Supporting Information: Information requirements under the essential-use concept: PFAS case studies

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S1. Contents

1) Data collected for substances in the alternatives assessment

The data collected from the ECHA Classification & Labelling (C&L) Inventory, the ECHA REACH registration database, and data generated with EPI Suite are listed in the accompanying MS Excel document "Gluege_et_al_SI-2.xlsx", separated according to the case studies.

2) Additional information on the case studies

2.1) Bicycle lubricants

Fluoroadditive powders are a class of fluoropolymers primarily based on PTFE.[1] They are of small particle size and relatively low molecular weight. It has been stated that fluoroadditive powders are also used in lubricants[1] and probably also in bike chain lubricants. Apparently, fluoroadditive powders enhance the abrasion resistance, reduce the coefficient of friction and mechanical wear and that they reduce surface contamination.[2]

The use of PTFE in lubricants (including lubricants for cars) is one of the major uses of fluoropolymers in the Nordic Countries. From the 13,800 t of PFAS polymers that have been used in between 2000 and 2017 in Sweden, Finland, Norway and Denmark, 1450 t were used in lubricants.[3,4]

2.2) Carpets

A recent publication estimated the stock of PFAS in California carpets. For 2017, they estimated that the total amount of PFAS in in-use carpets is ~60 tonnes.[5]

Some information on chemical synthesis processes and ingredients of carpets can be found in patents, for example in patent US005889138A [6] and patent US005889138A [7]. These two patents describe fibers that are sulfonated. According to information from a report from the U.S. Department of Toxic Substances Control (DTSC), sulfonation blocks the fiber dye sites with colorless sulfonates, making the carpet or rug impossible to stain by acidic colorants.[8] The first patent mentioned here describes a process for making stain-resistant nylon fibers from highly sulfonated nylon copolymers and discloses the use of 1,3-benzenedicarboxylic acid, 5-sulfo-, lithium salt (1:1), polymer with 1,6-hexanediamine and hexanedioic acid (CAS no. 222173-52-6). The latter one is a method for continuous production of stain-resistant nylon using 1,3-benzenedicarboxylic acid, 5-sulfo-, polymer with hexahydro-2*H*-azepin-2-one and 1,6-hexanediamine (CAS no. 31227-03-9). However, no information is available on these two substances in the public domain.

A patent from Investa (US20150004351)[9] describes compositions for the topical treatment of fibers containing clay nanoparticles and a wax. Additional information on alternatives to PFAS in carpets is provided in the report from DTSC.[8]

2.3) Cleaning products

Based on data from the SPIN Database, the use of PFAS in cleaning products accounted for 21 out of 20,160 t of PFAS used in Sweden, Finland, Norway and Denmark in between 2000 to 2017.

2.3.1) Floor polish

Non-fluorinated alternatives have been developed for floor polish. Patent CN101293999 [10] from 3M describes e.g. the use of a fluorine-free wetting agent comprising an organosilicon and an alkyne diol-based polyether or a fatty oil-alkene oxide copolymer. According to SciFinder^n, the alkyne diol-based polyether is poly(oxy-1,2-ethanediyl), α-hydro-ω-hydroxy-, ether with tetramethyldecynediol (2:1) (CAS no 175801-05-5). An alternative assessment of this polymer was not possible because there were no data in the C&L inventory and no REACH registration. Evonik advertises its Dynol 607 (poly(oxy-1,2-ethanediyl), α,α'-[1,4-dimethyl-1,4-bis(3-methylbutyl)-2-butyne-1,4-diyl]bis[ω-hydroxy-

, (9CI, ACI)) CAS no. 169117-72-0 as surfactant for floor polish.[11] According to the C&L inventory, this compound is harmful to aquatic life with long-lasting effects (see SI-2) and therefore not an ideal alternative.

2.3.2) Carpet spot cleaner and aftermarket carpet-care products

PFAS-free carpet-spot cleaner are available on the market. One example is the Stain + Odoer Remover from ECOS.[12] It is stated that a plant derived surfactant, caprylyl/myristyl glucoside (CAS no. 68515-73-1 and 110615-47-9) is used.[12] According to its REACH registration dossier, caprylyl/myristyl glucoside is neither persistent nor bioaccumulative. However, the C&L inventory has a notification that this compound is harmful to aquatic life with long-lasting effects (see SI-2).

