Chapter 2: Perfluorinated compounds – occurrence and uses in products

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Abstract

Perfluorinated compounds are a chemical family of all organic compounds consisting of a carbon backbone fully surrounded by fluorine and represent a large and complex group of organic substances with unique characteristics. They are used in several industrial branches, but they also occur in a large range of consumer products due to their extraordinary properties such as chemically inert, non-wetting, very slippery, nontoxic, nonstick, highly fire resistant, very high temperature ratings, highly weather resistant) they are applied in fluoropolymer coated cookware, sports clothing, extreme weather military uniforms, food handling equipment, medical equipment, motor oil additives, fire fighting foams, paint and ink as well as water repellent products. Currently, the knowledge of the exact chemical compositions in articles and preparations of perfluorinated compounds is very limited. Since the exact composition of perfluorinated compounds in consumer products are mostly confidential, a range of analytical studies concerning the content of perfluorinated compounds in consumer products have been carried out over the past years with the intention to better understand the intentional and residual content and release of fluorinated substances from consumer products and their impact to health and the environment.

Keywords: Perfluorinated compounds, consumer products, perfluorinated carboxylic acids, telomer alcohols

1.1 Introduction

Polyfluorinated chemicals (PFCs) do not occur naturally. They have been manufactured for 50 years and represent a large and complex group of organic substances with unique characteristics that are extremely versatile and used in a variety of industrial and household applications. Presently the knowledge of the exact chemical compositions in articles and preparations of perfluorinated compounds is very limited.

Recent years of research have substantially improved our knowledge of this wide range of compounds and their uses, but there is lot still a to explore concerning their uses, their intrisic properties and occurrence in the environment.

The main characteristics of polyfluorinated compounds are the replacement of most hydrogens by fluorine in the aliphatic chain structure. Some of these organic fluorine compounds are known as perfluorinated, which means that all hydrogens have been replaced with fluorine with a large variety of chemical forms and structures. Due to the diversity of fluoro organic substances it is important to understand the developed chemical terminology.

1.2 The family of PFCs

PFCs are a chemical family of all organic compounds consisting of a carbon backbone fully surrounded by fluorine, which makes them impervious to heat, acid or other forces that typically break down chemical compounds. They are used in several industrial branches, but they also occur in a large range of consumer products. Due to their extraordinary properties

(chemically inert, non-wetting, very slippery, nontoxic, nonstick, highly fire resistant, very high temperature ratings, highly weather resistant) they are applied in fluoropolymer coated cookware, sports clothing, extreme weather military uniforms, food handling equipment, medical equipment, motor oil additives, fire fighting foams, paint and ink as well as water repellent products.

Fluorotelomers are a range of chemicals with similar fluoride carbon backbones connected to a –CH₂-CH₂- chain and different functional heads. They are industrially produced applying a telomerisation process, coupling tetrafluoro-ethene, which leads to straight-chained products with an even number of carbon atoms. Fluorotelomers are probably the most commonly used perfluorinated substances in products. The hydroxyl group as functional group will give fluortelomer alcohols (FTOH). They are used to treat paper to improve its moisture and oil barrier properties. FTOHs are also used in waterproof outdoor clothing and in waterproofing agents for textiles. Fluorotelomeralcohols are manufactured as a raw material used in the synthesis of fluorotelomer-based surfactants and polymeric products.

The manufacture of FTOHs usually result in a mixture containing six to twelve fluorinated carbon congeners, the 8:2 FTOH being the dominant one. Release of the volatile FTOHs may occur all along the supply chain from production, application into consumer use and disposal. They have the potential to form stable perfluorinated carboxylates (PFCAs) such as perfluorocctaoic acid (PFOA) and perfluorononaoic acid (PFNA) which is shown in figure 1 below.



Figure 1: Simplified mechanism for the atmospheric degradation of 8:2 FTOH into perfluorocarboxylic acids (red box), (Wallington et al. (2006).

