. According to the brochure, RM65 is in compliance with different 'eco labels' (TCO-99, Blue Angel (Germany), Eco Mark (Japan)) which require that monitors and computer cases are manufactured with chlorine and bromine-free plastics. The recommended use level of RM65 is 750 – 1200 ppm and the concentration of fluorine in the polycarbonate is max. 0.15%. Miteni SpA states on its website that the production capacity is several tons per year.

- 3M™ FR-2025 Flame Retardant Additive. K-PFBS constitutes 95-99% of the product according to the safety data sheet. According to the distributer in Korea, FR-2025 flame retardant additive has been found to be an effective flame retardant in polycarbonate at levels as low as 0.06-0.08% by weight.

- EFTOP EF-42 Potassium nonafluorobutanesulfonate, from Mitsubishi Materials Electronic Chemicals Company, is also marketed as a flame retardant for polycarbonate resins that are required to be transparent. According to the webpage, EF-42 is also widely used as a raw material (the anion fraction) for photo acid generating agents (Mitsubishi, n.d.).

- BAYOWET® C4 from Lanxess is marketed for use as a flame retardant for polycarbonate, but also has other indicated uses in plastics. Recommended use level of the product is not indicated.

Articles containing the substances

The product information generally makes reference to flammability requirements for electrical and electronic equipment (EEE); it is presumed that the majority of the flame retarded polycarbonate is used in EEE. Examples of final applications of the flame retarded polycarbonate mentioned in technical data sheets include monitors and computer casings.

Information on quantities used

The global manufacture of K-PFBS in 2015 was reported at 46 tonnes; of these, 32 tonnes are used in China (without indicated uncertainties). One European manufacturer states that their production capacity is several tonnes per year. The substance is not registered under REACH, but may still be used in volumes up to 100 t/year (registration deadline for volumes 1-100 t/year in 2018). As the majority of electrical and electronic equipment used in Europe is imported from Asia, it is estimated that the majority of K-PFBS used in final articles would be imported. On this basis, it is estimated that the use of K-PFBS in flame retardants for the manufacture of flame retarded polycarbonate within the EEA likely is in the range of 1-10 t/year, while the total quantity in articles placed on the market is estimated to be in the range of 2-20 t/year.

3.2.3 Oil, water and stain repellent protection of fabrics, carpets, leather, etc.

Various side-chain-fluorinated polymers are used as agents for oil, water and stain repellent protection of fabrics, carpets, and leather. Many of these agents are based on polymers prepared on the basis of fluorine chemistry without the sulphur groups. To the knowledge of the authors, 3M is the only supplier of such products based on PFBS-chemistry, where the most well-known product line is Scotchgard™. The Scotchgard™ products were originally based on PFOS-related substances, but in June 2003, PFOS-related substances were replaced by PFBS-related substances. Not all of the Scotchgard™ brand products are based on fluorine chemistry.

The impregnating agents are applied as a thin film on the surface of the materials by a process in which the polymerization and curing occurs on the surface of the material. The side chains of the two-dimensional polymer structure formed during curing protrude as small hairs from the material, and aid in providing the dirt- and water-repellent effect. The side-chains may be a combination of polyfluoroalkylated (providing repellency) and non-fluorinated chains (providing e.g. film forming softness). The substances in the applied repellent agents may be present in the final film at trace levels. As described in Section 1.2.3., the side chains of these polymer types may possess the ability to sever from the polymer chain to become PFBS precursors. Actual measurements of impregnation agents and treated articles have demonstrated that the agents and articles often contain a mix of different PFAS with varying lengths of the perfluorinated chain (Section 3.2.8).

Besides the abovementioned uses, PFBS-based substances may also be used during the manufacturing of synthetic fibres as polymer melt additives. During the manufacturing process (the polymer melt process), a fluorochemical polymer may be added to impart oil and water repellency to the finished fibres.

Life cycle stages

The following life cycle stages exist for this application:

- Manufacture of the substances
- Production of repellent agents
  - a) Use of repellent agents in production of articles (fabric, carpets, leather etc.) (industrial)
  - b) Use of repellent agents for treatment of finished articles (fabric, carpets, leather etc.) (consumers)
- Use of articles
- Disposal of articles

Substances used

The formula of the Scotchgard™ products is generally confidential and the identities of many of the relevant fluorochemicals are not disclosed in the safe data sheets for the products, but stated as, for instance:

- Fluorochemical acrylate polymer
- Fluorochemical urethane
- Perfluorobutanesulfonamide and polyoxyalkylene containing polyurethane

Other substances in low concentrations in some of the repellent agent mixtures are:

- *N*-Methyl perfluorobutanesulfonamidoethyl acrylate (MeFBSAC, CAS No. 67584-55-8)
- *N*-Methyl perfluorobutanesulfonamidoethanol (MeFBSE, CAS No. 34454-97-2)
- *N*-Methyl perfluorobutanesulfonamide (MeFBSA, CAS No. 68298-12-4)

Wang *et al.* (2013) specifies the following Scotchgard™ products:

- PM-3622 containing CAS No. 949581-65-1
- PM-490 containing CAS No. 940891-99-6 and PM-930 containing CAS No. 923298-12-8.

It has not been possible to verify the information from Wang *et al.* (2013); therefore, the substances have not been included in the gross list of PFBS-related substances in Appendix B. The substances are not included in the lists of PFAS published by the OECD. Searches on the abovementioned CAS-numbers in several databases also did not yield any results on the identity of the substances.

Mixtures containing the substances

The Scotchgard™ product brand from 3M comprises products both for consumer and non-consumer use. Some of the products do not include PFBS chemistry but are based on other chemistries. The following mixtures identified from the website of the manufacturer are assumed to be based on PFBS chemistry (the list is not considered to be exhaustive but represent examples of different application areas):

For consumer use the following products are supplied in aerosols for spray application (the list may not be exhaustive):

- Scotchgard™ Fabric Protector – oil, water and stain repellent protection of fabrics based on a fluorochemical urethane
- Scotchgard™ Suede and Nubuck Protector used for protection of leather products, based on a polyfluoroalkyl acrylate polymer.
- Scotchgard™ Protector for Rugs & Carpet - oil, water and stain repellent for rugs and carpets, based on a fluorochemical urethane

For non-consumer use, the following has been identified:

- Scotchgard™ Protective Material PM-97, PM-93 and PM-95, which are all protective treatments for carpets containing perfluorobutanesulfonamide and polyoxyalkylene containing polyurethane

For industrial use, the following 3M Mixtures have been identified:

- 3M™ Protective Material for Fabric PM-4950: Repellent treatment for fabric. Contains a fluorochemical acrylate polymer (65-75%) and MeFBSAC (CAS No. 67584-55-8) (<0.12%)
- 3M™ Protective Material PM-1690: Carpet treatment. Contains an urethane (25-35%), MeFBSE (CAS No. 34454-97-2 (<0.15%) and MeFBSA (CAS No. 68298-12-4) (<0.1%)
- 3M™ Protective Chemical PM-490. Protective treatment for textiles and carpet. Contains a fluorochemical polyurethane.
- 3M™ Protective Material PM 4700, PM-4701 and PM-4800, which are all recommended for use as leather protectors. The mixtures contain a fluorochemical acrylate polymer.
- 3M™ Repellent Polymer Melt Additive PM-870, which is used during the manufacturing of synthetic fibres to impart oil and water repellency to the finished fibres. The mixture contains a fluoroalkyl derivative (88-90%) and MeFBSE (CAS No. 34456-97-2) (<0.5%). No information on recommended use levels is available.

Industrial applications - As an example of industrial applications, TFL Ledertechnik GmbH (Germany), an authorized distributor of 3M™protective materials for the leather industry, supplies Scotchgard™ Protector in three products: "*PM-4700 is an aqueous based product for drum application, PM-4701 is an aqueous based product for spray application and PM-4800 is a solvent based formulation for spray application*" (TFL, 2016). When applied in the drum at tanneries, the mixture may be applied by co-application before or after the introduction of the fat liquors or as an after-treatment in the drum. According to the technical description, the protectors are applied for leather articles of suede and nubuck for shoes (upper leather), coats and sofas. The company states that "*the polymers are developed in such a way that they will contain very low levels of residual monomers that have the potential to degrade further to PFBS (Perfluorobutanesulfonate). Concerning the ultimate degradation product of this new chemistry, PFBS, test findings provide evidence that this substance is persistent".*

Specific information on industrial application of the mixtures for production of apparel and carpets has not been identified, but for the study it has been confirmed that such application takes place within the EEA.

Recommended use levels have not been specified for any of the mixtures.

Articles containing the substances

Repellent films based on polymers with PFBS-related side chains may be present in apparel (rain- and outerwear, workwear, uniforms), technical textiles (medical, non-wovens, military, antiballistic fabrics, coated fabrics), home textiles (upholstery, awnings etc.), carpets, industrial leather articles (nubuck and suede) and in consumer textiles and leather applications (e.g. shoes, handbags etc.). Many types of repellent agents based on different fluorine-, silicone- and other chemistry are available on the market, so only a small number of the treated articles are actually based on PFBS chemistry.

According to contact with Norwegian trade associations for the textile industry and their members, the substances are not used for textiles on the consumer market, and the companies generally avoid the use of the substances. No data has been received from the European trade association Euratex.

Actual measurements of e.g. treated leather have demonstrated levels of extractable PFBS of up to 308 µg/m² but studies have typically not tested for a wider range of PFBS-based substances (Section 3.2.8). The content of PFBS moieties of polymers may be much higher. No specific data for PFBS-based polymers have been identified, but in a study of agents based on fluorotelomer chemistry, an increase of more than a factor of 1000 in the amount of extractable PFAS after oxidation of the side chains was demonstrated (Eschauzier and Knepper, 2013).

Information on quantities used

Based on the information made available throughout the survey, the quantities of agents for repellent protection for these purposes placed on the EEA market for industrial, professional and consumer applications correspond to 20-40 t/year PFBS moieties. It is assumed that import with articles is significant for this application area as the majority of outdoor textiles and leather articles placed on the EEA market is imported from Asia; however, some export of articles, especially leather articles manufactured within the EEA also takes place. Based on the available information, the content in final articles and mixtures used for consumer applications placed on the EEA market is estimated to be in the range of 20-60 t/year PFBS moieties.

3.2.4 Repellent agents for porous hard surfaces

PFBS-based substances and polymers are used to impart functional oil and water repellency when applied to porous hard surfaces such as concrete, grout, unglazed tile, granite, clay, slate, limestone, marble and terracotta. The repellent agents can be used either as penetrating sealers or as additives in various coating and sealer formulations.

The function of the repellent agents is essentially as described for the articles above. Repellents for porous hard surfaces based on other fluorine, siloxane and other chemistries are available for the same applications.

Industrial, professional and consumer sectors are indicated as end-users of the final products.

Life cycle stages

The following life cycle stages exist for this application:

- Manufacture of the substances
- Production of the repellent agents
- Application of the repellent agents on porous hard surfaces in buildings or incorporated into construction materials
- Use phase of the buildings
- Removal and disposal by maintenance or demolition of the buildings

Substances used

Identified substances being used for these applications are:

- PFBS-related polymers, such as fluoroacrylate modified urethane and fluorochemical acrylate polymer

- *N*-Methyl perfluorobutanesulfonamidoethanol (MeFBSE) (CAS No. 34454-97-2

The MePBSE is present at low concentration (<0.5%), probably as a residual raw material.

Mixtures containing the substances

The following repellent mixtures for porous hard surfaces have been identified:

- 3M™ Stain Resistant Additive SRC-220: aqueous fluorinated polyurethane dispersion that provides stain resistance and release characteristics to various coating formulations, sealer formulations and construction materials. The product is suitable for both indoor and outdoor use. When used as a penetrating sealer the recommended concentration is 2 – 5%. The mixture can also be used as a stain resistant additive to a variety of acrylic and urethane based coatings at 0.2 to 1.0% active solid levels, to improve the water and oil repellency. Additionally, SRC-220 additive can be incorporated into construction materials, such as caulk or putty, to improve the stain resistance and release characteristics of these materials.

- 3M™ Stain Resistant Additive and Sealer PM-1680. The product is a water soluble general-purpose fluorochemical emulsion designed for application to porous hard surfaces. PM-1680 can be added to an existing formulation or can be diluted with water and used as a penetrating sealer. For use as a penetrating sealer, it is recommended that PM-1680 should be mixed with water, solvents and 3M™ Novec™ Fluorosurfactant FC-4434. The recommended concentration of PM-1680 for such applications is 10%. PM-1680 can also be added directly to a number of commercially available water-based coatings and sealer formulations. PM-1680 additive enhances the oil, water and stain resistant properties of the formulations. Typical recommended additive levels are from 0.2-3.0%. PM-1680 can be applied with most commercially available application equipment such as brushes, sponges, rollers and spray applicators.

- SILRES® BS 38 from Wacker Chemie. According to the National Industrial Chemicals Notification and Assessment Scheme (NICNAS) in Australia, the polyfluorinated side-chain polymer in SILRES BS 38 is a potential precursor for PFBS in the environment (NICNAS, 2014). According to the notification, degradation products of the notified polymer, along with associated impurities and residual monomers of the notified polymer, are potential precursors of PFBS. SILRES® BS 38 is a solvent-based mixture of silane-based substances, siloxane and fluoropolymer (< C8). In diluted form, it serves to render inorganic substrates such as mineral construction materials water-repellent and oil-repellent (Wacker, 2015). The maximum introduction volume of the notified chemical in Australia is 0.1-0.8 t/year (NICNAS, 2015). According to the notification, the product is applied in factory settings (33%), by tradesmen (33%) or by the public (34%). For tradesmen and domestic users, the product containing the notified polymer (up to 8% concentration) is applied to stone and tiles using a brush, roller or mop. According to the technical data sheet for SILRES BS 38 (Wacker, 2015), the product is used for:

    - Treatment of façades of natural or synthetic stone, concrete, or fibrous cement in order to allow easier removal of dirt, grease, graffiti, posters, etc. from monuments, exterior and interior walls.
    - Water-, oil- and dirt-repellent treatment of low-porosity natural stone, e.g. marble, travertine and granite.

  - Treatment of floors of natural or synthetic stone, or unglazed ceramic tiles for easy care.
  - Treatment of windowsills and tabletops of natural or synthetic stone, or fibrous cement to avoid staining.
- 3M™ Protective Material PM-803 for use as tile grout additive. The mixture contains *N*-methyl perfluorobutanesulfonamidoethanol (MeFBSE) (CAS No. 34454-97-2) and a fluorochemical urethane.

A number of other mixtures from 3M™for this application area contain fluorinated polyurethane and acrylate dispersions, which may be PFBS-related polymers, but no information on the actual polymers is provided. The applications for these mixtures are similar to the applications described above.

Articles containing the substances

These repellent agents are typically used for treatment of building materials on site and would typically not be present in articles placed on the market. It is possible that some building materials, e.g. marble, travertine and granite tiles, could be pre-treated before they are placed on the market.

Solid materials

The PFBS-based repellent agents are present on surfaces or within building materials and PFBS may be released from the surfaces. No data on actual levels of extractable PFBS-based substances are available.

Information on quantities used

Based on the information made available throughout the survey, it is estimated that the total tonnage in terms of PFBS moieties in mixtures placed on the EEA market likely is in the range of 5-10 t/year. The import and export with articles, e.g. treated stones, is assumed to be small for this application area.

3.2.5 Metal plating

One PFBS-related substance is registered for industrial use for metal (chromium) plating.

Historically, salts of PFOS have been used as wetting agents and mist-suppressing agents in decorative plating and non-decorative hard plating (Wang *et al.,* 2013). Recent technology development using chromium-III instead of chromium-VI has made PFOS-related substances' use in decorative chrome plating obsolete. Chromium-III, however, cannot be used for hard chrome plating. In Europe, salts of 6:2 fluorotelomer sulfonic acid (6:2 FTSA, CAS no. 27619-97-2) are applied as alternatives to PFOS in non-decorative chromium plating (Danish experience described in Poulsen *et al*., 2011). However, they can only partly be applied in decorative plating due to their surface tension, slightly higher as compared to PFOS (UNEP, 2012).

Life cycle stages

The following life cycle stages exist for this application:

- Manufacture of the substances
- Production of plating agents
- Industrial use of the agents for plating
- Disposal of plating bath

Substances used

The identified substance being used for this application is:

- Tetraethylammonium perfluorobutanesulfonate (CAS No. 25628-08-4) is registered for this application (name of registrant confidential).

Mixtures containing the substances

The following mixture for hard chrome plating has been identified:

- Bayowet FT 248 liquid (50% solution) is used as a spray mist inhibitor for the chromium galvanic industry. The mixture consists of 5% tetraethylammonium perfluorobutanesulfonate and 45% tetraethylammonium heptadecafluorooctanesulfonate (CAS No. 56773-42-3) (Lanxess, 2016). According to the technical data sheet, the mixture is applied to the chromium electrolyte in an active substance concentration of 125 mg/L (Lanxess, 2008).

For the professional use of mist suppressing agents containing PFOS in the hard chrome plating industry, the agents have typically consisted of a 5–10% solution of PFOS (Poulsen *et al*., 2011). According to Poulsen *et al.* (2011), the PFOS-containing agents were added in total amounts of 7.2 L/m^3.