Alternatives exist also to PFAS in aftermarket carpet-care products. Non-PFAS chemical solutions on the market include silicone dioxide in nanoparticle form[13] and proprietary anionic non-fluorinated polymers.[14,15]

2.4) Additional case study: Climbing ropes

Uses: PFAS, probably C6 side-chain fluorinated polymers, are used in climbing ropes to protect the ropes from water and dirt.

Availability of alternatives: The rope producer Edelrid introduced in 2018 a hydrophobic coating for climbing ropes that is PFAS free.[16] Ropes with this coating meet the water-repellency standard of the International Climbing and Mountaineering Federation and absorb only 1–2% of their own weight in water.

Alternative assessment: The composition of the PFAS-free coating is confidential business information, so no assessment of alternatives is possible. The rope producer themselves have not performed a hazard or risk assessment, but rely on the chemical safety data sheet provided by the chemical manufacturer of the waterproofing chemical for chemical hazard information (Edelrid, personal communication).

Conclusion: Technically, PFAS are not needed in climbing ropes and an alternative is on the market so that this use of PFAS is non-essential. However, an assessment of alternatives was not possible because no information on the composition and properties of the alternative was made available.

2.5) Chrome plating

As a general note, chromium (VI) was assessed as chromium trioxide and chromium (III) as chromium chloride as described in the authorisation process for chromium trioxide use.[17]

There are basically two processes in which chromium (VI) is used for the plating on plastics: in the etching of plastic (pre-treatment process) and for applying a metallic chrome coating on top of the plastic substrate (electroplating). In the alternative assessment of Gerhardi Kunststofftechnik it is pointed out that both steps are interlinked and cannot be seen as standalone processes. They also state that without an adequate pre-treatment, the high-quality of the final product cannot be reached.[18]

2.5.1) Pre-treatment (etching) process

PFAS are used as effective wetting agents in the etching pre-treatment process. Hauser et al. (2020)[19] stated that if chromium (VI) and thus also the fluorosurfactants are to be dispensed with, substitution is possible by a two-stage process. The first step would involve swelling (e.g. with ethylene and butyl diglycol), the second step oxidation (e.g. with potassium permanganate). An optional third step could be neutralization.[19]

In their alternative assessment, Gerhardi Kunststofftechnik concluded that as of 2016, "permanganate based alternatives for etching of plastic substrates is not technically feasible. From a technical point of view, the major drawback is the clearly insufficient adhesive properties, leading to delamination and an unacceptable aesthetic appearance of the final coating. Furthermore, the permanganate process leads to deposition of sludge, which causes high maintenance and costs."[18] So, according to Gerhardi Kunststofftechnik, the pre-treatment process is not yet possible without chromium (VI). Whether or not the fluorosurfactants can be replaced in the etching process with chromium (VI) is unclear.

2.5.2) Electroplating

PFAS are used as surfactants in chrome plating baths. They reduce the exposure to chromium (VI) vapour as the surfactant forms a barrier over the electrolyte solution and lowers the surface tension causing a reduction in the size of the bubbles formed. This reduces the amount of hexavalent chromium emitted into the air.[4]

As stated in the main article, there are a few companies that have developed hard chrome plating processes with chromium (III). Gerhardi Kunststofftechnik GmbH and other companies have analysed these processes and summarized their findings in a report called "Analysis of alternatives for chromium trioxide - non confidential report".[18] We refer to this report here as "Alternative assessment of Gerhardi Kunststofftechnik" although other companies have been involved as well.

For the electroplating, two processes were considered in the alternative assessment of Gerhardi Kunststofftechnik as promising alternatives: Trivalent chromium electroplating and PVD-based processes.[18] For trivalent chromium plating, they concluded that "Cr(III) derived coatings still have technical limitations when it comes to corrosion resistance, especially after combined stone-chip / climate change testing. Furthermore, color changes are still an issue."[18] However, they also showed that in the corrosion resistance tests, a few of the systems performed close to chromium trioxide derived metallic chrome coating. On the aesthetics aspect, the color of trivalent chromium plating is slightly more yellowish/brownish than that of the chromium (VI). But Gerhardi Kunststofftechnik state also that single Chromium (III) coated products have recently been accepted by some automobile manufacturers for one car model (e.g., front grill from Peugeot A9 MiVi). So research and development are going on and it seems that trivalent chromium electroplating might be a possible alternative in the future.