The general chemical structure of perfluorinated sulphonates (PFS) contains a perfluorinated carbon chain connected to a sulphonate group. In addition to this, fluorotelomer sulphonates (FTSs) contain two carbon atoms adjacent to the functional group that are not fluorinated. FTS are used among other fluorotelomers in fire fighting foam for their film forming properties and the ability to decrease fuel absorption. These foams are especially useful for major fires, e.g. chemical fires (Stockholm Convention on POPs Review committee, 2009). The quantities in the foams are low, but the foams are released directly into the environment.

FTS is also used as a component in more complex structures (e.g. in water proofing agents) and as a substitute for perfluorooctane sulfonate (PFOS).

Fluorinated surfactants are used in very low levels in a large number of cleaning products, e.g. polish, waxes, all-purpose cleaners, window cleaners etc. Their use is widespread and directly released into wastewater.

Perfluorinated carboxylates (PFCA) is another important PFC group. The main use of perfluorooctanoate (PFOA) is as a process aid in the manufacture of various fluoropolymers, such as polytetrafluoroethylene (PTFE). These polymers are among other things, used to coat cookware intended for stovetop cooking and baking.

The substances PFOS and PFOA are part of a group of old-generation PFCs which will be used to a lesser extent in the future due to their potential hazards. These hazards have resulted and will result in a number of international legislative bans worldwide. New generations of PFCs are developed continuously and applied in industrial amounts already.

Polyfluorinated sulphonamides are considered the most important PFCs because of their intentional industrial production and global distribution. PFOS and related substances are well known degradation products from substituted sulphonamides that are used commercially for numerous applications. However, the potential toxicity, extreme persistence and accumulation potential of their degradation product PFOS has resulted in prohibition for new uses or import by chemical regulatory authorities worldwide based on international restrictions by the United Nations Environmental Programme (UNEP) Stockholm convention, where PFOS is going to be classified as a POP (Persistent Organic Pollutant)

Other polyfluorinated chemicals, such as perfluoroalkylsulfonic acid derivatives (e.g. PFOSF), are probably used as paper additives/coatings to prevent oil from soaking through or staining the paper.

2. Physical properties of PFC

Surface energy is the most critical parameter in the action of PFCs. Due to their extraordinary properties (chemically inert, non-wetting, very slippery, nontoxic, nonstick, highly fire resistant, very high temperature ratings, highly weather resistant) they are applied in fluoropolymer coated cookware, sports clothing, extreme weather military uniforms, food handling equipment, medical equipment, motor oil additives, fire fighting foams, paint and ink as well as water repellent products.

Therefore it is essential to define these surface properties in order to achieve the appropriate surface protective properties or otherwise the purpose of the surface treatment is lost.

PFCs can therefore be used to provide water repellence, stain resistance and soil release properties to a treated surface is related to the physical properties of these fluorinated materials. The critical surface tension is the determining physical parameter why fluorinated chemicals can repel both water and oil substances (J.F. Colbert et al 1983) (J. M. Corpart et al. 1997).

The critical surface energy γ_c of the CF₃ and CF₂ groups are much lower compared to the surface energy of the corresponding hydrocarbons (CH₃ and CH₂), which is described in table 1 below.

| Liquids | Surface energy : γ _c (mN/m) | Surface tension : | <u>γ_L(mN/m)</u> |
|----------|---|---|---|
| | 6 | | |
| | 15 | | |
| | 18 | | |
| | 22 | | |
| | 31 | | |
| - | 39 | | |
| | 42 | | |
| | 46 | | |
| | 44 | | |
| water | | | 72 |
| n-Octan | e | | 22 |
| Olive of | 1 | | 32 |
| | - water n-Octan Olive oi | Liquids Surface energy : γ_c (mN/m) 6 15 18 22 31 - 39 42 46 44 water n-Octane Olive oil | Liquids Surface energy : γ_c (mN/m) Surface tension : 6 15 18 22 31 - 39 42 46 44 water n-Octane Olive oil |

Table 1: Surface energies for characteristic polymer backbone structures

One of the fundamental laws of physics states that every system strives for a minimal surface energy. Therefore when a PFC is coated on a textile substrate and exposed to water with its surface tension of 72 mN/m or oily substances with surface tensions of 20 mN/m and more, they will not spread on the textile surface. The consumer can observe this phenomenon as "water and oil repellence".