For the 2005 OECD survey, a company in Germany reported that in 2003, 20-50 tonnes bis[2-(*N*-methyl perfluorbutanesulfonamido)ethoxy] phosphoric acid ester (CAS No. 120945-47-3) were used as a defoamer in the electroplating industry (OECD, 2005). However, the OECD (2006) survey indicated the consumption as 20-50 kg. The substance has not been included in other surveys, and it is not clear as to whether the kg or tonnes measure is correct. The CAS number is indicated in ECHA's database of preregistered substances as: "Name confidential or not available". No current uses of this substance have been identified.

Articles containing the substances

The substances are not expected to end up in the final articles but are rather disposed of along with the plating bath.

Information on quantities used

Tetraethylammonium perfluorobutanesulfonate is registered in volumes of 1-10 t/year for industrial use in metal (chromium) plating. It is not indicated whether the substance is used for hard or decorative plating. The only identified mixture contains a PFOS related substance; furthermore, production and placing chromium plating on the market has been prohibited in the EU since 26 August 2015. It cannot be excluded that other mixtures are marketed, but not identified; consequently, the quantities used are still estimated at 1-10 t/year.

3.2.6 Surfactants and solder paste for electronics

A number of PFBS-related substances are included in surfactants and solder paste used in the electronic industry. The surfactants are not necessarily much different from surfactants used for other applications, but are described separately in this context, as the life cycle stages for this application are different from other applications of surfactants.

Life cycle stages

The following life cycle stages exist for this application:

- Manufacture of the substances
- Production of surfactants
- Production of electronics
- Disposal of used surfactant and solder paste

Substances used

Identified substances used for these applications are:

- 1-Propanesulfonic acid, 3- [hexyl[(nonafluoro-butyl)-sulfonyl]amino]-2-hydroxy-, monoammonium salt (CAS No. 606967-06-0)
- Ammonium perfluorobutanesulfonamidoethanolate (CAS No. 484024-67-1)
- Fluoroacrylate copolymer (CAS No. 1017237-78-3)
- *N*-Methyl perfluorobutanesulfonamidoethyl acrylate (MeFBSAC, CAS No. 67584-55-8)

Mixtures containing the substances

The following surfactants and soldering flux mixtures have been identified:

- 3M™ Novec™ 4300 Electronic Surfactant, recommended for use in metal etch solutions and in other aqueous microelectronic process chemicals
- 3M™ Novec™ 4200 Electronic Surfactant, intended for use in semiconductor wafer fabs. Novec™ 4200 is intended to improve wet-out, levelling and flow-control for a variety of applications including buffered HF (BHF)/buffered oxide etch (BOE) applications
- ECOFREC 200; Flux for the soldering of electronic components on printed circuit boards
- LOCTITE LF 318M solder paste

Articles containing the substances

It is assumed that only trace levels of the substances are left on printed wiring boards and other electronic components.

Information on quantities used

It has not been possible to obtain any specific information on the quantities of PFBS-related substances used for the production of electrical and electronic articles. Based on the available information it is roughly estimated that the total consumption in the EEA is likely limited and in the range of 0.1-1 t/year.

3.2.7 Other applications

A number of other applications have been identified or described in the literature. Specific data on consumption of PFBS-related substances for these applications are not available, but considering the applications, releases to the environment and consumer exposure, consumption is expected to be limited as compared with some of the applications described above.

Curatives in fluoroelastomer formulations

According to 3M, PFBS-related substances may also be used in curatives for fluoroelastomer fomulations. The PFBS-based curatives are present in the product formulation in concentrations of <5%. The curative will react with the fluoroelastomer backbone to a three-dimensional network, and is thus fully incorporated into the polymer matrix. The curatives are only deployed in industrial applications for the manufacturing of O-rings, seals, tubing inner linings, etc. No detailed information on the substances or quantities used has been obtained.

Manufacture of synthetic leather

MeFBSE (CAS No. 34454-97-2), MeFBSAC (CAS No. 67584-55-8) and MeFBSA (CAS No. 68298-12-4) are found at low levels in 3M™ Protective Material PM-1000, used for manufacture of synthetic leather and resins utilized in the production of synthetic leather. No information on recommended use levels and use volumes is available.

Acid catalysts

PFBS is found in the mixture EFTOP EF-41 from Mitsubishi Materials Electronic Chemicals Company, for use as an acid catalyst, as well as in raw material for photo-acid-generators and synthetic raw material (Mitsubishi, n.d.). Photo-acid generators are components of photoresist formulations used in optical lithography.

Anti-static additive for plastics

Tetrabutylphosphonium perfluorobutanesulfonate (CAS No. 220689-12-3) has been found in the mixture Anti-Stat FC-1 Fluor surfactant from DuPont (in the literature also referred to as Zonyl FASP-1), which was used as an anti-static additive for plastics. Anti-Stat FC-1 seems to have been replaced by antistatic additives in DuPont's Entira AS product range, but safety data sheets for these products have not been available.

Tetrabutylphosphonium perfluorobutanesulfonate is registered under REACH in volumes of 1+ t/year by Miteni SpA. (chemical manufacturer) and SABIC Innovative Plastics BV (large provider of engineering plastics) for manufacture of plastics. Further information has been requested from both companies on use, but no information has been obtained. The substance is not included on the websites of the companies.

Laboratory agent

In principle, all of the substances may be marketed for use as analytical standards.

N-Methyl perfluorobutanesulfonamidoethyl acrylate is registered for use as a laboratory agent. The environmental release category for this application is indicated as "Industrial use of monomers for manufacture of thermoplastics". The specific use of the substances in laboratories has not been identified.

Other applications

Some additional mixtures from 3M are based on fluoroalkyl substances with confidential CAS numbers. Applications included 3M™ Acid Mist Suppressant FC-1100, used in copper electrowinning tank houses and 3M™ Well Stimulant WS-1200, used to mitigate condensate and/or water blockages in sandstone natural gas wells.

Other applications not demonstrated to take place in the EEA today

Other applications mentioned in the literature for which it has not been possible to confirm actual uses in the EEA are listed below.

Pesticides - According to a market report from Prof Research Global (2016a), the second largest application of PBSF globally was the production of pesticides. Furthermore, the market report on PFBS indicates that this substance is used to some extent for manufacturing of pesticides. According to a search in the EU Pesticides Database, the only two active substances in approved pesticides in the EU with the text string "fluor" in the name are sulfonyl fluoride and oxyfluorfen (Pesticide Database, 2016). None of these occur within the groups of PFBS-related substances. Traditionally, a PFOS-related pesticide sulfluramid has been widely applied for controlling leaf-cutting ants. No data have been identified indicating that sulfluramid has been replaced by a C4 homologue.

Firefighting foams - No actual use of PFBS in firefighting foams has been identified. Some old-generation aqueous firefighting foams (AFFF) contained PFBS. For example, an analysed firefighting foam (Table 7) contained 0.2 g/L of PFBS, as well as higher concentrations of the higher homologues PFHxS, PFHpS and PFOS. According to a bulletin from Tyco Fire Protection Products, since 2002, virtually all perfluorinated surfactants contained in firefighting foam agents have been produced only by the telomerisation process (Tyco, 2016). New-generation aqueous firefighting foams are not expected to contain PFBS, and in accordance with this expectation, analysis of two new-generation AFFFs in Norway demonstrated PFBS levels below the detection limit (Herzke *et al.*, 2012). According to an assessment of alternatives to PFOS, PFBS has never been applied or successfully used in firefighting foams due to its non-dispersive properties (POPRC, 2012). However, it cannot be excluded that PFBS is present at trace levels in firefighting foams based on other PFAS.

PFBS has been demonstrated to be present in surveys of fire-fighting training grounds around the world, but its presence may be due to historical use of fire-fighting foams with PFBS. In Denmark, 17-20 ng/L was demonstrated at one location out of seven where the dominant PFASs were PFHxA and PFHpA (Tsitonaki et al., 2014). In a study from the US, PFBS (and PFBA) was found in surface soil, subsurface soil, sediment, surface water, and groundwater (Anderson *et al.* 2016). In Australia, PFAS were also measured at fire-fighting grounds. The highest levels in soils were of PFOS but PFBS was also identified (Baduel *et al.* 2015).

In another study from the US, PFAS (including PFBS) levels in drinking water was linked to industrial sites, fire training areas and wastewater treatment plants (Hu *et al.* 2016).

Heap leaching mining - Perfluorobutanesulfonamide *N*-(*N′,N′,N′*-trimethyl-propanaminium) chloride (CAS No 53518-00-6) has previously been used in FC-1129 Fluorad Brand Leach Mining Additive from 3M. Heap leaching is a mining process to extract metals from ore via a series of chemical reactions that absorb and re-separate specific minerals.

3.2.8 Actual PFBS levels in analysed products

During the application of the mixtures with PFBS-related substances, the substances may be transformed and built into two and three-dimensional polymer structures, where the parent substances are only present in trace amounts. This prospect means that the substances identified by analysis of the final coated articles are not necessarily the same as the substances applied. This issue complicates significantly a quantification of the amounts of the substances traded using final articles and the potential for releases of the compounds.

The following section reviews existing information on PFBS identified in surveys of various products. Within the group of PFBS-related substances, the surveys have generally included PFBS but not precursors and degradation products.

Chu and Letcher (2014) studied the i*n vitro* formation of perfluoroalkyl sulfonamides from Scotchgard Fabric Protector Products. These products represent the major application of PFBS-related substances in articles for consumers. The tests demonstrated that the main *in vitro* metabolite of the PFBS-related products was perfluorobutane sulfonamide (FBSA), which, according to the authors, was coincident with the detection of the major fabric protector components that contains the N-methyl-perfluorobutane sulfonyl chemical moiety. The PBSA concentration increased progressively over the incubation period, but with no concomitant formation of PFBS, indicating that it would be relevant to analyse for FBSA. Furthermore, date sheets for some of the agents for repellent protection contain low levels of residual MeFBSAC, MeFBSE and MeFBSA, which may also be present at low levels in the final articles. However, these substances have generally not been included in the surveys.

In most surveys of polyfluoroalkyl substances (PFAS) in articles, the concentrations of PFBS have been relatively low. As an example, the concentration of PFBS in 15 sample textiles for children in Denmark were below the detection limit in 14 samples and below 0.01 µg/m^2 textile in one case (Lassen *et al*., 2015a). Similar results have been found in several other studies of clothing, whereas a study by Norges Naturvernforbund (2006) found concentrations up to 0.3 µg/m^2 textile in some clothing (Table 7). In these samples, the PFBS only accounted for a small amount of the total content of PFAS. Other reports (SFT, 2006 and Hanssen and Herzke 2014, 2015) show similar results. In a study on the presence of perfluoroalkyl substances in consumer articles imported from China and sold in Norway, PFBS was only detected in a single sample (paper plates food contact material) at a concentration of 0.069 µg/m² (Vestergren *et al.,* 2015).

Becănová *et al.* 2016 investigated the presence of PFASs in consumer articles, building materials, car interior components and wastes of electrical and electronic equipment (WEEE). Consumer articles were divided into different categories, i.e. textiles, floor covering, electrical and electronic equipment (EEE) and plastics. PFBS was detected in 15 out of 24 textile samples with a maximum concentration of 6.14 µg/kg; in 4 out of 9 floor covering samples, with a maximum concentration of 0.97 µg/kg; in 11 out of 18 EEE samples, with a maximum concentration of 11.4 µg/kg, and in one out of 4 plastic samples at a concentration of 0.38 µg/kg. Building materials were divided into oriented strand board (OSB), other composite wood and wood, insulation materials, mounting and sealant foam, façade materials, polystyrene and air conditioning components. No PFBS was detected in the latter two categories. See Table 7 for details on the findings in the remaining categories. PFBS was detected in 7 out of 10 samples of car interior components, with concentrations ranging from 0.068 to 2.18 µg/kg. The substance was also detected in 6 out of 7 WEEE samples, with a maximum concentration of 1.38 µg/kg. Therefore, the levels of PFBS in the analysed samples were very low, suggesting that the presence of PFBS was not caused by intentional addition of the substance to the materials during manufacturing (Becănová *et al.,* 2016). Samples containing PFBS also contained other perfluoroalkyl sulfonates such as PFHxS (C6), PFHpS (C7), PFOS (C8) and PFDS (C10) at similar concentrations, indicating that the applied side-chain-fluorinated polymers contain a mix of moieties with varying chain lengths.

In a study by Kotthoff *et al.* (2015) the presence of several perfluoroalkyl sulfonic acids was investigated in a number of consumer articles (82 in total). PFBS was identified in carpets, gloves, ski wax and leather samples, at higher concentrations than were demonstrated in most of the abovementioned studies. In the leather samples, PFBS was found at a maximum concentration of 143 µg/m² and in the carpet samples the maximum concentration was 26.8 µg/m². It should be noted, however, that the samples used for analysis in this study were purchased in 2010.

In a study from 2013, Greenpeace investigated the presence of different groups of substances, including different per- and poly-fluorinated chemicals in branded textile articles on sale in 25 different countries/regions. PFBS was detected in two footwear articles and two samples of waterproof clothing (Brigden et al., 2013). In 2016 Greenpeace published a follow-up to this study (and other investigations of per- and polyfluorinated chemicals), where 40 outdoor items (clothing, footwear and gear (tents, sleeping bags and hiking gear)) were investigated. PFBS was detected in 8 out of 13 jacket samples, with the highest concentration being 673 µg/m²; in 4 out of 9 trouser samples, in 7 of 13 shoe samples and 2 of 15 backpack samples. The PFBS levels (see Table 7) found in this study were generally much higher than in the other studies mentioned, and in several of the samples, PFBS was the predominant PFC detected.

In a recent Nordic survey of per- and polyfluorinated substances in articles, PFBS were only found in a few samples (in baking ware) just above the detection level (Blom and Hanssen, 2015).

As mentioned above, studies have shown that the total content of PFAS moieties in e.g. treated textiles are thousands of times higher than the measured concentrations of free PFAS. No specific data for PFBS-based polymers have been identified, but in a study of agents based on fluorotelomer chemistry, an increase by more than a factor of 1000 in the amount of extractable PFAS after oxidation of the side chains was demonstrated (Eschauzier and Knepper, 2013). Consequently, actual measurements of PFBS in articles provide very limited information on the actual content of PFBS-related substances and the potential for release of PFBS, but rather indicate the quantities that may be immediately released without further breakage of the links between the polymer backbone and the PFBS-based side chains.

Table 7 Measured levels of PFBS in various mixtures and articles

Consumer product	Level of PFBS	Reference	Comment
Firefighting foam (aqueous film forming foams)	253,700 ug/L	Herzke *et al.*, 2012	The product contained a mixture of several different PFAS, including PFBS. The concentrations of PFOS, PFHxS and PFHpS were higher than the concentration of PFBS in the product. The brands of AFFF belong to old generation foams and have been phased out of products in Norway.
Waterproofing agent	38.65 µg/L	Herzke *et al.*, 2012	The product also contained 118 µg/L PFBA
Leather articles	1.36 µg/m² (shoe leather) 308 µg/m² (furniture leather)	Herzke *et al.*, 2012	Both articles also showed levels of PFOS above the allowable level of 1 µg/m² according to EU Directive 2006/122/EC (38.0 and 21.2 µg/m² for furniture and shoe leather, respectively). The shoe leather also contained PFHxS (4.81 µg/m²)
Non-stick ware	2.84 µg/kg	Herzke *et al.*, 2012	The product contained higher concentrations of PFOS and PFBA (805 and 415 µg/kg, respectively)
Snowsuit for children	0.01 µg/m²	Lassen *et al.*, 2015a	Total amount of PFASs detected in the product was 100.69 µg/m²
Textile (outdoor wear)	< 0.05 – 1.01 µg/m²	Norges Naturvernforbund, 2006	

Consumer product	Level of PFBS	Reference	Comment
Textile (clothes and tablecloth)	< 0.01 – 0.02 µg/m^2	SFT, 2006	
Textile (outdoor wear)	0.055 µg/m^2	Hanssen and Herzke, 2014	
Swimsuit	0.05 µg/m^2	Hanssen and Herzke, 2015	
Food contact material	0.069 µg/m^2	Vestergren *et al.*, 2015	PFOA and 8:2 FTOH were also identified in low concentrations in the sample
Textiles (e.g. upholstery fabric, foam, curtains, bed cover, teddy bear coir, bed cover, blanket)	0.159 – 6.14 µg/kg	Bečănová *et al.*, 2016	Samples containing PFBS contained other perfluoroalkyl sulfonates such as PFHxS (C6), PFHpS (C7), PFOS (C8) and PFDS (C10) at similar concentrations
Floor covering (carpets)	0.348 – 0.966 µg/kg	Bečănová *et al.*, 2016	
EEE (e.g. keyboards, screens, vacuum cleaner, switch, coffee maker, insulation foam in fridge door, printed wiring)	0.028 – 11.4 µg/kg	Bečănová *et al.*, 2016	
Plastics (DVD cover)	0.384 µg/kg	Bečănová *et al.*, 2016	
Building materials (wooden board	0.201 µg/kg	Bečănová *et al.*, 2016	
Insulation material	0.086 – 3.87 µg/kg	Bečănová *et al.*, 2016	
Façade materials (water resistant paint)	0.536 µg/kg	Bečănová *et al.*, 2016	
Car interior material (textile and plastic material)	0.068 – 2.18 µg/kg	Bečănová *et al.*, 2016	
WEEE	0.074 – 1.38 µg/kg	Bečănová *et al.*, 2016	
Food contact material (baking ware)	0.019 – 0.029 µg/m^2	Blom and Hanssen 2015	
Footwear	0.623 – 19.7 µg/m^2	Brigden *et al.*, 2013	In one of the footwear articles, PFBS was the only per- and poly-fluorinated substance present
Waterproof clothing	0.192 – 2.10 µg/m^2	Brigden *et al.*, 2013	
Footwear	0.29 – 195 µg/m^2 (mean 42.2 µg/m^2)	Brigden *et al.*, 2016	
Backpack	3.18- 9.42 µg/m^2 (mean 6.3 µg/m^2)	Brigden *et al.*, 2016	

Consumer product	Level of PFBS	Reference	Comment
Outdoor clothing (trousers)	5.04 – 51.4 µg/m² (mean 28.3 µg/m²)	Brigden *et al.*, 2016	PFBS was the predominant ionic PFC detected in some of the samples
Outdoor clothing (jackets)	0.11 – 673 µg/m² (mean 92.2 µg/m²)	Brigden *et al.*, 2016	PFBS was the predominant ionic PFC detected in some of the samples
Textile, carpet	26.8 µg/m²	Kotthoff *et al.*, 2015	The concentration of PFBS was the highest of all perfluoroalkyl sulfonic acids detected in the samples. Different FTOHs were also detected in the samples
Textile, gloves	2.0 µg/kg (median 0.5 µg/kg)	Kotthoff *et al.*, 2015	Higher concentrations of other PFASs were detected in the samples as well
Ski wax	3.1 µg/kg	Kotthoff *et al.*, 2015	
Leather	143 µg/m²	Kotthoff *et al.*, 2015	The samples also contained high concentrations of PFBA and PFPA

3.2.9 Quantities in imported mixtures and articles

Import of the substances in mixtures - The substances may be imported in two types of products: 1) surfactants and other mixtures used in production of other mixtures or used as process chemicals; and 2) as surfactants of paints, adhesives, inks, and other final mixtures. No data on import of the substances on their own or in mixtures have been obtained from the three companies registering PFBS-related substances or from any other companies. Without this information it is difficult to estimate to what extent the mixtures used in the EEA are imported or produced in the EEA.