2.6) Chemical-driven oil production

Figure S1 shows the structure of the surfactant iC18S(FO-180).

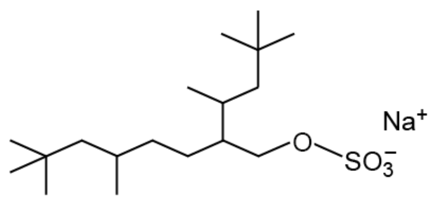
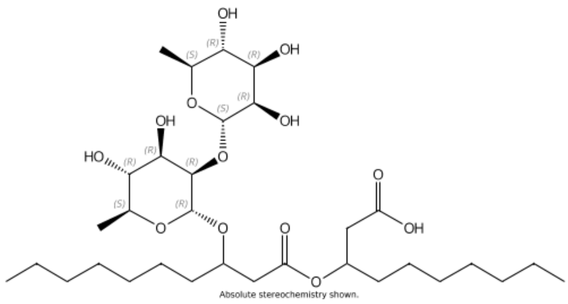
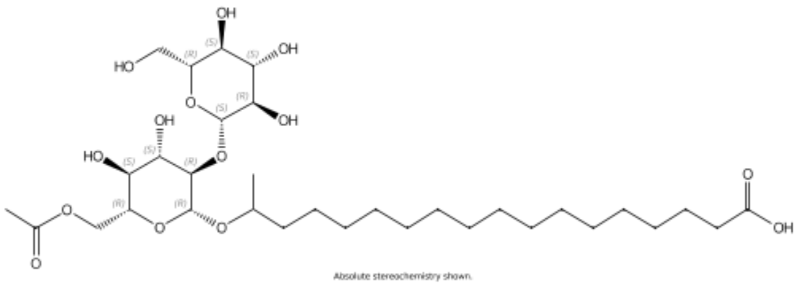
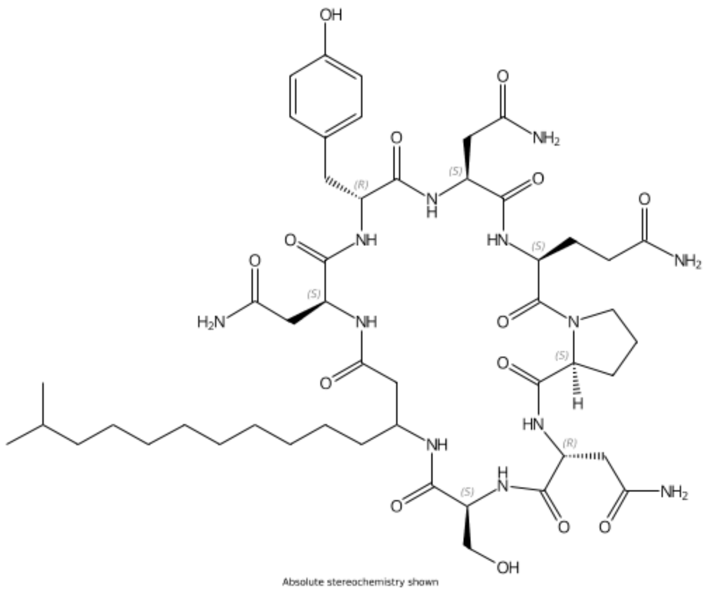