The spreading of a liquid on a surface is measured via contact angles and demonstrates well when a fabric is being wetted or not.

When : - angle Θ is > 90° : liquid will not wet the surface

- angle Θ is < 90° : liquid will wet surface partially

- angle $\Theta = 0^\circ$: complete spreading & wetting of the surface by the liquid.



 γ_{SL} = Interfacial tension

Figure 2: Contact angle versus wettability of a substrate surface

As can be seen from the formula for spreading $S = \gamma_c - (\gamma_L + \gamma_{cL})$ it is observed that if the surface energy of the substrate is lowered sufficiently, the liquid will not be able to wet the surface.

Practice shows that it is not sufficient to have only terminal CF₃ groups in a fluorinated chemical. Optimum reduction of the surface energy γ_c is achieved with perfluorinated chains with a sufficient chain length to obtain a large enough density of fluorinated carbons on the surface.

This is demonstrated in literature (J.F. Colbert et al 1983) (J. M. Corpart et al 1997) of fluorochemicals that there is a relationship of the chain length of the perfluorinated chains that is related to the critical surface energy of the surface as described in figure 13 below.



Figure 3 : Surface energy versus number of carbons in PFC backbone structure, where 4 on the x-axis means four perfluorinated carbons etc.

Based on the already explained surface energy properties of fluorinated chemicals, it is understood that for instance a non fluorine surface treatment, such as silicones on treated polymers, can provide rather good water repellency but no oil repellency due to the fact that the oil has lower surface energy than the silicone layer. The surface energy obtained with a silicone surface can not be lower than 22 mN/m, which is comparable to the surface tension of hydrocarbon oily substances. This means that fluortelomers are not always possible to replace with a non fluorine surface treatment if oil or soil repellence is required.

3. Historic emissions of PFCs

PFCs have been manufactured for more than 50 years where the substances PFOS and PFOA are part of a group of old-generation PFCs which will be used to a lesser extent in the future due to their potential hazards. These hazards have resulted and will result in a number of international legislative bans worldwide.

In the European Union in the REACH regulation, PFOS and its precursors is the only EU regulated PFC substance and PFOA is assessed concerning its intrinsic properties which resulted in a classification as toxic (T; R48/23), carcinogenic (Carc Cat2, R45), and a reproductive toxicant (Repr Cat2, R61). Presently, no national or European regulation of the use of PFOA exists but may be the case in the future.

United States Environmental Protection Agency (US EPA) banned PFOS and its precursors since 2001 and has a voluntary agreement with the fluoropolymer industry for emissions of PFOA and its homologues. In this global stewardship programme on perfluorooctanoic acid (PFOA) and related chemicals, the industry commit to reducing PFOA and related chemicals by 95% no later than 2010, and to work toward total eliminating PFOA from emissions and in products no later than 2015.

Australia is developing definitions of and limit uses to non-dispersive applications, similar to restrictions in EPA consent orders with companies.

Due to this pressure from the international society, new generations of PFCs are developed continuously and applied in industrial amounts already.

Due to identified hazards for PFOS and PFOA in context to their long history of production their historical global use and emissions of perfluorinated compounds in the last 50 years are of major environmental importance.

Prevedouros and his research group published a model in 2006, where cumulative global emissions between 2005 and 2050 have been predicted to be at least 80% lower than the estimated cumulative emissions between 1950 and 2004.

By composing an initial global-scale mass balance model to evaluate identified direct emissions of PFCs from manufacture and use this model could account for observed concentrations of PFCs in the environment, (Prevedouros et al. (2006).