Import of the substances in articles - Three main uses of the substances in articles have been identified:

1) Side-chain-fluorinated polymers in impregnating agents used on leather (nubuck and suede), outdoor textiles and carpets,

2) Flame retardants in polycarbonates mainly used in electrical and electronic articles, and

3) Small quantities in coatings produced from paints and lacquers in which the substances have been used as surfactants (i.e. without a function in the final articles).

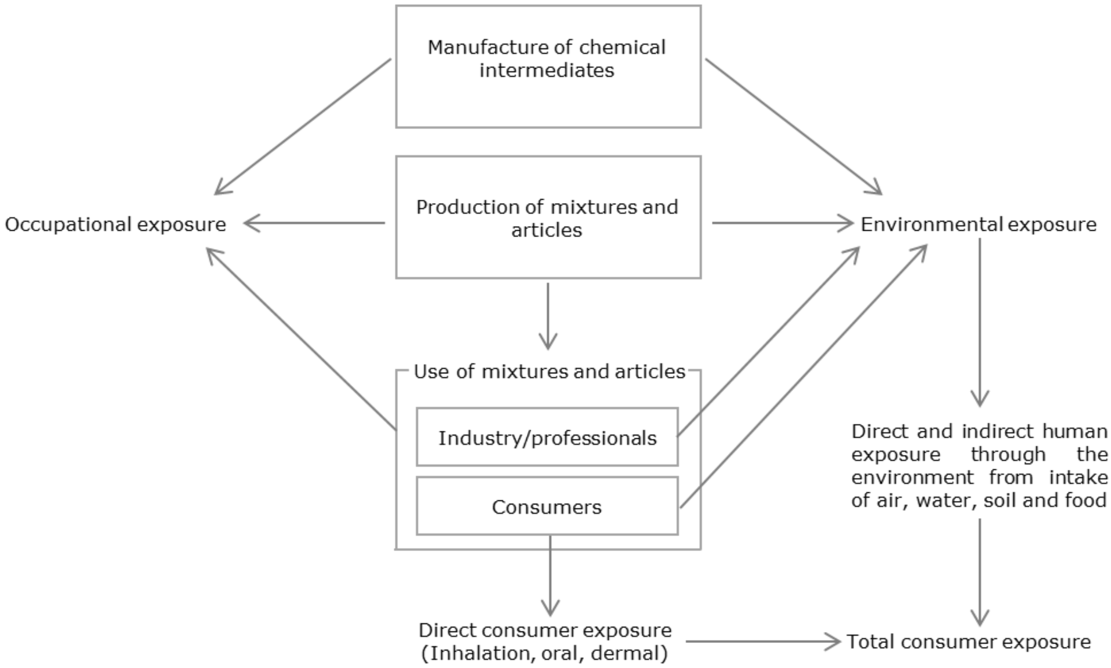
The available data do not allow for an exact estimate of the total quantities in imported articles. Outdoor textiles, leather and electronic articles used in the EEA are largely imported from China; a significant proportion of the PFBS-related substances and side-chain-fluorinated polymers produced in China may end up on the EEA market. With consumption of these substances of approximately 150 t/year for non-pesticide applications, the amount of the PFBS-related substances in imported articles, in terms of weight of PFBS moieties, is likely in the range of 5-50 t/year.

4 Potential for releases and exposure to the environment and consumers

4.1 Potential for releases during product life

Industrial production of commercial intermediates, mixtures and articles containing PFBS-related substances may occur in several steps and possibly many more locations, each giving rise to potential exposure of workers and releases to the surrounding environment of PFBS-related chemicals. The tendency is that PFBS is more often identified in newer studies (Buch et al., 2012). The various potential exposure routes for environmental, occupational and consumer exposure are illustrated in the figure below:

Figure 3 Potential exposure routes



Occupational exposure to the substances is beyond the scope of this study.

In the following sections, the potential sources of release to the environment and exposure of consumers are described qualitatively, and to some extent semi-quantitatively, if data are available.

The description does not include an examination of the fate of the released substances in the environment or the uptake of these substances in the human body.

4.2 Releases to the environment

4.2.1 Potential releases to the environment by application area

Potential routes for releases to the environment by application area are summarised in Table 8. The objectives of the table are to indicate the main sources of releases to the environment, described in more detail in the following sections. The information in the table is further described in the text after the table, where full references are provided.

No surveys of emissions of PFBS to the environment have been identified, but the surveys of the releases of PFOS and PFOS-related (POSF-derived) products may indicate possible sources of releases of the PFBS-related substances which have substituted for some of the applications of PFOS-related products. According to Alexander et al. (2009), estimates indicate that direct emissions from POSF-derived products are the major source to the environment, resulting in releases of 450-2700 tonnes PFOS into wastewater streams, primarily through losses from stain repellent treated carpets, waterproof apparel, and aqueous firefighting foams. Compared to these sources, releases from "performance chemicals", e.g. surfactants and flame retardants, were considered to be low.

For all applications, some releases may occur through the manufacture of substances and mixtures (e.g. production of surfactants). These releases are not included in the table, but described afterward.

The overall environmental release pathways and transport mechanisms can briefly be described as follows, whereas, as mentioned, a more detailed description of the fate is beyond the scope of the study:

- **Atmospheric emissions** of non-polar, volatile PFBS derivatives, results in long-range air transport and spread by wind to remote areas, for instance to the Arctic, where it precipitates from the atmosphere and contaminates this susceptible environment and its food chains. Polar bears living in the Arctic are especially highly exposed to PFAS chemicals. Locally, close to point sources, direct inhalation exposure may contaminate humans and wildlife, and air fallout can pollute soils, surface waters and food. This contamination contributes to exposure of livestock and, in addition, indirect exposure of humans through foodstuff. For example, a study has shown that PFBS was highly abundant in French food (Rivière *et al.*, 2014). Since PFBS-derivatives, due to their shorter perfluoroalkyl chain length, are more volatile than their homologue PFOS-derivatives, air releases are more important for PFBS-derivatives

- **Through discharge of water-soluble PFBS-salts to wastewater,** at wastewater treatment plants, the PFBS-moiety is not degradable, and it ends up in outlet water, or accumulates in the sludge. If the sewage sludge is used to fertilise agricultural land, agricultural soil is polluted with PFBSand PFBS-related substances which may leach to the groundwater or be taken up by the crops and end up in foods. PFBS in the outlet water would pollute rivers, lakes and marine waters and accumulate in the sediments. . In soils, PFBS is less bound/adsorbed than PFOS and PFOA (Milinovic *et al.*, 2015). Furthermore, the PFBS-related chemicals may enter aquatic food chains and end up in fish to be eaten by consumers. A recent study found low levels of perfluorobutane sulfonamide (FBSA) in almost all analysed freshwater fish species in Canada (Chu *et al.*, 2016). In South Korea, PFBS was abundant in various aquatic organisms (Hong *et al.,* 2015). In addition, the potential exists for long-range transport of PFBS derivatives by sea currents.

- **Through disposal and treatment** - various solid wastes contain mainly less volatile, less soluble and more bound PFBS. If landfilled there may be a risk of evaporation or leaching of PFBS to groundwater. PFBS and related chemicals degrade during combustion processes, and the high combustion temperatures in municipal waste incinerators destroy the PFBS derivatives.

Table 8 Potential for environmental exposure and release pathways by application of mixtures and articles (see reference in main text after the table)

	Industrial and professional application of mixtures	Consumer application of mixtures	Service life	Disposal of waste
Surfactants for inks, paints, adhesives, waxes, etc.	Releases to wastewater and air from manufacture of paints, inks, etc. Spill from outdoor application of paints (if any) is considered potentially to be the main source of direct releases to the environment from this application Releases to wastewater from cleaning of tools	Spills from outdoor applications of paint (if any) may be the main release pathway Releases to wastewater from cleaning of tools	Releases to the environment and wastewater from weathering of painted surfaces	Surfactants are present in municipal solid waste (e.g. paper waste); building waste (painted surfaces); waste metal for recycling Incineration and metal recycling: Substances are destroyed Landfilling: Potential long-term releases to the environment
Agents for oil, water and stain repellent protection of fabrics, carpets, leather, etc. (Scotchgard™)	Releases to wastewater from application of repellent agents in industrial settings	Releases to the environment and wastewater in aerosols by spray applications (the fraction not ending up on the product)	Releases to the environment and wastewater from abrasion of treated surfaces	Waste from impregnated fabric, carpets, leather etc. containing small amount of PFBS-related substances Incineration: Substances are destroyed Landfilling: Potential long-term releases

	Industrial and professional application of mixtures	Consumer application of mixtures	Service life	Disposal of waste
Tile grout additive/ surfactants and repellent agents for porous hard surfaces	Potential local releases to wastewater and the local aquatic environment (spills, cleaning etc.)	Same as professional use, but these types of products are used by the general consumer only to a limited extent	Releases to the environment and wastewater from weathering and abrasion of treated surfaces	Fraction of disposed building waste. Potential long-term releases
Flame retardant for polycarbonate	Releases to wastewater and air from manufacture of polycarbonate	The flame retardants are not expected to be applied by consumers	In final articles, the substances are bound in the plastic material and releases are likely relatively limited as compared to applications where the substances are used for surface treatment	Included in plastic fractions of electrical and electronic waste Incineration: Substances are destroyed Landfilling: Potential long-term releases Recycling: Exposure routes similar to new applications
Mist suppressing agent for hard chrome plating	Potential releases of PFBS-related substances from open vessels and emissions to air ventilation canals	This process is not relevant for the consumer	Not relevant, the substances do not remain with the articles	Chromate solution containing the mist suppressing agent has a limited usage lifetime and has to be changed regularly. The used solution is treated as chemical waste, where chromium is isolated and the rest disposed of with the risk of long-term leaching of PFBS to the groundwater or emission of PFBS-contaminated wastewater.

4.2.2 Releases from manufacture of substances and production of mixtures

Considerable amounts of PFBS-related substances are handled during manufacture of substances and production of mixtures; thus, potential significant local releases to the environment (evaporation, ventilation, spills) are possible.

No data on releases from manufacture of the substances and production of mixtures in the EEA has been available.

High emissions of short chain perfluoroalkyl acids were reported from around a fast developing fluorochemical industry in China (Wang *et al.,* 2016). Levels of PFBS were very high in surface waters. In river water, measured levels were >400 times higher of PFBS than of PFOS and PFOA, showing a changed product pattern with focus on short-chain PFAS. In groundwater, perfluorobutanoic acid

(PFBA) dominated in the upper layers, while PFOS was more significant in lower layers (Wang *et al.,* 2016).

4.2.3 Releases from application of mixtures with surfactants

No specific information on the releases of PFBS-related substances from professional and industrial application of mixtures with surfactants has been identified.

One of the applied mixtures, Fluorosurfactant FC-4430, has been notified under the Australian NICNAS programme (NICNAS, 2015). The data from the notification will be used as an indicator for potential releases of the substances from this application area. In FC-4430, and other mixtures on the market, the main constituent is fluoroacrylate copolymer (CAS No. 1017237-78-3), whereas MeFBSE, MeFBSA, and MeFBSAC are present at low levels of <1%. In the notification for FC-4430 these other constituents are indicated as "*residual polyfluoroalkyl starting constituents and/or impurities of the notified polymer*" (NICNAS, 2015).

During the various processes and life cycle steps, the substances or their degradation products may either:

- Evaporate to the air - dependent on physical/chemical properties of the specific substances, or
- be released to wastewater and soil and to air by aerosols - mainly due to the general handling of mixtures and degradation of the final materials.

Emission factors

The potential releases to wastewater and soil and emission to air in aerosols, as mentioned, are dependent on the general handling of the mixtures and materials. For the standardized supply chain communication of environmental assessments under REACH, a number of industry sector groups and trade associations have developed Specific Environmental Release Categories (SPERCs) which describe typical operational conditions that are relevant with regard to the emissions of substances to the environment. The European Industry Associations for Paints (CEPE) and the Association for Sealants (FEICA) have prepared SPERCs for paint and adhesives, respectively. These will be used to indicate the main releases pathways for this application area. The emission factors are for "solids", i.e. non-volatile constituents of the mixtures, and consequently do not include the possible evaporation of the substances to air. The releases would mainly occur in the fluorinated polymer form, which may later be degraded by wastewater treatment or in the environment.

The following SPERC emission factors (indicating the percentage of applied substances released by the different pathways) are applied for formulation and uses of paint by consumers, professionals and industry (CEPE, 2013):

- Formulation - liquid coatings and inks (where specific formulation not known) - solids: 0.0097% to wastewater

- Professional application by spray: 2.2% to air, 2% to wastewater, soil indicated as "to be advised"

- Consumer use, all applications and professional application by brush and roller: 1% to wastewater and 0.5% to soil for applications outdoors.

For formulation and use of adhesives and sealants, FEICA (2013) SPERCs are as follows:

- Formulation of adhesives; 0.01% to air and 0.005% to wastewater

- Wide dispersive use of substances other than solvents in adhesives and sealants: 1.5% to wastewater (same for solvent and water-based adhesives).

Formulation of paint, inks, adhesives, etc.

During formulation of paint, inks, adhesives, tile grout additives and repellent agents for porous hard surfaces, PFBS-related substances in the surfactants may be handled; therefore, some local releases to the environment (evaporation, ventilation, spills) are possible. The SPERCs for formulation of liquid coatings and inks for solids is 0.0097% to wastewater, whereas for formulation of adhesives it is 0.01% to air (as aerosols) and 0.005% to wastewater. The FC-4430 notification assumes a release factor to waste of 0.5% for an on-site treatment plant during reformulation and equipment cleaning of paint and adhesives. The notification states that no significant release of the notified polymer to the water compartment is expected.

As indicated by the SPERCs above, emissions from the formulation processes are generally considered to be limited as compared to the releases from the application of the final mixtures.

The expected evaporation of the polymer from the process is limited. The NICNAS notification for FC-4430 notes that inhalation exposure is unlikely during factory application based on the expected low vapour pressure of the notified acrylate polymer given its relatively high molecular weight (>1000 Da). The notification does not mention the possible evaporation of the residual content of MeFBSE, MeFBSA and MeFBSAC. As these substances are relatively volatile (Buck et al., 2011), it must be assumed that they will ultimately be released to air, either during application or later from the materials. The data does not allow an estimate of how much of the content is released during formulation.

Application of paint, inks, adhesives, etc.

Inks, paint, waxes etc. contain small concentrations of surfactant (<0.01-0.3%). The releases during application depend on application method. As indicated by the SPERC emission factors, professional application by spray may result in significant emissions to the air (emission factor of 2.2% to air). For other applications of paint, adhesives and sealants the main releases are to wastewater. The emission factors for both consumer use and professional application are on the order of magnitude of 1-2% to wastewater e.g. by cleaning of brushes and other application tools. For adhesives, an emission factor of 1.5% to wastewater is assumed.

In accordance with the abovementioned factors, the FC-4430 notification assumes a release to domestic wastewater of 2% for industrial, commercial and private applications of paint and 0.5% from the use of adhesives.