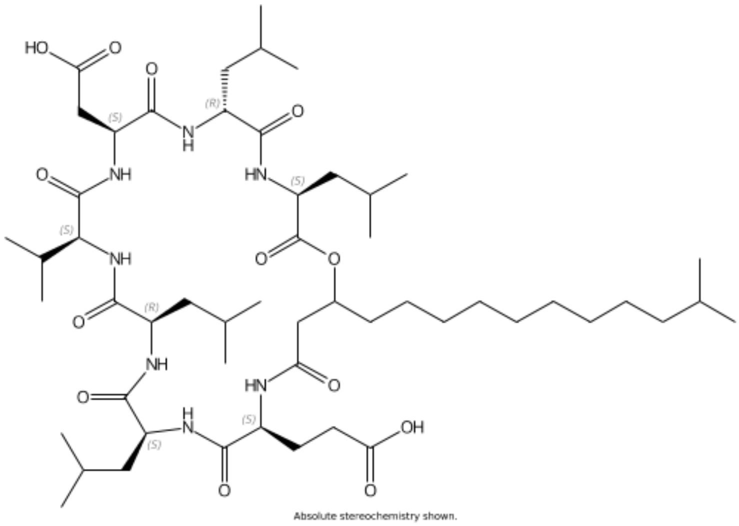
Figure S1: Surfactant iC18S(FO-180), according to Alexander et al. (2014),[20] and Kiani et al. (2019).[21]

Table 2 shows major biosurfactant classes for microbial enhanced oil recovery (MEOR). The examples shown have not necessarily been tested for their suitability for MOER. They are simply examples of the different classes of biosurfactants mentioned.

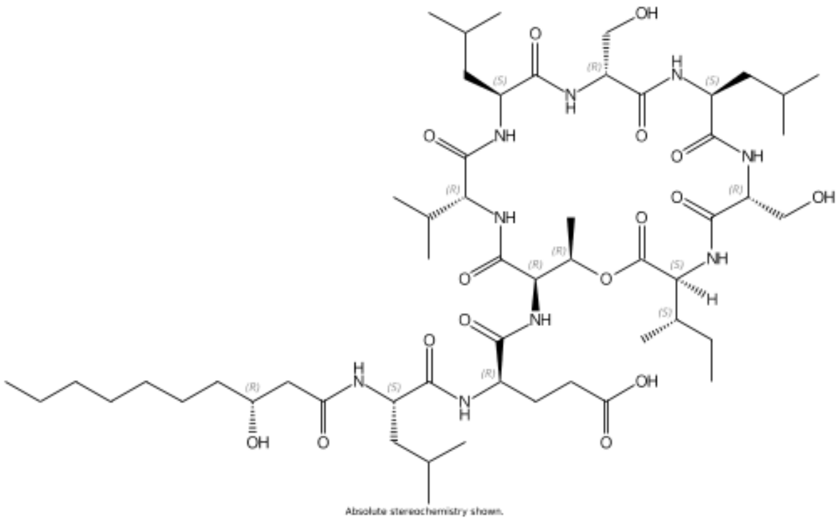
Table S1: Major biosurfactant classes for MEOR, adapted from Varjani (2017) and Desai and Banat (1997)*. Not for all biosurfactants listed chemical structures are provided.*

Biosurfactant	Example
<u>Glycolipids</u>	
Rhamnolipids (e.g. CAS no. 4348-76-9)	
Trehalolipids	
Sophorolipids (e.g. CAS no. 117854-19-0)	
Cellobiolipids	
<u>Lipoproteins or Lipopeptides</u>	
Iturin (e.g. CAS no. 64667-10-3)	

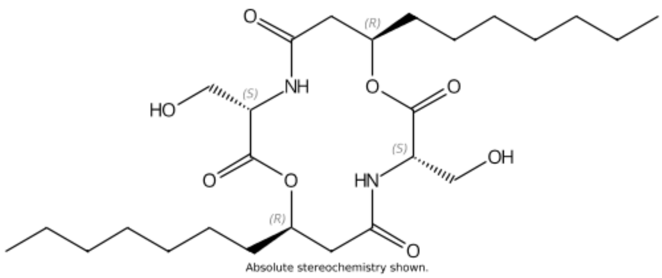
Surfactin
(e.g. CAS no. 24730-31-2)



Viscosin
(e.g. CAS no. 27127-62-4)

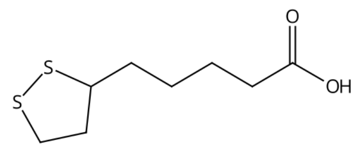


Lichenysin
Peptide-lipid
Serrawettin
(e.g. CAS no. 5285-25-6)



Subtilisin

Phospholipids, fatty acids or natural lipids
Surface-active antibiotics
Gramicidin
Polymixin
Fatty acids or natural lipids