Table 2: Global Historical PFCA Production and Emissions Summary, taken from (Prevedouros et al., 2006)

| Environmental input source | Historical time period (years) | Estimated total global historical PFCA emissions (metric tons) | Estimated total global production (metric tons) | |
|--|-----------------------------------|--|---|--|
| Direct PFCA Sources : | | | | |
| 1) PFCA manufacture | | | | |
| PFO/APFO | 1951-2004 | 400-700 | 3600-5700 | |
| PFN/APFN | 1975-2004 | 70-200 | 800-2300 | |
| Total manufactured | | 470-900 | 4400-8000 | |
| 2) Industrial and Consumer Uses | | | | |
| Fluoropolymer manufacture (APFO) | 1951-2004 | 2000-4000 | | |
| Fluoropolymer dispersion processing (APFO) | 1951-2004 | 200-300 | | |
| Fluoropolymer manufacture (APFN) | 1975-2004 | 400-1400 | | |
| Fluoropolymer processing (APFN) | 1975-2004 | 10-20 | | |
| Aqueous fire fighting foams (AFFF) | 1965-1974 | 50-100 | | |
| Consumer and industrial products | 1960-2000 | 40-200 | | |
| Total direct | 3200-6900 | | | |
| Indirect PFCA Sources: | | | | |
| 1) POSF-based products | | | | |
| PFCA residual impurities | 1960-2002 | 20-130 | | |
| POSF-based precursor degradation | 1960-2002 | 1-30 | | |
| POSF-based AFFF | 1970-2002 | 3-30 | | |
| 2) Fluorotelomer-based products | | | | |
| PFCA residual impurities | 1974-2004 | 0.3-30 | | |
| Fluorotelomer-based precursor degradation | 1974-2004 | 6-130 | | |
| Fluorotelomer-based AFFF | 1975-2004 | < 1 | | |
| Total indirect | | 30-350 | | |
| Total source emissions (direct + indirect) | | 3200-7300 | | |

^{*a*} Low and high estimated values as well as the period of use/production for each source are based upon publicly available information cited in the text.

Not: APFO = ammonium perfluorooctanoate; APFN = ammonium perfluorononanoate; AFFF = aqueous fire-fighting foam; POSF = perfluorooctylsulfonyl fluoride

According to the modelling work of Prevedouros and his team for the long-term (1950-2050) global fate of PFOA, they identified direct emissions of PFOA from manufacture and use that could account for observed concentrations of PFOA in the environment (Prevedouros et al. 2006).

Table below lists both direct and indirect PFOA emission sources to the global environment. This table also presents estimated minimum and maximum projected cumulative emissions between 2005 and 2050 for each source together with the contribution of each source to the total PFOA emissions for the time period.

| PFOA emission | 1950-2004 min- | % of total PFOA | 2005-2050 min- | % of total PFOA |
|-----------------------------------|-------------------|--------------------|----------------|---------------------|
| Direct Sources | max (metric tons) | emission (average) | | emissions (average) |
| FP manufacturing (APFO) | 2060-4090 | 72.3% | 410-815 | 86.0% |
| APFO manufacturing | 370-590 | 11.8% | 20-40 | 4.2% |
| FP dispersion (APFO) | 215-340 | 6.8% | 45-75 | 8.7% |
| AFFF-ECF | 50-100 | 1.8% | 0 | 0% |
| FP manufacturing (APFN) | 3-10 | 0.1% | <1-2 | 0.1% |
| Consumer & Industrial Products | 2-10 | 0.1% | 0 | 0% |
| APFN manufacturing | 1-2 | 0% | <1 | 0% |
| PVDF (APFN) | <1 | 0% | <1 | 0% |
| Direct sources: | 2700-5140 | 92.9% | 475-932 | 99.0% |
| Indirect Sources | | | | |
| POSF raw material degradation | 4-585 | 5.0% | 0 | 0% |
| POSF impurities | 14-110 | 1.2% | 0 | 0% |
| POSF-AFFFs | 2-23 | 0.2% | 0 | 0% |
| FT raw material degradation | 3-60 | 0.6% | 1-14 | 0.8% |
| FT impurities | <1-17 | 0.1% | <1-4 | 0.2% |
| Indirect sources: | 23-795 | 7.1% | 1-18 | 1.0% |
| Direct and indirect sources: | 2723-5935 | 100.0% | 476-950 | 100.0% |

Table 3: Estimated Historical between 1950 and 2004 and estimated emissions between 2005 and 2050 of PFOA Emissions (Armitage et al. 2006).