As part of the NICNAS notification for FC-4430, a test was carried out to ascertain to what extent MeFBSE was liberated into the gas phase as the applied paint cures at room temperature. The results indicated that the rate of release of the fluorinated species from the dried coating was lower than the detection limit. With a detection limit of approximately 2% of the notified polymer to MeFBSE due to alcoholysis, some amount should be detected if liberated into the gas phase. (NICNAS 2015). Release rates below 2% cannot be detected.

Releases from the cured products during use

Releases from cured products are assumed mainly to be due to releases from outdoor uses of paint. It should be noted that the purpose of these surfactants, contrary to the agents used to provide repellency described in the next section, is to provide some properties to the mixture when the substances are embedded in the matrix in the cured materials as described in the NICNAS notification for FC-4430. The notification states, regarding adhesives, that *"Once the adhesive is cured into a solid mass, exposure will no longer be possible as the notified polymer will be trapped within the solid matrix"* (NICNAS, 2015). The same is assumed to be the situation for sealants.

As the acrylate polymer is embedded in the matrix, it is released as part of emitted paint particles. Danish substance flow analyses have usually assumed that some 3-4% of paint applied outdoors is lost to the environment by maintenance (re-painting) and abrasion during the lifetime of the paint, whereas the OECD Emission Scenario Document for the painting industry assumes that approximately 2-3% of the coating will be lost to industrial soil by flaking/chipping during the useful life of the product (as cited by Lassen et al., 2015b). The released particles will be released partly to wastewater and partly to the soil in the surroundings.

As part of the NICNAS notification for FC-4430, it was investigated to what extent fluorinated species were released from the dry film containing the notified polymer under test conditions. During the test, a scrubbing process was conducted twice, each for 25 cycles of scrubbing with the sponge under liquid scrub media. The rate of release of the fluorinated species from the dried coating under these conditions was below the detection limit and are indicated in the notification to be "insignificant". This indicates that the releases of the polymer by migration/leaching are likely minor as compared to the releases as part of the released paint particles.

The acrylate polymer may furthermore be degraded during use to various fluorinated species. According to the FC-4430 notification, the polymer is known to rapidly undergo a primary cleavage of the perfluoroalkyl chain in a sewage treatment plant. Likely this degradation is limited as long the polymer is embedded in the matrix during use of the articles/materials, but no data on possible degradation rates during use has been identified.

The NICNAS notification for FC-4430 (2015) indicates that the primary degradant of the polymer is MeFBSE (NICNAS , 2015). This primary degradation product is then expected to further degrade through a number of possible perfluoroalkyl-containing intermediates to ultimately produce PFBS (NICNAS, 2015). It is noted that some volatile, sulfonate-containing degradation products have the potential to undergo long range atmospheric transport and thus may result in translocation of PFBS in the environment.

The polymers and impurities not released during the application or use phase may be disposed of along with the articles. In disposal, the materials are either incinerated (and thereby degraded) or landfilled. Compared to the agents for repellent treatment described in the next two chapters, releases during the use phase are considered to be significantly lower as the polymers for this application area are embedded in a matrix. The total potential for releases of PFBS-related substances from this application area during the entire life cycle is relatively small if the end products are incinerated, whereas the substances may be released from the matrix over time when landfilled. Considering that no more than 1-3 t/year PFBS moieties are applied in the EEA, the total releases during the entire lifecycle for these applications are estimated to be minor as compared to the releases due to the use of PFBS-related agents for repellent protection.

4.2.4 Releases from agents for oil, water and stain repellent protection of fabrics, carpets, leather, etc.

Agents for oil, water and stain repellent protection of fabrics, carpets, leather, etc. represent the largest volume of use of PFBS-related substances in the EEA.

As mentioned above, a survey of the releases of PFOS-related substances indicates that losses from stain repellent treated carpets, waterproof apparel, and aqueous fire fighting foams were the major emission sources. The releases associated with the use of PFBS-related agents for oil, water and stain repellent protection of fabrics, carpets, leather, etc. are therefore likely to represent a major release source.

As described in section 3.2.3, the impregnating agents are applied as a thin film on the surface of the materials by a process in which the polymerization and curing occur on the surface of the material. The side chains of the two-dimensional polymer structure formed during curing protrude as small hairs from the material, and aid in providing the dirt and water-repellent effects.

The applied agents are typically urethane and acrylate polymers in some mixtures with low levels (<1%) of residual MeFBSAC, MeFBSE and MeFBSA.

For one of the applied agents (a "fluorochemical urethane" used as a component in "Scotchguard Heavy Duty Carpet Protector"), a NICNAS notification is available (NICNAS, 2003). Regarding residual content of raw materials, it is indicated that "*all residual monomers are below the relevant cut-off*" (not further specified). The information on the carpet protector is used in this study as an indicator for similar products used for protection of apparel, leather and carpets.

Formulation of agents for repellent protection

No data are available regarding the releases of the agents by formulation or by production of spray cans containing the agents. Compared to the releases from the application of the mixtures and from the final products, the release from the formulation process is assumed to be fairly insignificant.

Application of mixtures for repellent protection

The releases from the applications of the mixtures are highly dependent on the application conditions, which can broadly be divided into:

- Industrial use of repellent agents in production of articles (fabric, carpets, leather etc.) - applied in drums and as aerosol sprays
- Consumer use of repellent agents for treatment of finished articles (fabric, carpets, leather etc.) - typically applied in aerosol sprays

Emission factors for the industrial use of the repellent agents have not been identified. No SPERCs for the leather and textile industry have been developed. The OECD Emission Scenario Document for the textile finishing industry does not provide specific emission factors for repellent agents (OECD, 2004). Furthermore, no OECD Emission Scenario Documents are available for the leather industry.

From the industrial use of the repellents in drums, some release to wastewater can be assumed. The Best Available Techniques (BAT) Reference Document for the tanning of hides and skins indicates that emissions to wastewater from fatliquoring agents and impregnating agents contribute to the COD (Chemical Oxygen Demand) and BOD (Biological Oxygen Demand) in the effluent from the tanning process, but does not provide any emission factors (BREF, 2010). During industrial spray applications, the agents may be released to the surroundings via aerosols in exhaust air and to wastewater via aerosols ending up on the floor. No data are available for quantifying the releases.

According to the NICNAS notification for the PFBS-related fluorochemical urethane "*The majority of the notified polymer will be applied to carpet and rugs as a foaming aerosol which when dry remains on the treated article. A maximum of 5% overspray has been estimated*." (NICNAS 2003).

Aerosol sprays used by consumers for treatment of apparel and leather are often applied outdoors and a significant part of the agents do not end up on the treated articles, but are rather released to the surroundings in aerosols. A maximum of 5% overspray was assumed for treatment of carpet and rugs, as above, but likely the percentage overspray for smaller articles as shoes and apparel is significantly higher, and may be a major pathway for release of these substances to the environment.

Releases from articles in use

Release of the fluorinated polymers and degradation products from treated articles in use may be major pathways for release of PFBS related substances to the environment.

According to the NICNAS notification for fluorochemical urethane in foaming spray "*Up to 75% of the polymer may, over time, be extracted from the carpet through steam cleaning and be disposed of to the sewer." (NICNAS, 2003).* The notifier (the 3M Company) indicates that "*over time the polymer may, through mechanical action, slowly wear off the carpet surface and be either vacuumed away over a period of 3-10 years or be walked-off onto surrounding ground* ". It is not indicated to what extent the polymer is released in polymeric form or as degradation products.

A similar wear can be expected from apparel and leather articles during use. It is likely that a significant part may be released by washing.

Lassen et al. (2015) investigated releases of PFAS from PFAS-treated children's clothing and discussed the possible long-term releases from the clothing. The investigated textiles were mainly treated with other types of perfluorinated polymers (telomer-based PFAS) but the release mechanisms are probably more or less the same for the different polymer types. Laundry tests showed that, of the total PFAS content, about 1 % was released to laundry water in a single wash, but higher release rates have been observed in other studies (as discussed by Lassen et al., 2015). The study notes, with reference to Wang et al. (2014b), that PFASs may be continuously formed from the degradation of the products during use and that a significant source of PFAS could be the release of the substances later in the life cycle of the textile by decomposition of PFAS-based polymers. The fact that, over time, the water and dirt repellency properties of garments become less efficient and require retreatment may indicate that the polymers are possibly degraded by breakage of the perfluorinated side chains.

Chu and Letcher (2014) studied the *in vitro* formation of perfluoroalkyl sulfonamides from copolymer surfactants of pre- and post-2002 Scotchgard Fabric Protector Products. The pre-2002 products were based on PFOS-related chemistry whereas the post-2002 products were based on PFBS-related chemistry. The main *in vitro* metabolite of the post-2002 product was perfluorobutane sulfonamide (FBSA, CAS No 30334-69-1), which according to the authors was coincident with the detection of the major fabric protector components that contains the N-methyl-perfluorobutane sulfonyl chemical moiety. The FBSA concentration increased progressively over the incubation period, but with no concomitant formation of PFBS. According to the authors, the *in vitro* metabolism assay results clearly demonstrated that the detected FBSA in the incubation solutions did not come from any small molecular product impurities in the Scotchgard, as low molecular weight FBSA precursors such as MeFBSA and EtFBSA were not detectable in the incubation solution. Therefore, they conclude that it was more likely that the detected FBSA in the study's in vitro incubation solutions were metabolites of the copolymer products. The results do not allow for any quantification of the releases in comparison to the total content of N-methyl-perfluorobutane sulfonyl moieties, but demonstrate that PBSA is formed and released from the products under certain circumstances.

As mentioned in section 3.2.8, most studies of releases of PFAS from products have analysed for PFBS, but not for PBSA, MeFBSAC, MeFBSE and MeFBSA.

The fraction of the polymers and impurities not released during the application or use phases may be disposed of along with the articles. In disposal, the materials are either incinerated (and thereby degraded) or landfilled. The total potential for release of PFBS-related substances from this application area during the entire life cycle is likely more than half the applied volume, and the application area represents the major release source of the PFBS-related substances.

4.2.5 Releases from treated hard surfaces in buildings

The agents used to provide repellent properties for hard surfaces on buildings have a similar function as the agents used for textiles, leather and carpets mentioned in the previous section.

Many of the agents are based on PFBS-based polymers, such as fluoroacrylate modified urethane and fluoro-chemical acrylate PFBS-related polymers. In one of the mixtures, MePBSE is present at low concentration (<0.5%), probably as residual raw material.

For one of the agents, SILRES® BS 38 from Wacker Chemie AG, a notification of the polyfluorinated side-chain polymer for the Australian NICNAS programme is available (NICNAS, 2014). SILRES® BS 38 is a solvent-based mixture of silane-based substance, siloxane and fluoropolymer. In diluted form, it serves to render inorganic substrates such as mineral construction materials water-repellent and oil-repellent. In the notification, it is indicated that the product is expected to be applied in factory settings (33%), by professionals (33%) or by consumers (34%) in Australia. The product containing the notified polymer (up to 8% concentration) is applied to stone and tiles using brushes, rollers or mops. The polymer of a molar weight > 10,000 Da and a purity of >90% is indicated as a potential precursor of PFBS. This indicates that the polymer has PFBS-related side-chains.

Formulation of agents for repellent protection of hard surfaces

No data are available regarding the releases of the agents by formulation or by production of spray cans containing the agents. Compared to the releases from the application of the mixtures and from the final products, the release from formulation is assumed to be minor.

Application of mixtures for repellent protection of hard surfaces

The mixtures are typically applied outdoors. The agents can be applied with most commercially available application equipment such as brushes, sponges, rollers and spray applicators. No SPERCs or other emission factors for this application have been identified. For professional application of spray paint, the SPERC (as described in section 4.2.3) indicates 2.2% to air and 2% to wastewater, while soil is indicated as "to be advised". Spray application of repellent agents probably gives rise to similar releases while application by rollers and brushes may result in release to the soil below the treated surface. For SILRES® BS 38, NICNAS (2014) assumes that "During spray application of the notified polymer in industrial settings, engineering controls are expected to be used to limit release of the notified polymer to the environment". For consumer application, NICNAS (2014) states that "A small proportion of the notified polymer may be released to sewer via improper disposal by do-it-yourself (DIY) users".

For application of water-based products, some release to wastewater of approximately 1% can be expected from cleaning of tools. Tools from solvent based products are expected to be cleaned using hydrocarbon-based solvents which are disposed of as hazardous waste (as described for SILRES® BS 38 in NICNAS, 2014).

The main releases occur as PFBS-related polymers, which may be further degraded by waste treatment and in the environment. The NICNAS (2014) notification does not indicate any releases of perfluoralkyl impurities in the polymer but does indicate a concentration of such impurities of 0.0048% in end-use articles. From other agents where MePBSE is present at low concentrations (<0.5%), the volatile MePBSE is likely released to air either during application or later in the use phase of the treated surfaces.

Releases from articles in use

As described above for the agents used for textiles, leather and carpets, a significant fraction of the applied polymer may be released as a polymer by abrasion during use or PFBS-related degradation products may be released from treated surfaces.

The NICNAS notification for SILRES® BS 38 states that *"The notified polymer applied to treated stone and tile surfaces is expected to adhere to the surface to which it has been applied. However, abrasion of the floor surface by foot traffic is expected to result in some relocation of the notified polymer. Estimates for losses due to abrasion from these uses are not available.....The notified polymer applied to surfaces may also degrade as a result of weathering upon being exposed to environmental conditions. Degradation may result in the widespread release of perfluorobutanesulfonic acid (PFBS) to surface waters, landfill and landfill leachates, soils, and other regions where release is not foreseen."* (NICNAS 2014)

As the agents are used outdoors, and the agents as well as the treated surfaces are subject to UV light and weathering, it is anticipated that a significant fraction of the applied agents are likely released over time to wastewater and soil below the treated surfaces. It is also likely that some PFBS-related substances are released because of degradation of the PFBS-related side-chains in the polymers (as described above for a Scotchgard Fabric Protector product), but no data on releases from agents used for hard surfaces, apart from the SILRES® BS 38, have been identified.

The fraction of the polymers and impurities not released during the application or use phase may be disposed of along with the building waste. As the materials are typically not incinerated during disposal, the total potential for releases of PFBS-related substances from this application area is similar to the total consumption for the area. As noted in the NICNAS notification for SILRES® BS 38 "*degradants of the notified polymer, along with associated impurities and residual monomers of the notified polymer, are potential precursors of the persistent chemical, perfluorobutanesulfonic acid (PFBS). The assessed use pattern of the notified polymer does not control the release of breakdown products into the environment after disposal and the long-term environmental risk profile of PFBS is currently unknown. Consequently, the long-term risk profile for the notified polymer and its degradation products are unknown.*" (NICNAS 2014)

4.2.6 Releases from hard chrome plating

According to the data sheet for a mist-suppressing surfactant for chromium plating, the surfactant is applied to the chromium electrolyte in an active substance concentration of 125 mg/L (please note that the use of the surfactant may have ceased in recent years).

Data on releases from the use of the specific surfactant have not been identified, but some data are available for a similar application of another surfactant. For professional use of mist suppressing agents with PFOS in the hard chrome plating industry, agents have typically consisted of a 5–10% solution of PFOS (Poulsen *et al.*, 2011). According to Poulsen *et al.* (2011), the PFOS-containing agents were added in concentrations of 7.2 L/m^3.

The application of the mist suppressing agents potentially gives rise to releases of PFBS-related substances from the open vessels and emissions to air ventilation canals.

According to Poulsen *et al.* (2011), "*hard chrome plating is a surface treatment process where a layer of chromium is electrochemically deposited on the surface of metals. The electrochemical process produces a significant amount of gases to be released from the process tank. These gases rise to the surface as bubbles. Most bubbles burst at the surface and when they burst, they form aerosols, which are released to the atmosphere. The aerosols consist of process liquid containing chromic acid/chromate and thus may expose the work environment more, if no mist suppressant agent is used*."

According to Poulsen *et al.* (2011), "*the German national metal plating association (ZVO) states that in the case of Germany only 20% of the applied is lost. The US EPA has recently discovered that the metal plating industry is a major contributor to the pollution of perfluorinated chemicals into sewage water in the US, and this is especially alarming as the chemicals pass un-degraded through sewage treatment plants into lakes and streams.*"

A chromate solution containing the mist suppressing agent has a limited usage lifetime and has to be changed regularly. The used solution is treated as chemical waste, where remaining chromium (VI) is isolated, reduced to chromium (III) and stored. The liquid remainder may be disposed of with a risk of long-term leaching of PFBS to groundwater or emissions of PFBS-contaminated wastewater.

4.2.7 Releases from the use of flame retardants

No data on the releases from the use of K-PFBS as a flame retardant in polycarbonate have been identified. The K-PFBS may be released during production of the substance, production of the polycarbonate, from flame retarded polycarbonate during use and from the disposal of the polycarbonate.

Production of polycarbonate

No SPERC for production of polycarbonate has been identified. The OECD Emission Scenario Document on plastics additives (OECD, 2004) may provide some first indication about the emissions of the flame retardant by production of plastics even though the emission factors may be outdated and should be considered as worst case scenarios.