Polymeric biosurfactants	
Emulsan	
Alasan	
Liposan	
(e.g. CAS 1077-28-7)	
Biodispersan	
Mannan-lipid protein	
Carbohydrate-protein-lipid	
Particulate biosurfactants	
Vesicles and fimbria	
Whole cells	

2.7) Processing aids for aqueous emulsion polymerization of fluoropolymers

2.7.1) General notes

Fluoropolymers can be produced by several methods, including suspension polymerization (e.g. patents DE2416452,[24] DE3135598,[25] and EP649863 [26]); aqueous emulsion polymerization (e.g. patents DE2052495,[27] and DE2639109 [28]); solution polymerization (e.g. patents DE2019150,[29] US4535136,[30] US5663255 [31]); polymerization using supercritical CO (e.g. patents JP4601103 [32] and EP964009 [33]); and polymerization in the gas phase (e.g. patent US4861845 [34]).

2.7.2) Fluorine-free processing aids for the polymerization of vinylidene fluoride (VDF) patented by Arkema

Arkema has developed a whole toolbox of methods and emulsifiers to produce PVDF without fluorosurfactants. Table S2 and Table S3 show fluorine-free emulsifiers patented by Arkema in between 2004 to 2020. One set of substances are emulsifiers containing blocks of polyethylene glycol (PEG), polypropylene glycol (PPG) and/or polytetramethylene glycol (PTMG) (Table S2). They are included inter alia in the patents US20060281845,[35] US20070135546,[36] US20070082993,[37] US20120142858,[38] and WO2020101963.[39] Beside the Chemical Abstract Service (CAS) numbers, Table S2 also contains a short summary on their alternative assessment (AA). More details on the AA can be found in the accompanying excel spread sheet (Gluege_et_al_SI-2.xlsx).

Table S2: Emulsifiers containing blocks of PEG, PPG and/or PTMG that are included in patents US20060281845,[35] US20070135546,[36] US20070082993,[37] US20120142858,[38] and WO2020101963.[39]

Substance name	CAS No.	Summary of AA	Ref
Polyethylene glycol (PEG)	25322-68-3	reduced hazard	35–39
Polyethylene glycol acrylate (PEGA)	60182-11-8	no information	35
Polyethylene glycol monoacrylate	26403-58-7	no C&L notifications	36–39
Polyethylene glycol monomethacrylate	25736-86-1	reduced hazard	39
Polyethylene glycol methacrylate (PEG-MA)	9056-77-3	no information	37
Polyethylene glycol monobutyl ether (PEGBE)	9004-77-7	reduced hazard	36,37,39
Polyethylene glycol phenol oxide (Triton X-100)	9002-93-1	endocrine disrupting	35–37,39
Polyethylene glycol dimethyl ether	24991-55-7	CLP Reproductive	39

		toxicant 2	
Polypropylene glycol (PPG)	25322-69-4	reduced hazard	35–39
Polypropylene glycol acrylate (PPGA)	58856-72-7	no information	35–37,39
Polypropylene glycol monoacrylate	50858-51-0	CLP Aquatic Chronic 2	38
Poly(propylene glycol) methacrylate (PPG-MA)	62851-97-2	no information	36–39
Polypropylene glycol dimethacrylate	25852-49-7	no C&L notifications	36–38
Polytetramethylene glycol (PTMG)	25190-06-1	no information	36–39

Additional patents from Arkema describe the use of alkyl phosphonate surfactants (US20070032591 [40]), vinyl/acrylic acids or a salt thereof (WO2012030784 [41]), polyvinyl/acrylic acid or a salt thereof (WO2007018783 [42]), alkanesulfonates (US20050239983 [43]), siloxane surfactant (EP1462461 [44]), and 3-allyloxy-2-hydroxy-1-propane sulfonic acid salts as surfactants (EP1475395 [45]). According to information provided by Arkema in a personal communication, the emulsifier used in a process is selected on the basis of the desired properties of the PVDF polymer.