^{*a*} AFFF = aqueous film forming foams (also aqueous fire fighting foams); APFN = ammonium perfluorononoate; APFO = ammonium perfluorooctanoate; ECF = electrochemical fluorination, a process used to produce fluorinated chemicals; FP = fluoropolymer; FT = fluorotelomer; POSF = perfluorooctanesulfonyl fluoride; PVDF = polyvinylidene fluoride.

Direct sources with up to 6 900 tons emitted perfluorinated carboxylic acids (PFCA) were representing the vast majority of PFCAs emitted to the global environment compared to indirect sources which contributed up to 350 tons.

The contribution of indirect sources is expected to decrease both in absolute numbers and relative to direct sources within the year 2050 (Armitage, 2006).

4. PFCs in articles and their exposure

The potential health risks associated with perfluorocarboxylic acids (PFCAs) have promoted intensive research on the sources, transport, transformation, and distribution of these chemicals and their precursors in environmental media, as well as research related to ways to reduce the health risks. Despite the significant progress that has been made so far, researchers are yet to reach a consensus on what are the most important routes by which the general population is exposed to these chemicals. In particular, there are different opinions on whether PFCA-containing products are significant contributors to the total exposure.

A risk characterization from the potential exposure to PFOA in consumer articles has been published (Washburn *et al.*, 2005). The authors investigated potential human exposure to PFOA in a wide variety of consumer articles, including treated textiles and concluded that the trace levels of PFOA present would not be expected to cause adverse human health effects not contribute to quantifiable levels of PFOA in human blood. The authors noted that PFOA was present in a number of consumer articles, which were not treated with fluorinated products. This may result from the presence of PFOA contamination globally (Yamashita *et al.*, 2005).

A more recent study by Fromme, et al. 2009, used the data from indoor measurements in Canada and Norway and estimated that, for the general population in Western countries, the inhalation of house dust contributed only 0.6% of the mean PFOA daily intake and 8.2% of the high PFOA daily intake.

Tittlemier, et al 2007, identified treated carpeting as the second most important source of exposure for PFOA after ingestion of food. A study by Trudel, et al. found that the consumption of contaminated food is the most important pathway causing exposure to PFOA, followed by ingestion of dust and inhalation of air in low- and intermediate-exposure scenarios. Their study also found that direct, product-related exposure is dominant in high-exposure scenarios, in which consumers regularly use PFC-containing products, such as impregnation sprays, or have treated carpets in their homes.

Trudel and his co-workers also observed that product-related exposure tends to be more important for PFOA than for PFOS, most likely because PFOS is no longer used in consumer products. It is, therefore, apparent that the paucity of indoor source and exposure data contributes to the significant uncertainty and differences of opinion about the most prevalent exposure routes for these compounds.

The fact that elevated levels of PFCAs have been detected in house dust in Japan, Canada and the United States strongly suggests the presence of indoor sources. It is well known that fluorotelomer and fluoropolymer products are sources of PFCAs and that PFCAs may exist in fluorotelomer products as unwanted by-products and in fluoropolymer products as residuals Because a broad range of commercial products either contain or are treated with fluorotelomer and fluoropolymer products, they can be potential sources of PFCAs. Given that products are often used in close proximity to humans, it is hypothesized that they can contribute to human exposure to PFCAs either directly by dermal contact and hand-to-mouth transfer or indirectly through inhalation of suspended particles from treated carpet and other interior surfaces.