Releases may take place from raw materials handling, compounding and conversion. Polycarbonate is typically converted by moulding. During the conversion, the polycarbonate is heated up and some evaporation of the flame retardants takes place. According to the OECD Emission Scenario Document "*Initially some emissions will be to atmosphere, but ultimately all particulates will be removed or settle, and vapours will condense to some extent, resulting in losses to both solid waste and wastewater (via aqueous washing). It will be assumed here that all particulate losses will eventually be to wastewater and that volatilisation loss will condense to some extent and eventually be released 50% to air and 50% to wastewater.*" According to document, for organic flame retardants the emission factors depend on the volatility of the substance, particle size of powders, to what extent the processes are open and the machinery. In any case, the total emission factor for releases to wastewater from compounding and conversion is below 1% and the actual releases may likely be well below this. For materials handling the emission scenario document applies an aggregate factor for releases to wastewater and solid waste of 0.2-0.5% depending on particle size.

Releases from polycarbonate during use

In the final polycarbonate, the flame retardant is embedded in the polycarbonate matrix and the releases depend on the migration of the flame retardant to the surface of the material and evaporation or washing off from the surface. For organic flame retardants, the OECD Emission Scenario Document applies an emission factor from indoor application of the materials of 0.05% to wastewater and the atmosphere, respectively, during the entire lifetime of the products. No actual data on migration of the K-PFBS in the polycarbonate has been identified. Emission of brominated flame retardants during service has been demonstrated by several studies, but the results cannot be used to further qualify the estimate on the service life emission factor for K-PFBS.

4.2.8 Releases from wastewater and solid waste treatment

Wastewater

PFBS-related chemicals are to some extent released with wastewater. The fate of the substances depends on the treatment of the wastewater.

Some wastewater is discharged directly to the environment. Even in countries with efficient wastewater treatment systems, a portion of the wastewater is discharged directly to the environment via overflows during heavy rain. PFBS-related chemicals in the untreated wastewater pollute surface waters, and enter aquatic food chains or accumulate in sediments.

In industrial- or municipal wastewater treatment plants, the PFBS-moiety is not degraded but either passes through the plant in outlet water or accumulates in sludge. If the sludge is later used to fertilize agricultural land, the PFBS-related chemicals end up in the soil and may leach to the groundwater or be taken up by the crops.

A significant fraction of the PFBS-related substances reaching wastewater treatment plants may be in the form of polymers. The partitioning of the polymers between the water phase (leading to discharges) and the solid phase (sludge) is still not well understood. Furthermore, the available information indicates that the fluorinated side chains are released to some extent as degradation products from the polymers during wastewater treatment, and their fate during the process may be different from the fate of the polymers as exemplified below.

The NICNAS notification for Fluorosurfactant FC-4430 notes that "*Predictions of the environmental partitioning behaviour of poly- and perfluoroalkyl polymers remain uncertain based on current knowledge because of limited data and their unique properties. In particular, the usual predictive models for partitioning during sewage treatment are inapplicable for chemicals containing perfluoroalkyl functionality as they assume lipophilicity for hydrophobic functionality, whereas the perfluoroalkyl functionality is both hydrophobic and lipophobic. However, the notified polymer consists of predominantly hydrophilic components and a minor amount of perfluoroalkyl functionality. Tests on water solubility prove that the notified polymer is miscible in water and is unlikely to adsorb on soil/sediment. Therefore, the notified polymer may potentially be mainly present in STP effluent and released to public water. The non-hydrophilic degradates (e.g. perfluoroalkyl functionalities) may also potentially be present in biosolids that will* *be reused and applied to agricultural soils throughout Australia."* (NICNAS, 2015). Furthermore, the notification makes reference to a biodegradation study and states "*The results indicate rapid transformation of the notified polymer, involving an initial cleavage of the pendant perfluoroalkyl chain, in media designed to imitate exposure to municipal wastewater treatment sludge. However, the fate of the perfluoroalkyl functionality was not investigated in this study*". The notification concludes that "*Taken together, the information suggests that biodegradation of the backbone of the notified polymer is expected to occur slowly under environmental conditions due to its high molecular weight. However, the notified polymer contains pendant chains that are expected to be rapidly cleaved from the notified polymer."*

According to the notification for "Fluorochemical Urethane""*Any polymer entering receiving waters at a sewage treatment plant is initially unlikely to become associated with either the aqueous or the sludge and sediment compartment, given the likely surface active nature of the polymer. In time, the hydrocarbon moiety may become assimilated with the organic phase, while the fluorinated moiety will remain in solution."* (NICNAS, 2003)

The notification of the polyfluorinated side-chain polymer in SILRES BS32 notes that "*In particular, the usual predictive models for partitioning during sewage treatment are inapplicable for chemicals containing perfluoroalkyl functionality as they assume lipophilicity for hydrophobic functionality, whereas the perfluoroalkyl functionality is both hydrophobic and lipophobic. The assumption that surface activity and/or high molecular weight results in efficient removal by sorption to sludge during conventional wastewater treatment has not been verified by supporting data for this class of chemical. However, the notified polymer will be incorporated in a product that is expected to potentially solidify upon contact with water, increasing the likelihood that the notified polymer will be removed from the aqueous phase during sewage treatment plant (STP) processes via adsorption to sludge. Therefore, the notified polymer may potentially be present in STP effluent and biosolids that will be reused and applied to agricultural soils throughout Australia.*" (NICNAS, 2014)

Solid waste

Incineration of PFBS-containing waste in conventional municipal solid waste incinerators operating at combustion temperatures ≥850˚C according to EU regulation is likely to destroy the PFBS molecule, as it does for its long-chain analogues. In laboratory combustion tests, both the potassium perfluorooctanesulfonate (K-PFOS) and perfluorooctanesulfonamides began to degrade at about 400ºC and at 600ºC, >99% of the substance had destroyed. The destruction was even more efficient at higher temperatures (Yamada & Taylor, 2003).

On disposal to landfill, the hydrocarbon- and nitrogen-containing portions of the polymers are likely to be degraded slowly through biotic and abiotic processes.

PFBS has the potential to leach from solid waste disposed of to landfill in the long term. A study has shown that the perfluorobutanesulfonate (PFBS) concentration in municipal landfill leachate from the United States may be as high as

2300 ng/L (Huset *et al.,* 2011). In China, PFBS was one of the most abundant perfluoroalkyl acids (PFAAs) in landfill leachate; as well, leachate is a significant source (>3 tons/y) of PFAAs to groundwater in China (Yan *et al.,* 2015).

The notification for "Fluorochemical Urethane" (NICNAS, 2003), states regarding disposal to landfill, "*The hydrocarbon and nitrogen containing portions of the polymer are likely to be slowly degraded by biotic and abiotic processes. The notified polymer is likely to be surface active and under normal conditions would be expected to bind to the surfaces of soil and sediment, and be immobile.*" (NICNAS, 2003).

The notification of the polyfluorinated side-chain polymer in SILRES BS32 notes that "*The majority of articles are expected to ultimately be disposed of to landfill. The notified polymer applied to surfaces may also degrade as a result of weathering upon being exposed to environmental conditions. Degradation may result in the widespread release of perfluorobutanesulfonic acid (PFBS) to surface waters, landfill and landfill leachates, soils, and other regions where release is not foreseen.*"

4.2.9 Long-range transport

Limited information on long-range transport of PFBS-related substances is available, whereas more information is available on the mechanisms of long-range transport of the long-chain PFOS-related substances.

According to the US EPA Long-Chain Perfluorinated Chemicals (PFCs) Action Plan, "*owing to its chemical and physical properties, PFOS is typically found at higher concentrations in water compared with air, and can travel long distances by oceanic currents. In contrast, PFOS precursors are more volatile and can be transported through air to areas far from initial release, where they subsequently degrade to PFOS." (US EPA 2009)*

The Australian NICNAS (2005) Chemical Hazard Assessment Report for K-PFBS notes that it has been hypothesized that PFOS is globally distributed via more volatile, neutral airborne contaminants that undergo long-range transport and then degrade to yield free acids. The volatile precursors of PFOS are mainly MeFOSA, MeFOSE and EtFOSE. It is further noted that the lower molecular weight PFBS precursors are expected to be more volatile, and therefore more readily subject to long-range transport, before they break down to PFBS (NICNAS, 2005 and further quoted in NICNAS, 2015). PFBS itself remains mainly in the water column due to the much higher water solubility compared with higher homologues.

According to Buck et al. (2011), commonly detected PFBS-related substances in the atmosphere and its associated particulate matter include the relatively volatile MeFBSA, MeFBSE and EtFBSE, as well as their long-chain homologues. Furthermore, sewage treatment plant effluents and river, coastal, and ocean waters were found to contain some N-alkyl sulfonamido derivatives including MeFBSA and MeFBSE.

As an example, del Vento et al. (2012) measured volatile per– and polyfluoroalkyl compounds in air in the vicinity of the Western Antarctic Peninsula during February 2009 (Australian summer). MeFBSA and MeFBSE were among the most abundant compounds with average concentrations of ~3 to 4 pg/m^3. According to the authors, the relatively high levels of MeFBSE were surprising given the reported reactivity of this chemical and short atmospheric residence time. The authors note that it is likely that this compound, alongside MeFBSA, provides a source of C2–C4 perfluoroalkyl acids (PFAAs) to Antarctic surface waters.

MeFBSAC, MeFBSA, and MeFBSE are used as intermediates in the production of side-chain fluorinated polymers and found in low concentrations in some surfactants and repellent agents. No information on MeFBSAC in the atmosphere has been identified, but the volatile substance is probably transported by the same mechanisms as the sulfonamido derivatives. Releases from manufacture of the polymers and releases of residual content in mixtures and articles are the likely sources of the substances found in the atmosphere and a transport mechanism for transport of PFBS-related substances to remote areas.

Furthermore, the NICNAS notification for the Fluorosurfactant FC-4430 (2015) indicates that the primary degradant of the polymer is MeFBSE (NICNAS, 2015). This primary degradation product is then expected to further degrade through a number of possible perfluoroalkyl-containing intermediates to ultimately produce PFBS (NICNAS, 2015). Without specifically indicating MeFBSE, it is noted that some volatile, sulfonate-containing degradation products have the potential to undergo long range atmospheric transport and thus may result in translocation of PFBS in the environment.

The substances have different half-lives in the atmosphere, influencing their potential for long-range transport but the fate of the substances in the atmosphere is beyond the scope of this study.

The US EPA Long-Chain Perfluorinated Chemicals (PFCs) Action Plan notes that the oceans have been suggested as being the final sink and route of transport for perfluorinated carboxylic and sulfonic acids (among these PFBS), where they have been detected on the surface and at depths > 1,000 meters (US EPA, 2009). In accordance with this, the NICNAS notification for the Fluorosurfactant FC-4430 notes that the PFBS is expected to be recalcitrant in the environment, and potentially undergo long-range transport while mainly staying in the water column (NICNAS, 2005).

4.3 Consumer exposure

4.3.1 Potential routes for exposure of consumers

The potential routes for direct exposure of consumers to PFBS-related substances are summarised in Table 8. The information in the table is further described in the text after the table, where full references are provided.

Indirect exposure to the substances via the environment, e.g. in food and drinking water, is beyond the scope of this assessment.

Table 9 Potential for direct exposure of consumers and exposure pathways (excluding indirect exposure via the environment)

	Application of mixtures	Sevice life of articles and materials
Surfactants for inks, paints, waxes, etc.	Consumers may to some extent apply paints, adhesive, waxes and inks with PFBS-based surfactants and undergo exposure during the application Dermal exposure from contact with the mixtures Possible inhalation by spray application of paints	PFBS-related substances in cured paint inks, sealants etc. are bound in the matrix, but may be released e.g. by the abrasion of the surfaces and sanding and consumers may be exposed to the substances as components of dust particles Possible releases of impurities in the polymers of the surfactants.
Flame retardant for polycarbonate	Not applied by consumers	Consumers may be exposed to the flame retardant, if it is released from the polycarbonate, but compared to other sources this exposure is considered to be relatively insignificant (see description below)
Agents for oil, water and stain repellent protection of fabrics, carpets, leather, etc. (Scotchgard™)	Consumers' impregnation of outdoor clothes, shoes etc. to achieve repellence with Scotchgard™ products in spray cans without sufficient ventilation may result in significant consumer inhalation exposure to PFBS-related substances Dermal exposure e.g. when small items are held in the hand during spray application	Consumer use of PFBS-impregnated clothing items may result in skin exposure to PFBS-related substances present as impurities or from weathering of the polymers. Infants and toddlers may be exposed by sucking the impregnated fabrics Storage of newly impregnated clothes and shoes in shops and homes may result in PFBS-related substances in indoor air and dust
Repellents for porous hard surfaces incl. tile grout additive	These products are not typically applied by consumers If used by consumers, they may be exposed to the substances in applying the agents to the wall or by mixing tile grout May result in inhalation exposure if applied by spray	For outdoor applications, consumers are not expected to be significantly and directly exposed to the polymers during service life Possible dermal exposure to impurities of the polymers and degradation products from indoor application on floors
Metal plating	Not applied by consumers	The substance is not expected to be present in final articles
Surfactants and solder paste for electronics	Not applied by consumers	The substance is not expected to be present in final articles
Other applications	These products are generally not applied by consumers to any significant extent	The substance is not expected to be present in final articles used by consumers

Main potential for consumer exposure

Applications of surfactants and water, oil and stain repellent agents for various uses might represent the main direct pathways of potential consumer exposure to the substances, and are described in more detail in the following. Such applications may result in direct inhalation of PFBS derivatives from indoor- or outdoor pollution or skin absorption from exposures to the skin.

4.3.2 Surfactants containing PFBS-related substances

Exposure by application of mixtures containing surfactants that are PFBS-related substances

Dermal exposure - Some inks, paint, waxes etc. contain small concentrations surfactants containing PFBS-related substances (<0.01-0.3 %). Specifically, it has been indicated that some paints and adhesives used by consumers may contain these surfactants.

As described in the section on environmental release, consumer application of paints may result in some releases to the environment, corresponding to a few percent of the products. Consumer use of these products may result in dermal exposure by the application e.g. by spill and by cleaning of equipment.

According to a notification for Fluorosurfactant FC-4430, the polymer was notified for use as a surfactant in consumer applications, in decorative domestic paints and coatings and adhesives, at concentrations of up to 0.3% (NICNAS, 2015). According to the notification "*Paints and coatings containing the notified polymer will be available to the public for application by brush, roller, and possibly by spraying. For these uses, exposures to the notified polymer via the dermal and inhalation routes are possible. Furthermore, adhesives containing the notified polymer will also be available to the public for application to surfaces using a cartridge applicator with potential exposures via the dermal, oral and ocular routes*." (NICNAS, 2015).

Inhalation - By spray application, consumers may, as quoted above, be exposed to the substances in aerosols.

As well, some volatile impurities may evaporate during use, but no data indicating to what extent such evaporation takes place is available.

Exposure to PFBS-based substances in cured paints, inks, etc.

Dermal exposure – Aside from dermal exposure from application, some dermal exposure to PFBS-related substances on the surface of materials may take place. As the polymers are embedded in the matrix and not intended to modify the surface of the materials, dermal exposure is considered to be insignificant as compared to the dermal exposure from the surface treatment agents described in the next section. The low exposure level is confirmed by the notification of Fluorosurfactant FC-4430, *"Public exposure via dermal contact with dried coatings or adhesives containing the notified polymer will be minimal as the notified chemical is present in low concentrations and bound within a matrix once the product has dried."* (NICNAS, 2015)

Inhalation - Fresh paint and coatings, or storage of newly impregnated items in the home may result in evaporation of the volatile PFBS-related impurities from the materials and contaminate indoor air and dust. No data are available to quantify the possible releases during the service life of the materials.

4.3.3 Agents for oil, water and stain repellent protection of fabric, carpets, leather, hard surfaces etc.

This section includes all applications of agents for repellent protection of both soft and hard surfaces.

Application of repellent spray products

Dermal exposure - Dermal exposure of consumers by application of repellent spray products and application of agents by brush is possible e.g. small items held in the hand during application.

Inhalation - The main exposure routes through consumer use of repellent spray products is inhalation of the impregnation agents in aerosols. The exposure levels and possible effects depend on the size and type of the aerosols formed, the solvents and propellants and the extent to which the agents are applied as foams.

A Danish survey and Health Assessment of Possible Health Hazardous Compounds in Proofing Sprays concluded that the use of textile proofing agents sprayed with propellant results in considerable exposure to fine (< 1 µm) and ultra-fine aerosols (nanoaerosols) (< 100 nm) (Feilberg et al., 2008).

The mechanisms of exposure of the general public are also discussed in an Annex XV restriction report of agents for repellent protection with another chemistry but similar application pattern (Danish EPA, 2016). The report notes that "*Typical consumer exposure situations involve indoor spraying in small rooms, such as bath-rooms, and with poor ventilation. In many of the case descriptions .... it is mentioned that windows and doors have been closed. Although some of these product types, e.g. for leather and textile impregnation, may carry a warning text such as "Use only outdoors or in well-ventilated areas" it is likely that these instructions are not always followed, e.g. if the consumer is living in an apartment building in the city.*" (Danish EPA, 2016).

The NICNAS notification for a carpet protector notes "*There is potential for public exposure to the notified polymer prior to binding to carpet fibres, but this will be limited by the manner of application. Inhalation exposure during application will be limited due to the physical form (foam) of the product*" (NICNAS, 2003)

Releases from treated surfaces and articles

As mentioned in section 3.2.8, some Nordic studies reported concentrations of PFAS, including low concentrations of PFBS, in impregnated outdoor clothes.