Table S3: Additional fluorine-free emulsifier for the polymerization of PVDF patented by Arkema. The patents are US20070032591,[40] WO2012030784,[41] WO2007018783,[42] US20050239983,[43] EP1462461,[44] and EP1475395.[45]

Substance name	**CAS No.**	**Summary of AA**	**Ref**
Dodecylphosphonic acid	5137-70-2	Reduced hazard	40
Sodium vinylsulfonate	3039-83-6	CLP Aquatic Chronic 3	41
Vinylphosphonic acid	1746-03-8	Reduced hazard	41
Vinylsulfonic acid	1184-84-5	Reduced hazard	41
Itaconic acid	97-65-4	CLP Aquatic Acute 1, CLP Aquatic Chronic 1	41
Methacrylic acid	79-41-4	Reduced hazard	41
Acrylic acid	79-10-7	CLP Aquatic Acute 1	41
Poly(vinylphosphonic acid)	27754-99-0	Reduced hazard	42
Poly(vinylsulfonic acid)	26101-52-0	No information	42
Poly(methacrylic acid)	25087-26-7	Reduced hazard	42
Poly(acrylic acid)	9003-01-4	CLP Carcinogen category 1A, CLP Mutagen category 1B	42
Sodium 1-octanesulfonate monohydrate	207596-29-0	Reduced hazard	43
1,2-Octanedisulfonic acid, sodium salt (1:2)	139473-92-0	No information	43
Sodium decanesulfonate	13419-61-9	Reduced hazard	43
Sodium octanesulfonate	5324-84-5	Reduced hazard	
Dimethylsilanediol-ethylene oxide block copolymer	156309-06-7	No information	44
Polyethylene glycol monomethyl ether mono[3-[methylbis(trimethylsiloxy)silyl] propyl] ether	27306-78-1	CLP Aquatic Chronic 2, CLP Aquatic Chronic 3	44
Poly(dimethylsiloxane)	9016-00-6	CLP Aquatic Chronic 4	44

1-Propanesulfonic acid, 2-hydroxy-3-(2-propen-1-yloxy)-, ammonium salt (1:1)	101324-88-3	No information	45
1-Propanesulfonic acid, 2-hydroxy-3-(2-propen-1-yloxy)-, sodium salt (1:1)	52556-42-0	Very persistent; CLP Reproductive toxicant 2	45
Dimethylsilanediol-ethylene oxide block copolymer*	156309-06-7	No information	45
Dimethylsilanediol-ethylene oxide-propylene oxide block copolymer*	156309-05-6	No information	45
Ethylene oxide-propylene oxide block copolymer*	106392-12-5	Reduced hazard	45
Polyethylene glycol*			
1,1,1,3,3,5,5-Heptamethyltrisiloxane*	2895-07-0	Reduced hazard	45
1,1,1,3,5,5,5-Heptamethyltrisiloxane*	1873-88-7	Very Persistent, very bioaccumulative	45
Betaine*	107-43-7	Reduced hazard	45

* (possible/optional cosurfactant in ref. 45)

2.7.3) Fluorine-free processing aids for the polymerization of VDF by other manufacturers than Arkema

Other manufacturers of fluoropolymers beside Arkema have also patented fluorine-free processing aids for the polymerization of VDF. It is not known if these processes are used in practice. Du Pont has developed a process that uses allylphosphate esters (US20080262177 [46]) and another process that uses hydrocarbon anionic surfactants (US20080125558 [47]) for the polymerization of VDF. 3M has developed at least two processes, one with carbosilane surfactants (US7678859 [48]) and one with derivatives of sugar (polyol compounds) (WO2011014715 [49]).

2.7.4) Processing aids for the polymerization of fluoropolymers in general

Patent US20120116003 [50] describes a process where fluorosurfactants are greatly reduced in the aqueous emulsion polymerization of fluoromonomers to form e.g. non-melt-processible perfluoroplastics such as polytetrafluoroethylene (PTFE) and melt-fabricable perfluoroplastics such as tetrafluoroethylene/hexafluoropropylene copolymer (FEP) and tetrafluoroethylene/perfluoro(alkyl vinyl ether) (PFA).

The patents also show the development and improvement of fluorine-free emulsifiers. It was stated in a patent from 2007 (US20070015865 [51]) that although emulsifier-free polymerization processes are known, the presence of fluorinated surfactants is still desirable because "it can yield stable fluoropolymer particle dispersions in high yield and in a more environmental friendly way than for example polymerizations conducted in an organic solvent". However, the newly developed processes, e.g. patent US20120116003 [50] yield solid contents of > 45% wt and use an aqueous medium. It was stated in another patent (WO2013169571 [52]) that fluoropolymer resins polymerized with hydrocarbon surfactants are prone to thermally induced discoloration, which is unwanted. However, patents WO2013169571 [52] and WO2013169581 [53] describe processes for reducing thermally induced discoloration that seem to solve the problem.