Dermal exposure - Consumer use of PFBS-impregnated clothing and other treated items may result in skin exposure to PFBS-related substances present as impurities in polymers and from weathering of polymers.

As described in section 4.2.4, studies of *in vitro* formation of PFBS-related substances by degradation of Scotchgard^{TM} Fabric Protector Products demonstrated that perfluorobutane sulfonamide (FBSA) was the main degradation product. The PFBA was formed from the PFBS-related side-chains which protrude from the surface and are responsible for water and dirt repellent properties. FBSA has not been included in most (if any) studies of PFAS in consumer products.

In a recent study, 18% of 50 outdoor clothing samples contained PFBS in the range of 0.02-42 µg/m^2 with a median of 0.69 µg/m^2, or 7 times higher than the measured median concentration of PFOS (Van Der Veen *et al.,* 2016).

Infants and toddlers may be exposed by sucking on impregnated fabrics. In a migration test, about 6% of the PFAS content of the material migrated (Lassen *et al.,* 2015). The study did not specifically include migration of PFBS-related products.

According to the NICNAS notification for the side-chain-fluorinated polymer in SILRES BS 38, *"The public may also be exposed to the notified polymer from direct dermal contact with tiles or stone that has been treated with products containing the notified polymer. This exposure will be on a long term, albeit infrequent basis. Also, following application the product containing the notified polymer is expected to adhere to stone and tile articles, thereby limiting long term exposure. In addition, based on the high molecular weight of the notified polymer (> 10,000 Da) and the low proportion of low molecular weight species, dermal absorption is unlikely to occur. Thus the risk to public health due to long term exposure to the notified polymer from treated tiles or stone is not considered to be unreasonable. Due to the low level of perfluoroalkyl impurities present in the notified polymer, the risk to public health due to long term exposure to perfluoroalkyl impurities of the notified polymer from tiles or stone is not considered to be unreasonable.".* The notification does not include a discussion of possible dermal exposure to degradation products. The products are mainly applied outdoors where consumer exposure during service life is limited. Dermal exposure to impurities in the polymers and degradation products from indoor application on floors of tile or stone is more likely.

Exposure by inhalation to the air - Storage of newly impregnated clothes and shoes in shops and homes may result in PFBS-related substances in indoor air and dust.

Presence of PFAS in indoor air, released from treated articles, has been demonstrated in several studies but the focus has been mainly on longer chain homologues.

In a German study, it was found that >7 % of the materials' content of extractable PFAS was emitted to air over a period of 5 days (Knepper *et al*., 2014). The study did not specifically include PFBS or PFBS-related substances. The evaporated substances were all within the group of fluorotelomer alcohols (FTOH), whereas MeFOSE and EtFOSE were not measured in the air.

A mean concentration of 1 pg PFBS/m^3 was measured in a children's bedroom in Finland. The concentration of PFOS was similar (Winkens *et al.,* 2016).

4.3.4 Flame retardants in polycarbonate

As discussed in section 4.2.7, no data on the releases of K-PFBS from flame-retarded polycarbonate have been identified.

Releases of other organic flame retardants, e.g. additive brominated flame retardants, from plastics during use have been demonstrated; it is possible that K-PFBS may be released to indoor air from polycarbonate during use.

The flame-retarded polycarbonate is mainly used in electrical and electronic equipment. Dermal exposure to K-PFBS on the surface of the polycarbonate cannot be excluded, but the contact would typically be infrequent and short- term. Compared to exposure to PFBS-related substances in apparel, where the PFBS-related polymers are applied to the surface, and dermal contact is frequent and long-term, the dermal exposure to K-PFBS in polycarbonate is considered to be minor.

5 Abbreviations and acronyms

AFFF	Aqueous firefighting foams
BP	Boiling point
BOD	Biological Oxygen Demand
CAS	Chemical Abstracts Service
CDR	Chemical Data Reporting (US EPA)
CEPE	The European Council of Paint, Printing Ink and Artists' Colours
COD	Chemical Oxygen Denmand
ECHA	European Chemicals Agency
EEA	European Economic Area - consists of the EU Member States, Iceland, Liechtenstein and Norway
EEE	Electrical and electronic equipment
ERC	Environmental Release Category
EtFBSE	N-Ethyl perfluorobutanesulfonamidoethanol
EtFBSAA	N-Ethyl perfluorobutanesulfonamidoacetic acid
EtFBSAC	N-Ethyl perfluorobutane sulfonamidoethyl acrylate
EtFBSE	N-Ethyl perfluorobutane sulfonamidoethanol
EtFOSE	N-Ethyl perfluorooctane sulfonamidoethanol
EtFBSMAC	N-Ethyl perfluorobutane sulfonamidoethyl methacrylate
FBSA	Perfluorobutanesulfonamide
FBSAA	Perfluorobutane sulfonamidoacetic acid
FEICA	Fédération Européenne des Industries de Colles et Adhésifs
FTOH	Fluorotelomer alcohols
FTSA	Fluorotelomer sulfonic acid
K-PFBS	Potassium perfluorobutane sulfonate
MeFBSA	N-Methyl perfluorobutane sulfonamide
MeFBSAC	N-Methyl perfluorobutane-sulfonamidoethyl acrylate
MeFBSB	N-(4-Hydroxybutyl) N-methyl perfluorobutane sulfonamide
MeFBSE	N-Methyl perfluorobutane-sulfonamidoethanol
MeFOSE	N-Methyl perfluorooctane-sulfonamidoethanol
MeFBSMAC	N-Methyl perfluorobutane-sulfonamidoethyl methacrylate
Mono-PAP	N-Ethylperfluorobutane-sulfonamidoethyl phosphate

MP	Melting point
Na-PFBSi	Sodium perfluorobutanesulfinate
NICNAS	National Industrial Chemicals Notification and Assessment Scheme
NIVA	Norwegian Institute for Water Research
NJTS Reg. No.	New Jersey Trade Secret registration number
OECD	Organisation for Economic Co-operation and Development
PBSCl	Perfluorobutanesulfonyl chloride
FBSA	Perfluorobutane sulfonamide
PBSF	Perfluorobutane sulfonyl fluoride
PEG N-EtFBSE	Polyethylene glycol N-ethyl-perfluorobutanesulfonamide
PFAS	Entire group of perfluoroalkyl and polyfluoroalkyl substances
PFBA	Perfluorobutanoic acid
PFBS	Perfluorobutane sulfonic acid
PFBSi	Perfluorobutane sulfinic acid
PFHpS	Perfluoroheptane sulfonic acid
PFHxS	Perfluorohexane sulfonic acid
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctane sulfonic acid
PFPA	Perfluoropentanoic acid
POSF	Perfluorooctane sulfonyl fluoride
PPG N-EtFBSE	Polypropylene glycol N-ethyl-perfluorobutanesulfonamide
REACH	Registration, Evaluation, Authorisation and Restriction of Chemical substances
RMOA	Risk management option analysis
SDS	Safety Data Sheet
SPERC	Specific Release Category
TDS	Technical Data Sheet
WEEE	Waste electrical and electronic equipment

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Appendix A List of identified mixtures with PFBS-related substances

Product	Application (as described in datasheets)	Recommended use level	PFBS-related ingredients (abbreviation)	CAS No.	% by weight
Surfactants for inks, paints, waxes etc.					
3M™ Novec™ Fluorosurfactant FC-4430	3M™Fluorosurfactant FC-4430 may be used as a flow and levelling agent in various applications including architectural coatings, inks, paints, adhesives, caulks, high solids coatings, water reducible coatings, radiation curable coatings and other industrial coatings additives and solvents in the formulation.	Between 0.05% and 0.3% active surfactant. However, use level can vary depending on the application and concentration of other additives and solvents in the formulation.	Fluoroacrylate copolymer	1017237-78-3	85 - 95
			1-Butanesulfonamide, 1,1,2,2,3,3,4,4,4-nonafluoro-*N*-methyl-, (MeFBSA)	68298-12-4	< 1 Trade Secret*
			1-Butanesulfonamide, 1,1,2,2,3,3,4,4,4-nonafluoro-*N*-(2-hydroxyethyl)-*N*-methyl-, (MeFBSE)	34454-97-2	< 1 Trade Secret *
			2-Propenoic Acid, 2-[methyl[(nonafluorobutyl)-sulfonyl]amino]ethyl ester (MeFBSAC)	67584-55-8	< 1
3M™ Novec™ Fluorosurfactant FC-4432	Novec™ Fluorosurfactant FC 4432 may be used as a flow and levelling agent in various applications including architectural coatings, inks, floor polishes, waxes, caulks, high solids coatings, water reducible coatings and radiation curable coatings	Same as above	Fluoroacrylate copolymer	1017237-78-3	82 - 92
			2-Propenoic acid, 2-[methyl[(nonafluorobutyl)-sulfonyl]amino]ethyl ester (MeFBSAC)	67584-55-8	< 1
			1-Butanesulfonamide, 1,1,2,2,3,3,4,4,4-nonafluoro-*N*-Methyl-, (MeFBSA)	68298-12-4	< 0.1 Trade Secret *
3M™ Novec™ Fluorosurfactant FC-4434	Novec™ Fluorosurfactant FC 4434 is a dilute solution of 25% active fluorochemical surfactant in a water miscible diluent. It may be used as a flow and levelling agent in various applications including inks, paints and coatings, polymers, adhesives, waxes, polishes and caulks.	Same as above	Fluoroacrylate copolymer	1017237-78-3	23 - 26
			2-Propenoic acid, 2-[methyl[(nonafluorobutyl)-sulfonyl]amino]ethyl ester (MeFBSAC)	67584-55-8	< 0.125

Product	Application (as described in datasheets)	Recommended use level	PFBS-related ingredients (abbreviation)	CAS No.	% by weight
3M™ Fluorosurfactant FC-5120	Paints and coatings	Not indicated	1-Propanesulfonic acid, 3- [hexyl[(nonafluoro-butyl)sulfonyl]amino]-2-hydroxy-, monoammonium salt	606967-06-0	20-30
CHO-SHIELD® 4997, Part A, Parker Hannifin Corp, UK	Four part conductive paint system. Professional Use Only	Not indicated	Fluoroacrylate copolymer	1017237-78-3	< 0,8%
EverGlow TL300 Epoxy Coating - Part A (Resin), National Polymers Inc., USA	Epoxy coating [probably with Novec™ surfactant]	Not indicated	1-Butanesulfonamide, 1,1,2,2,3,3,4,4,4-Nonafluoro-N-(2-Hydroxyethyl)-N-Methyl- (MeFBSE)	34454-97-2	<0.1%
			2-Propenoic Acid, 2-[Methyl(Nonafluorobutyl)Sulfonyl]Amino]Ethyl Ester (MeFBSAC)	67584-55-8	<0.1%
EF-N441S-30 Mitsubishi Materials Electronic Chemicals Co. ltd; Japan	Surfactant, Acid catalyst, Raw material for ionic liquid	Not indicated	Bis(perfluorobutane-sulfonyl)imide	39847-39-7	Not indicated
Flame retardants for polycarbonate					
RM65, Miteni s.p.a., Italy	Flame retardant for polycarbonate	RM 65, utilized in the range of 750 ppm to 1200 ppm (minimum and maximum concentration suggested), gives the PC at 1/8" of thickness a V0 CLASSIFICATION for flame retardancy	Potassium 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate (K-PFBS)	29420-49-3	98% min
3M™ FR-2025 Flame Retardant Additive	Flame retardant additive for polycarbonate	Not indicated	Potassium 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate (K-PFBS)	29420-49-3	95 - 99

Product	Application (as described in datasheets)	Recommended use level	PFBS-related ingredients (abbreviation)	CAS No.	% by weight
BAYOWET® C4 Lanxess	› Flame-retardant agent for poly-carbonate Other applications: › Chemical Industry › Chemical synthesis › Manufacturing of plastics › Plastic- and Rubber polymers › Polymer auxiliaries › Silicon products	Not indicated	Potassium 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate (K-PFBS)	29420-49-3	Not indicated
EFTOP EF-42 Mitsubishi Materials Electronic Chemicals Co. ltd; Japan	EF-42 is excellent flame retardant for polycarbonate resins which are required to be transparenct EF-42 is also widely used as the anion part of such as photo acid generating agents (PAG)	Not indicated	Potassium 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate (K-PFBS)	29420-49-3	98% min
Ecoflame S-338, Unibrom Corp, China	Flame retardant for polycarbonate	UL 94 V0 at a dosage rate of 0.025 - 0.05%, while the transmittance is maintained at 90%	Potassium 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate (K-PFBS)	29420-49-3	98% min
Gsal FR-2025, Ocean Chem, China	Widely used as a flame retardant for synthetic materials, the best fire retardant for polycarbonate in particular	Not indicated	Potassium 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate (K-PFBS)	29420-49-3	98% min

Product	Application (as described in datasheets)	Recommended use level	PFBS-related ingredients (abbreviation)	CAS No.	% by weight
Oil, water and stain repellent agents for fabrics, carpets, leather, etc.					
Scotchgard™ Fabric Protector	Oil, water and stain repellent agents for fabrics in consumer market Sprayed on surfaces	Not indicated	Fluorochemical Urethane	Trade Secret*	< 3
Scotchgard™ Suede and Nubuck Protector	Aerosol for suede and nubuck leather Sprayed on surfaces	Not indicated	Fluorochemical Acrylate Polymer (NJTS Reg. No. 04499600-6885)	Trade Secret*	< 2
Scotchgard™ Protector for Rugs & Carpet	Water, oil and stain protector for carpet and rug Sprayed on surfaces	Not indicated	Fluorochemical Urethane (NJTS Reg. No. 04499600-7003)	Trade Secret*	
Scotchgard™ Protective Material PM-97	Protective Treatments for Carpet No. Consumer Spray Applications	Not indicated	Perfluorobutanesulfonamide and polyoxy-alkylene containing polyurethane	Trade Secret*	21 - 28
Scotchgard™ Protective Material PM-93	Protective Treatments for Carpet No. Consumer Spray Applications	Not indicated	Perfluorobutanesulfonamide and polyoxy-alkylene containing polyurethane	Trade Secret*	3 – 20
Scotchgard™ Protective Material PM-95	Protective Treatments for Carpet No. Consumer Spray Applications	Not indicated	Perfluorobutanesulfonamide and polyoxy-alkylene containing polyurethane	Trade Secret*	5 – 15
3M™ Protective Material PM-4700	Leather Protector	Not indicated	Fluorochemical acrylate polymer	Trade Secret*	26 – 30
3M™ Protective Material PM-4701	Leather Protector	Not indicated	Fluorochemical Acrylate Polymer NJTS Reg. No. (EIN) 04499600-6549	Trade Secret*	17 – 21
3M™ Protective Material PM-4800	Leather Protector	Not indicated	Fluorochemical Acrylate Polymer (NJTS Reg. No. 04499600-6882)	Trade Secret*	40 - 44

Product	Application (as described in datasheets)	Recommended use level	PFBS-related ingredients (abbreviation)	CAS No.	% by weight
3M™ Protective Material for Fabric PM-4950	Repellent treatment for fabric	Not indicated	Fluorochemical Acrylate Polymer (NJTS Reg. No. 04499600-7023)	Trade Secret*	65 – 75
			2-Propenoic Acid, 2-[Methyl[(Nonafluoro-butyl)Sulfonyl]Amino]Ethyl Ester (MeF-BSAC)	67584-55-8	<0.12
3M™ Protective Material PM-1690	Carpet treatment	Not indicated	1-Butanesulfonamide, 1,1,2,2,3,3,4,4,4-nonafluoro-*N*-(2-hydroxyethyl)-*N*-methyl- (MeFBSE)	34454-97-2	<0.15
			1-Butanesulfonamide, 1,1,2,2,3,3,4,4,4-Nonafluoro-N-Methyl-, MeFBSA	68298-12-4	≤0.1
3M™ Protective Chemical PM-490	Protective treatment for textiles and carpet.	Not indicated	Fluorochemical Urethane: +6523 (NJTS)	Trade Secret*	28-32
Repellents for porous hard surfaces					
3M™ Stain Resistant Additive SRC-220	SRC-220 additive provides water and oil repellency and stain resistance to porous surfaces such as concrete,	Applied at a 2 to 5% concentration to porous surfaces	1-Butanesulfonamide, 1,1,2,2,3,3,4,4,4-nonafluoro-*N*-(2-hydroxyethyl)-*N*-methyl- (MeFBSE)	34454-97-2	0 - 0.5

Product	Application (as described in datasheets)	Recommended use level	PFBS-related ingredients (abbreviation)	CAS No.	% by weight
	grout, unglazed tile, granite, clay, slate, limestone and terracotta SRC-220 additive can also be used as a stain resistant additive to a variety of acrylic and urethane based coatings at 0.2 to 1.0% active solid levels, to improve the water and oil repellency. Additionally, SRC-220 additive may be incorporated into construction materials, such as caulk or putty, to improve the stain resistance and release characteristics of these materials.	0.2 to 1.0% active solid levels	Fluorochemical Urethane (NJTS Reg. No. 0449960-6607)	Trade Secret*	14-16
3M™ Protective Material PM-1680	3M™ Stain Resistant Additive and Sealer PM-1680 is a water diluting general purpose fluorochemical emulsion designed for application to porous hard surfaces, such as terracotta, grout, marble and concrete	Suggested Formulation (by weight) as a penetrating sealer: Water: 81.6% PM-1680: 10% Dowanol™ DPM or Proglyde™ DMM (Dow Chemical: 8% 3M™ Novec™ Fluorosurfactant FC-4434: 0.4%	Fluoroacrylate Modified Urethane	Trade Secret*	14 - 18

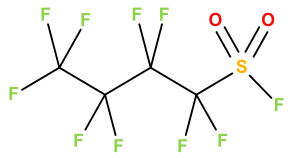
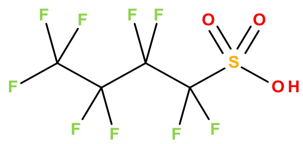
Product	Application (as described in datasheets)	Recommended use level	PFBS-related ingredients (abbreviation)	CAS No.	% by weight
SILRES® BS 38 Wacker Chemie AG	SILRES® BS 38 is a solvent-based mixture of silane, siloxane and fluoropolymer (< C8). In diluted form, it serves to render inorganic substrates such as mineral construction materials water-repellent and oil-repellent. The diluted solution should be liberally brushed onto substrate.	SILRES® BS 38 should be favourably diluted in a product:solvent ratio 1:6 to 1:10 (parts by weight). Suitable diluents are white spirit and isoparaffins.	Fluoropolymer (< C8) [Note: NICNAS (2015) indicates that the polymer may be degraded to PFBS indicating that the polymer contains PFBS-related side-chains]	Not indicated	Not indicated
Tile grout additive					
3M™ Protective Material PM-803	Tile grout additive	Not indicated	1-Butanesulfonamide, 1,1,2,2,3,3,4,4,4-nonafluoro-*N*-(2-hydroxyethyl)-*N*-methyl- (MeFBSE)	34454-97-2	0 - 0.5
			Fluorochemical Urethane (NJTS Reg. No. 0449960-6607)	Trade Secret*	14 - 16
Surfactants for electronics and flux for soldering					
3M™ Novec™ 4300 Electronic Surfactant	For use in metal etch solutions including Phosphoric/Acetic/Nitric ("PAN Etch") blends, and in other aqueous microelectronic process chemicals including low pH solutions.	Not indicated	1-Propanesulfonic acid, 3-[hexyl[(nonafluorobutyl)sulfonyl]amino]-2-hydroxy-, Monoammonium Salt	606967-06-0	15 - 25
3M™ Novec™ 4200 Electronic Surfactant	3M™ Novec™ Electronic Surfactants are intended to improve wet-out, levelling	Not indicated	1-Butanesulfonamide, 1,1,2,2,3,3,4,4,4-nonafluoro-N-(2-hydroxyethyl)-, monoammonium salt	484024-67-1	24-28

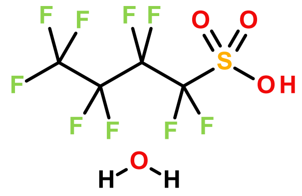
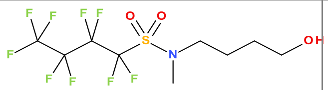
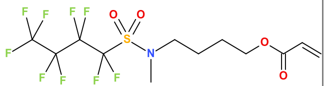
Product	Application (as described in datasheets)	Recommended use level	PFBS-related ingredients (abbreviation)	CAS No.	% by weight
	and flow-control for a variety of applications including buffered HF (BHF)/buffered oxide etch (BOE) applications. Novec™ 4200 surfactant is intended for use in semiconductor wafer fabs.		Ammoniated Fluoroalkyl Sulfonamide Impurities	Trade secret*	<1
ECOFREC 200, Inventec Performance Chemicals SA, France	Flux for the soldering of electronic components on printed circuit boards	Not indicated Applied by spraying, atomisation under air or nitrogen pressure, or with ultrasound.	Fluoroacrylate copolymer	1017237-78-3	< 0.5 %
Loctite 97SC LF318M DAP89V 500G, Henkel Corporation, USA	LOCTITE LF 318M is a halide-free, no clean, low voiding Pb-free solder paste, which has excellent humidity resistance and a broad process window both for printing and reflow	Not indicated	2-Propenoic acid, 2-[methyl(nonafluorobutyl)sulfonyl]amino]ethyl ester (MeFBSAC)	67584-55-8	0-0.1%
Metal chrome plating					
BAYOWET® FT 248 LANXESS Distribution GmbH, Germany	Chromium galvanic. Finishing of metals. Metal industry	Applied to the chromium electrolyte in an active substance concentration of 125 mg/L	Tetraethylammonium perfluorobutanesulfonate	25628-08-4	5%
Other applications					
3M™Repellent Polymer Melt Additive PM-870	Extrusion of synthetic fibers	Not indicated	Fluoroalkyl Derivative	Trade secret*	88-90
			1-Butanesulfonamide, 1,1,2,2,3,3,4,4,4-Nonafluoro-N-(2-Hydroxyethyl)-N-Methyl-	34454-97-2	<0.5
3M™ Protective Material PM-1000		Not indicated	1-Butanesulfonamide, 1,1,2,2,3,3,4,4,4-Nonafluoro-N-(2-Hydroxyethyl)-N-Methyl- (MeFBSE)	34454-97-2	<0.5

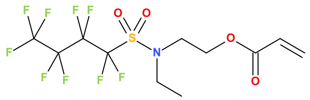
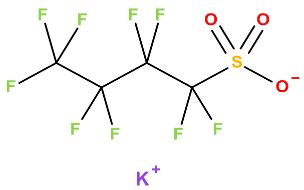
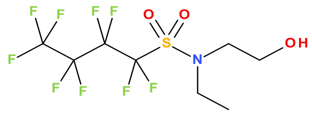
Product	Application (as described in datasheets)	Recommended use level	PFBS-related ingredients (abbreviation)	CAS No.	% by weight
	For manufacture of synthetic leather and resins utilized in the production of synthetic leather.		2-Propenoic Acid, 2-[Methyl[(Nonafluorobutyl)Sulfonyl]Amino]Ethyl Ester (MeFBSAC)	67584-55-8	<0.5
			1-Butanesulfonamide, 1,1,2,2,3,3,4,4,4-Nonafluoro-N-Methyl-, (MeFBSA)	68298-12-4	<0.4
			Fluorinated Oligomer Alcohol	Trade secret*	70-80
EFTOP EF-41 Mitsubishi Materials Electronic Chemicals Co. ltd; Japan	> Acid catalysts > Raw materials for photo acid generating agents > Synthetic raw materials	Not indicated	Nonafluoro-1-butanesulfonic acid	375-73-5	Not indicated
Anti-Stat FC-1 Fluorosurfactant (Zonyl FASP-1) DuPont Chemical Solutions Enterprise	Anti-static additive for plastics	Not indicated	Tetrabutylphosphonium Nonafluoro-1-Butanesulfonate	220689-12-3	99-100

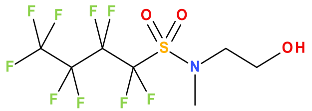
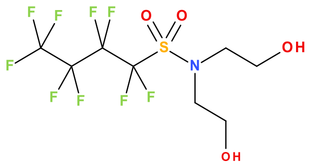
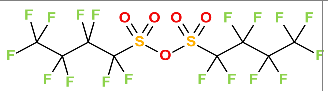
* The specific chemical identity and/or exact percentage (concentration) of this composition has been withheld as a trade secret (as indicated in the SDS).

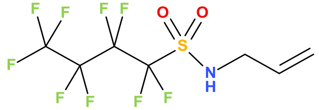
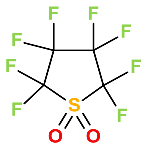
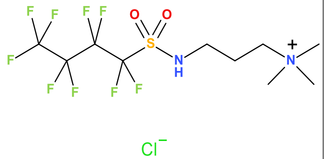
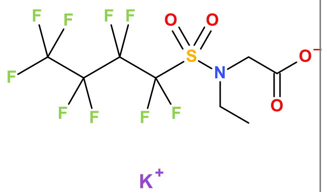
Appendix B Gross list of PFBS-related substances

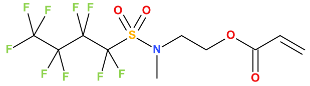
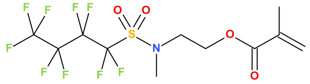
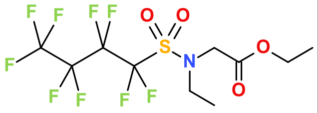
EC No	CAS No	Chemical Structure	Substance names and abbreviation	Chemical formula	MW	Melting and boiling point	Density	Other properties	C&L Inven-tory, Nov 2016
206-792-6	375-72-4		Perfluorobutane sulfonyl fluoride 1,1,2,2,3,3,4,4,4-No-nafluorobutane-1-sul-fonyl fluoride PBSF	$C_4F_{10}O_2S$	302.09	MP: -110 °C BP: 64-66	1.682 g/mL 25ºC 1,716 g/mL 20 ºC	Vapour pressure: 125 mm Hg 20 ºC; 16665 Pa Clear colourless liquid, moisture sensitive Solubility in water (23 ºC): <0.3 mg/L Refractive index: 1.3	Yes
206-793-1	375-73-5		Perfluorobutane sulfonic acid 1,1,2,2,3,3,4,4,4-No-nafluorobutane-1-sul-fonic acid PFBS	$C_4HF_9O_3S$	300.10	MP: 76-84 °C BP: 211 °C BP: 112-114 °C/ 14 mmHg	1.811 g/mL at 25 °C	Colourless liquid Solubility in water 0,5 g/L Refractive index: 1.3230	Yes

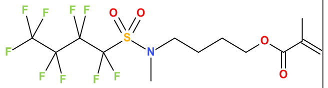
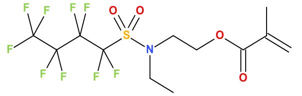
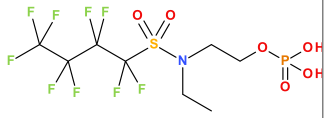
EC No	CAS No	Chemical Structure	Substance names and abbreviation	Chemical formula	MW	Melting and boiling point	Density	Other properties	C&L Inventory, Nov 2016
206-793-1	59933-66-3		Perfluorobutane sulfonic acid, hydrate 1,1,2,2,3,3,4,4,4-Nonafluorobutane-1-sulfonic acid , hydrate PFBS, hydrate	$C_4H_3F_9O_4S$	318.11				Yes
212-382-8	812-94-2		*N*-(4-Hydroxybutyl) *N*-methyl perfluorobutanesulfonamide 1,1,2,2,3,3,4,4,4-Nonafluoro-*N*-(4-hydroxybutyl) *N*- methyl butane-1-sulfonamide MeFBSB	$C_9H_{12}F_9NO_3S$	385.245	BP: 286.6 °C	1.528 g/cm³	Flash Point: 127.1°C Refractive index: 1.384 Vapour Pressure. 0.000296mmHg at 25°C	No
216-085-4	1492-87-1		*N*-Methyl perfluorobutane-sulfonamidobutyl acrylate 4-[Methyl[(nonafluorobutyl) sulfonyl]amino]butyl acrylate	$C_{12}H_{14}F_9NO_4S$	439.29	BP: 332.5 °C	1.451 g/cm³	Flash Point: 154.9°C Refractive index: 1.397 Vapour pressure: 0.000145 mmHg at 25°C	No

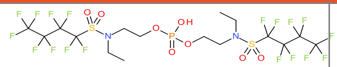
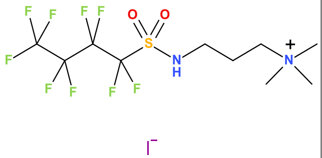
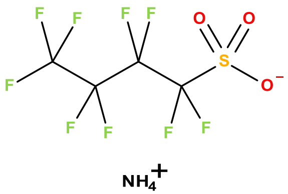
EC No	CAS No	Chemical Structure	Substance names and abbreviation	Chemical formula	MW	Melting and boiling point	Density	Other properties	C&L Inventory, Nov 2016
241-351-1	17329-79-2		*N*-Ethyl perfluorobutane sulfonamidoethyl acrylate 2-[Ethyl[(nonafluorobutyl)-sulfonyl]amino]ethyl acrylate EtFBSAC	$C_{11}H_{12}F_9NO_4S$	425.27	BP: 317.5 °C	1.485 g/cm^3	Flash Point: 145.8°C Refractive index: 1.393	No
249-616-3	29420-49-3		Potassium perfluorobutane sulfonate Potassium 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate K-PFBS	$C_4F_9KO_3S$	338.19	MP: 270 °C	0.69 g/cm^3	White crystalline powder/solid Solubility in water: 46 g/L at 20°C Vapour pressure: <1.22 × 10^{-5} Pa	Yes
252-035-8	34449-89-3		*N*-Ethyl perfluorobutane-sulfonamidoethanol EtFBSE	$C_8H_{10}F_9NO_3S$	371.22	BP: 265.9 °C	1.575 g/cm^3	Vapour Pressure: 0.00122 mmHg at 25°C Refractive index: 1.378 Flash point: 114.6°C	No

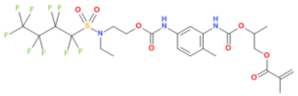
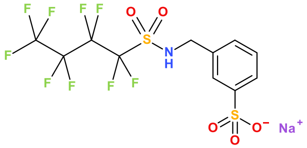
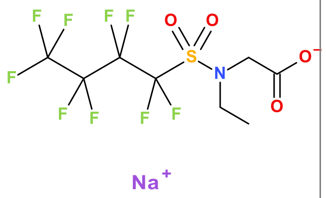
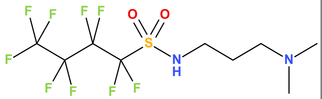
EC No	CAS No	Chemical Structure	Substance names and abbreviation	Chemical formula	MW	Melting and boiling point	Density	Other properties	C&L Inventory, Nov 2016
252-043-1	34454-97-2		*N*-Methyl perfluorobutane-sulfonamidoethanol 1,1,2,2,3,3,4,4,4-Nonafluoro-*N*-(2-hydroxyethyl)-*N*-methylbutane-1-sulfonamide MeFBSE	$C_7H_8F_9NO_3S$	357.19	MP: 64.7 °C BP: 258.9 °C	1.56 g/c m^3 at 23 C	White to yellow waxy solid Vapour pressure = $3.0x10^{-5}$ mm Hg at 20 °C LogPow = 2,67 Water solubility: 141 mg/L at 23-24 °C.	Yes
252-044-7	34455-00-0		*N,N*-Bis(2-hydroxyethyl) perfluorobutanesulfonamide 1,1,2,2,3,3,4,4,4-Nonafluoro-*N,N*-bis(2-hydroxyethyl)butane-1-sulfonamide	$C_8H_{10}F_9NO_4S$	387.22	BP: 319.7 ºC	1.661 g/cm^3	Flash Point: 147.1ºC Refractive Index: 1.395	Yes
253-270-9	36913-91-4		Perfluorosulfonic anhydride 1,1,2,2,3,3,4,4,4-Nonafluorobutane-1-sulfonic anhydride	$C_8F_{22}O_5S_2$	582.18	BP: 84 °C	1.898 g/mL 25°C	Refractive index: 1.3210	Yes

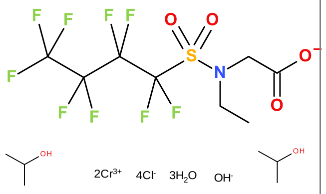
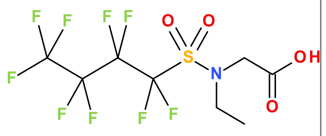
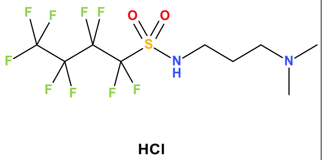
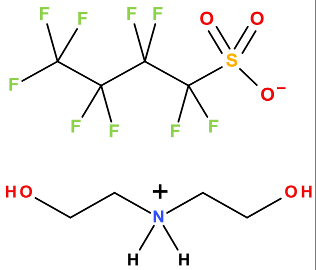
EC No	CAS No	Chemical Structure	Substance names and abbreviation	Chemical formula	MW	Melting and boiling point	Density	Other properties	C&L Inventory, Nov 2016
255-013-6	40630-65-7		*N*-Allyl perfluorobutanesulfonamide *N*-Allyl 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonamide	$C_7H_6F_9NO_2S$	339.177	BP: 201.1 °C	1.554 g/cm^3	Vapour Pressure: 0.314 mmHg at 25°C Refractive index: 1.356 Flash Point:75.4ºC	No
255-641-0	42060-64-0		Perfluorosulfolane Octafluorotetrahydro-thiophene 1,1-dioxide	$C_4F_8O_2S$	264.092	BP: 180.9ºC	1.88 g/cm^3	Flash Point: 63.2ºC Refractive Index: 1.327 Vapour Pressure: 1.19 mm Hg at 25°C	Yes
258-597-0	53518-00-6		Perfluorobutanesulfonamide*N*-(*N′*,*N′*,*N′*-trimethyl-propanaminium) chloride	$C_{10}H_{16}ClF_9N_2O_2S$	434.75				No
266-728-8	67584-51-4		Potassium *N*-ethyl-*N*-[(nonafluorobutyl)sulphonyl]glycinate	$C_8H_7F_9KNO_4S$	423.291				No