There are also other recent patents that disclose methods for manufacturing fluoropolymer using fluorine-free surfactants. Examples are the patents WO2018181898 [54], WO2018181904 [55], WO2019172382 [56], and WO2020136679 [57] from 3M.

2.8. Semiconductor industry

Beside the use of PFAS as photoacid generator in the photoresist, PFAS can also be part of the photoresist itself, act as a photosensitizer or quencher in the photoresist.[4] PFAS may also be used to add a thin coating to the photoresist to reduce reflections.[58] Additionally, PFAS may be used as surfactants in the developers, as etching agents or in ancillary products such as edge bead removers.[58] PFAS are also used in rinsing and cleaning solutions for wafers, and in working fluids for vacuum pumps and highly inert molds and pipes. Additional uses of PFAS in the semiconductor industry are described by Glüge et al. (2020).[4]

2.8.1) Photoacid generators

Some fluorine-free photoacid generators (PAGs) are described in patents. For example, aromatic PAGs in patent WO2009091704 [59] and heteroaromatic PAGs in patents WO2009091702 [60] and US20110183259.[61] The latter patent is currently active (owned by Global Foundries Inc.) and includes, among others, the PAG triphenylsulfonium benzo[b]thiophene-2-sulfonic acid, 4(or 7)-nitro-, ion(1-) (TPS TBNO).

2.8.2) Immersion liquid, developer solution and rinse solution

The identity of the fluorine-free alternative used in the BASF patent is vague. In patent WO2012127342 [62] the identiy is described as:

"[0040] Preferably, the potentially anionic and anionic groups of the fluorine-free anionic surfactants A are selected from the group consisting of carboxylic acid, sulfonic acid, phosphonic acid, sulfuric acid monoester, phosphoric acid monoester and phosphoric acid diester groups and carboxylate, sulfonate, phosphonates, monoester sulfate, monoester phosphate and diester phosphate groups.

[0041] Preferably, the counterions of the anionic groups are selected from the group consisting of ammonium, lithium, sodium, potassium and magnesium cations. Most preferably, ammonium is used as the counterion.

….

[0045] Preferably, the fluorine-free amphoteric surfactant A is selected from the group consisting of alkylamine oxides, in particular alkyldimethylamine oxides; acyl-/dialkylethylendiamines, in particular sodium acylamphoacetate, disodium acylamphodipropionate, disodium alkylamphodiacetate, sodium acylamphohydroxypropylsulfonate, disodium acylamphodiacetate, sodium acyl-amphopropionate, and *N*-coconut fatty acid amidoethyl-*N*-hydroxyethylglycinate sodium salts; *N*-alkylamino acids, in particular aminopropyl alkylglutamide, alkylaminopropionic acid, sodium imidodipropionate and lauroamphocarboxyglycinate"

3) Manufacturers contacted

Table S4: List of manufacturers contacted. All manufacturers included here provided information on the respective case studies, some of them also reviewed the case-study descriptions and provided feedback.

PFAS use	Manufacturer contacted	Date of contact	Review of case study description
Bicycle lubricants	Green Oil	August 2021	No
Bicycle lubricants	Fenwicks Bike	August 2021	Partial
Carpets	Aquafil	April 2021	No
Carpets	RAL Environment	June 2019	No
Carpets	Nordic Ecolabel	June 2019	No
Climbing ropes	Edelrid	March 2021	Yes
Chrome plating	Faraday Technology	May 2019, May and August 2021	Yes, extensive
Chrome plating	Atotech	May 2019 and May 2021	No
Chrome plating	MacDermid Enthone Industrial Solutions	June and August 2021	Yes, extensive
Processing aids for emulsion polymerization of fluoropolymers	Arkema	August 2021	Yes, extensive
Semiconductor industry (PAGs)	IBM	August 2021	Yes, extensive

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(15) TriPlex. Carpet Care http://www.tri-plextech.com/carpet-care/.

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