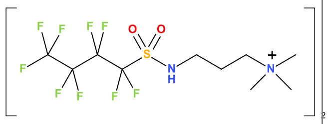
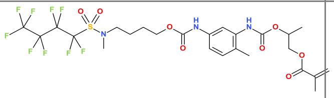
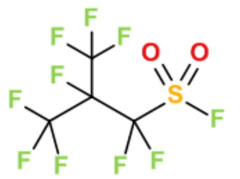
EC No	CAS No	Chemical Structure	Substance names and abbreviation	Chemical formula	MW	Melting and boiling point	Density	Other properties	C&L Inventory, Nov 2016
266-733-5	67584-55-8		*N*-Methyl perfluorobutane-sulfonamidoethyl acrylate 2-[Methyl[(nonafluorobutyl)-sulfonyl]amino]ethyl acrylate MeFBSAC C_4-acrylate	$C_{10}H_{10}F_9NO_4S$	411.239	MP: 54.7 °C BP: 300.5 °C	1.524 g/cm³	White waxy solid Vapour pressure: 0,25 Pa at 25 °C Water solubility: 2 mg/L at 22 °C Flash Point: 135.6°C Refractive index: 1.388	Yes
266-737-7	67584-59-2		*N*-Methyl perfluorobutane-sulfonamidoethyl methacrylate 2-[Methyl[(nonafluorobutyl)-sulfonyl]amino]ethyl methacrylate MeFBSMAC	$C_{11}H_{12}F_9N O_4S$ 36737450	425.27	BP: 317.2 ºC	1.486 g/cm³	Refractive Index: 1.392	No
266-741-9	67584-63-8		Ethyl *N*-ethyl-*N*-[(nonafluorobutyl)sulfonyl]-glycinate	$C_{10}H_{12}F_9NO_4S$	413.255	BP: 290.5 °C	1.504 g/cm³	Flash Point: 129.5°C Refractive index: 1.382	No

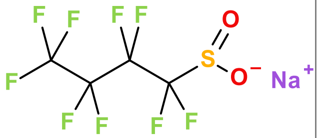
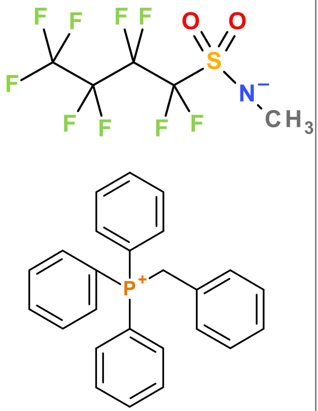
EC No	CAS No	Chemical Structure	Substance names and abbreviation	Chemical formula	MW	Melting and boiling point	Density	Other properties	C&L Inventory, Nov 2016
267-706-0	67906-39-2		*N*-Methyl perfluorobutane-sulfonamidobutyl methacrylate 4-[Methyl[(nonafluorobutyl)-sulfonyl]amino]butyl methacrylate	$C_{13}H_{16}F_9NO_4S$	453.32	BP: 348.2 °C	1.421 g/cm^3	Flash Point:164.4°C Refractive Index: 1.4	No
267-834-7	67939-33-7		*N*-Ethyl perfluorobutane sulfonamidoethyl methacrylate 2-[Ethyl[(nonafluorobutyl) sulfonyl]amino]ethyl methacrylate EtFBSMAC	$C_{12}H_{14}F_9NO_4S$	439.294	BP: 333.6 °C	1.452 g/cm^3	Flash Point: 155.6°C	No
267-861-4	67939-89-3		*N*-Ethylperfluorobutane-sulfonamidoethyl phosphate [Perfluorobutane sulfonamide-*N*-ethyl]-*N*-ethyl dihydrogenphosphate MonoPAP	$C_8H_{11}F_9NO_6PS$	451.20	BP: 391.7 °C	1.711 g/cm^3	Flash Point: 190.7°C Refractive index: 1.403	No

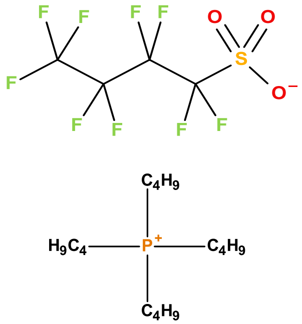
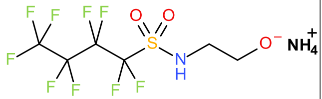
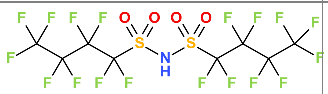
EC No	CAS No	Chemical Structure	Substance names and abbreviation	Chemical formula	MW	Melting and boiling point	Density	Other properties	C&L Inventory, Nov 2016
267-864-0	67939-91-7		Bis[2-[ethyl(perfluorobutanesulfonyl)amino]ethyl] hydrogenphosphate 1-Butanesulfonamide, N,N'-(phosphinicobis(oxy-2,1-ethanediyl))bis(N-ethyl-1,1,2,2,3,3,4,4,4-nonafluoro-	$C_{16}H_{19}F_{18}N_2O_8PS_2$	804.40 2				No
267-868-2	67939-95-1		Perfluorobutanesulfonamide*N*-(*N′*,*N′*,*N′*-trimethyl propanaminium) iodide	$C_{10}H_{16}F_9IN_2O_2S$	526.20				No
269-513-7	68259-10-9		Ammonium perfluorobutanesulfonate Ammonium 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate	$C_4H_4F_9NO_3S$	317.13				Yes

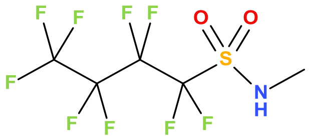
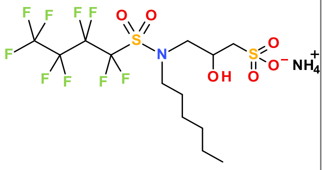
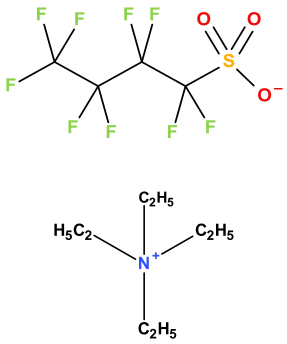
EC No	CAS No	Chemical Structure	Substance names and abbreviation	Chemical formula	MW	Melting and boiling point	Density	Other properties	C&L Inventory, Nov 2016
269-581-8	68298-76-0		2-[[[[5-[[[2-[Ethyl[(perfluoro-butyl)sulfonyl]amino]ethoxy]carbonyl]amino]-2-methylphenyl]amino]carbonyl]oxy]propyl methacrylate	$C_{24}H_{28}F_9N_3O_8S$	689.546		1.45 g/cm³	Refractive index: 1.485	No
269-601-5	68299-19-4		Sodium [[(perfluorobutyl)-sulfonyl]amino]toluene sulfonate	$C_{11}H_8F_9NO_5S_2Na$	491.282				No
271-445-8	68555-68-0		Sodium *N*-ethyl-*N*-[(perfluorobutyl)sulfonyl] glycinate	$C_8H_7F_9NNaO_4S$	407.185	BP: 300.2 °C		Flash point: 135.3°C Vapour pressure: 0.000269 mmHg at 25°C	No
271-455-2	68555-77-1		N-[3-(dimethylamino)propyl]-1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonamide	$C_9H_{13}F_9N_2O_2S$	384.262	BP: 263.7 °C	1.458 g/cm³	Flash Point: 113.3°C Refractive index: 1.381	No

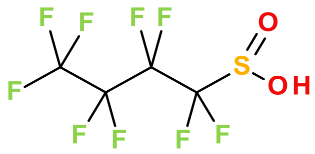
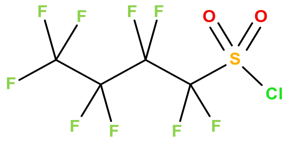
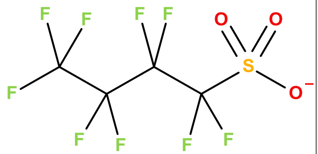
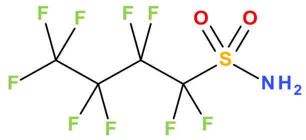
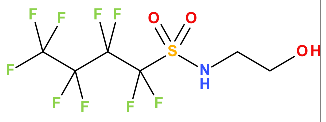
EC No	CAS No	Chemical Structure	Substance names and abbreviation	Chemical formula	MW	Melting and boiling point	Density	Other properties	C&L Inventory, Nov 2016
272-646-3	68900-97-0		Chromium (III) chloride hydroxide *N*-ethyl-*N*-perfluorobutyl sulfonyl glycinate	$C_{14}H_{28}Cl_4Cr_2F_9NO_9S$	803.228				No
273-332-9	68957-33-5		*N*-Ethyl perfluorobutane sulfonamidoacetic acid *N*-Ethyl-*N*-[(perfluorobutyl)-sulfonyl]glycine EtFBSAA	$C_8H_8F_9NO_4S$	385.201	BP: 300.2 ºC	1.655 g/cm^3		No
273-351-2	68957-59-5		*N*-(3-(dimethyl)amino-propyl)perfluorobutane-sulfonamide monohydrochloride	$C_9H_{14}ClF_9N_2O_2S$	420.72	BP: 263.7 °C		Flash point: 113.3°C Vapour Pressure: 0.0101 mm Hg at 25°C	No
274-465-5	70225-18-2		Bis(2-hydroxyethyl) ammonium perfluorobutanesulfonate 1,1,2,2,3,3,4,4,4-Nonafluorobutane-1-sulfonic acid, compound with 2,2'-iminodiethanol (1:1)	$C_8H_{12}F_9NO_5S$	405.232				No

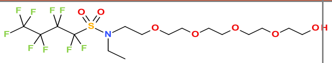
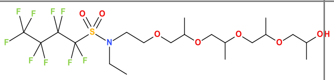
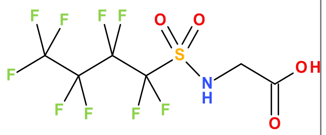
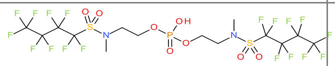
EC No	CAS No	Chemical Structure	Substance names and abbreviation	Chemical formula	MW	Melting and boiling point	Density	Other properties	C&L Inventory, Nov 2016
274-467-6	70225-22-8	 SO_4^{2-}	Di[Perfluorobutanesulfon-amide *N*-(*N′*,*N′*,*N′*-trimethyl propanaminium)] sulfate	$C_{20}H_{32}F_{18}N_4O_8S_3$	894.647				No
275-008-2	70900-38-8		2-[[[[2-methyl-5-[[[4-methyl-[(perfluorobutyl)sulfonyl]-amino]butoxy]carbonyl]-amino]phenyl]amino]-carbonyl]oxy]propyl methacrylate	$C_{25}H_{30}F_9N_3O_8S$	703.573		1.43 g/cm^3	Refractive Index: 1.484	No
290-846-9	90268-45-4	 * *Isobutanesulfonyl fluoride – one of the theoretically three isomers of the substance. The actual composition is not known.	Perfluorobutane sulfonyl fluoride, branched	$C_4F_{10}O_2S$	302.09				No

EC No	CAS No	Chemical Structure	Substance names and abbreviation	Chemical formula	MW	Melting and boiling point	Density	Other properties	C&L Inventory, Nov 2016
422-100-7	102061-82-5		Sodium perfluoro butanesulfinate Sodium 1,1,2,2,3,3,4,4,4-nonafluoro-1-butanesulfinate Na-PFBSi	$C_4HF_9O_2S.Na$	306.08		2.13 at 20 °C	Solid Vapour pressure: 2.1 Pa at 20 C	Yes
442-960-7	332350-93-3		Triphenyl(phenylmethyl)phosphonium 1,1,2,2,3,3,4,4,4-nonafluoro-N-methyl-1-butanesulfonamide (1:1)	$C_5H_3F_9NO_2S$ $C_{25}H_{22}P$	666.2		1.8 g/cm^3		Yes

EC No	CAS No	Chemical Structure	Substance names and abbreviation	Chemical formula	MW	Melting and boiling point	Density	Other properties	C&L Inventory, Nov 2016
444-440-5	220689-12-3		Tetrabutylphosphonium perfluorobutanesulfonate	$C_{20}H_{36}F_9O_3PS$	558	MP: 73.4 °C BP: ca. 285 °C	1.265 g/cm³ (20.1 °C)	Waxy solid Vapour pressure < 0.003 Pa at 25 °C $LogP_{ow}$ = 1.55-1.56 at 20 °C Water solubility: 824 mg/L at 20 °C, pH: 7.56	Yes
454-680-2	484024-67-1		Ammonium perfluorosulfonamido-ethanolate 1-Butanesulfonamide, 1,1,2,2,3,3,4,4,4-nonafluoro-N-(2-hydroxyethyl)-, monoammonium salt	$C_6H_8F_9N_2O_3S$	360,17				Yes
609-746-7	39847-39-7		Bis(perfluorobutane-sulfonyl)imide Bis(1,1,2,2,3,3,4,4,4-nonafluoro-1-butane-sulfonyl)imide	$C_8HF_{18}NO_4S_2$	581.19	BP: 274 °C	1.875 g/cm³	Vapour pressure: 0.006 mmHg at 25 °C Flash point: 119°C Refractive index: 1.326	Yes

EC No	CAS No	Chemical Structure	Substance names and abbreviation	Chemical formula	MW	Melting and boiling point	Density	Other properties	C&L Inventory, Nov 2016
614-396-3	68298-12-4		*N*-Methyl perfluorobutane sulfonamide *N*-Methyl 1,1,2,2,3,3,4,4,4-nonafluorobutane- 1-sulfonamide, MeFBSA	$C_5H_4F_9NO_2S$	313.138	BP: 159.2 °C	1.646 g/cm³	Flash Point: 50.1°C	Yes
643-022-1	606967-06-0		1-Propanesulfonic acid, 3- [hexyl[(nonafluorobutyl)sulfonyl]amino]-2-hydroxy-, monoammonium salt	$C_{13}H_{23}F_9N_2O_6S_2$	538	BP: 118 °C	1.1 g/ml	100% water soluble Vapour pressure 15.2 mm Hg at 20°C	Yes
700-536-1	25628-08-4		Tetraethylammonium perfluorobutanesulfonate *N,N,N*-Triethylethanaminium 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate,	$C_{12}H_{20}F_9NO_3S$	541.56 429.3	MP: 50-53 °C MP: 184 C BP: 315 C	1.35 at 20 °C	Crystalline solid Ionic liquid Water solubility: 880 g/L at 20°C and pH = 5 Vapour pressure: 0 Pa	Yes

EC No	CAS No	Chemical Structure	Substance names and abbreviation	Chemical formula	MW	Melting and boiling point	Density	Other properties	C&L Inventory, Nov 2016
468-070-9	34642-43-8 (the pre-registration does not indicate a CAS number)		Perfluorobutanesulfinic acid 1,1,2,2,3,3,4,4,4-Nonafluoro-butane-1-sulfinic acid PFBSi	$C_4HF_9O_2S$	284.10				Yes
-	2991-84-6		Perfluorobutanesulfonyl chloride 1,1,2,2,3,3,4,4,4-Nonafluoro-1-butane-1-sulfonyl chloride PBSCl	$C_4ClF_9O_2S$	318.55				Yes
-	45187-15-3		Perfluorobutane sulfonate anion	$C_4F_9O_3S$	299.10				No
-	30334-69-1		Perfluorobutanesulfonamide FBSA	$C_4H_2F_9NO_2S$	299.12				No
-	34454-99-4		Perfluorobutanesulfonamidoethanol	$C_6H_6F_9NO_3S$	343.167				No

EC No	CAS No	Chemical Structure	Substance names and abbreviation	Chemical formula	MW	Melting and boiling point	Density	Other properties	C&L Inventory, Nov 2016
-	68298-79-3		Polyethylene glycol *N*-ethyl-perfluorobutanesulfonamide PEG *N*-EtFBSE	$C_{16}H_{26}F_9NO_7S$ $C_{10}H_{14}F_9NO_4S$	547.43 415.27 2	BP: 328.8 °C	1.51 g/cm³	Refractive index: 1.391 Flash point: 152.7°C Vapour Pressure: 1.38 x 10^{-5} mm Hg at 25°C	No
-	68310-18-9		Polypropylene glycol *N*-ethyl-perfluorobutanesulfonamide PPG *N*-EtFBSE	$C_{20}H_{34}F_9NO_7S$	603.54				No
-	347872-22-4		Perfluorobutane sulfonamidoacetic acid FBSAA	$C_6H_4F_4NO_3S$	357.15				No
-	120945-47-3		Bis[2-(*N*-methyl-perfluorobutane sulfonamido)ethoxy] phosphoric acid	$C_{14}H_{15}F_{18}N_2O_8PS_2$					No

EC No	CAS No	Chemical Structure	Substance names and abbreviation	Chemical formula	MW	Melting and boiling point	Density	Other properties	C&L Inventory, Nov 2016
-	1017237-78-3	Polymeric	Fluoroacrylate copolymer 2-Propenoic acid, 2-[methyl[(1,1,2,2,3,3,4,4,4-nonafluorobutyl)-sulfonyl]amino]ethyl ester, telomer with 3-mercapto-1,2-propanediol, 2-methyloxirane polymer with oxirane di-2-propenoate (MSDS of 3M FC-4434)	Unspecified	NA	BP: 200 °C	1.15 g/mL at 25 °C	Vapour pressure 0.29 mm Hg at 20°C	Yes