There have been several studies of the PFCA content in products, but most of them report a single compound namely PFOA. In 2005, Washburn and his colleagues reported the PFOA content in 14 article groups based on theoretical calculations and analytical measurements.

Of these groups, pre-treated carpeting and carpeting treated with carpet-care solution had the highest PFOA loadings: 0.2 to 0.6 and 0.2 to 2 mg of PFOA per kg of article, respectively. Studies by other researchers reported PFOA content in nonstick cookware, food contact paper, thread sealant tape, and dental floss. Data for other PFCAs in commercial products are rather scarce. One study by Sinclair, et al. reported the C5 to C12 PFCA content in three brands of popcorn packaging paper.

Friends of the Earth, Norway, published a report about PFCs in impregnation fluids, covering PFCAs as well. Thirteen commercial products were analysed for a variety of PFCs. Seven of the investigated products contained PFOA, varying between 45 and 692 ng/mL (Naturvernforbundet, 2007).

In 2009 the US EPA analyzed 116 commercial articles purchased from retail outlets in the United States between March 2008 and May 2008 to determine the extractable content of C5 to C12 PFCAs (US EPA, 2009). Of the 13 article categories, the US EPA concluded that the most important PFCA sources were carpets, stone/tile/wood sealants, textiles and textile care products.

| Category | Samples | Maximum conc. of PFCAs | |
|--|---------|-------------------------------|--|
| Pre-treated carpeting | 9 | 292 ng/g fibre | |
| Commercial carpet-care liquids | 9 | 8860 ng/g liquid | |
| Household carpet/fabric-care liquids and foams | 12 | 1710 ng/g liquid | |
| Treated apparel | 16 | 235 ng/g product | |
| Treated home textile and upholstery | 14 | 437 ng/g product | |
| Treated non-woven medical garments | 5 | 334 ng/g product | |
| Treated floor waxes and stone/wood sealants | 11 | 939 ng/g product | |
| Treated food contact paper | 5 | 15,3 ng/g paper | |
| Membranes for apparel | 10 | 12,8 ng/g product | |
| Thread sealant tapes and pastes | 10 | 40,6 ng/g product | |
| Non-stick cookware | 14 | 0,00985 ng/cm2 coated surface | |
| Dental floss and plaque removers | 8 | 5,81 ng/g liquid | |
| Miscellaneous ¹ | 7 | 82,6 ng/g product | |

Table 4: Sample breakdowns of PFCAs by article category.

For most article categories, the PFCA content in a small number of the analyzed samples were significantly higher than in the rest of samples.

Polytetrafluoroethylene (PTFE) is, for example, used to coat cookware intended for stovetop cooking and baking. Other polyfluorinated chemicals, such as fluorotelomer and perfluoroalkylsulfonic acid derivatives (e.g. PFOSF), are or have been used to treat paper to improve its moisture and oil barrier properties. In particular, papers used in contact with high-fat content foods may be treated with fluorotelomer or perfluoroalkylsulfonyl-based paper additives/coatings to prevent oil stains or oil soak through the paper. Typically, these paper

¹ Includes four car-care products, two boat-care products, one deck cleaner, and one dry sack for outdoor use.

coatings/additives are phosphate esters or acrylic polymers containing polyfluoroalkyl functionality (Begley *et al.* 2005).

Larsen *et al.* (2005) detected small amounts of PFOA (up to 140 ppb) in extracts of polytetrafluoroethylene (PTFE) resins, obtained after applying pressure and increased temperatures to the material. Subsequent studies of cookware, coated with PTFE dispersions have shown no-detectable-levels of PFOA extractable from cookware under normal use conditions (Powley *et al.*, 2005). A later study by the Norwegian Institute of Public Health (2007) went in further details about these findings. In a worst case scenario the new study showed that an adult human would be exposed to 66 ng PFOA /kg bw, when drinking 100 ml water cooked in a PTFE coated pan. It was concluded that, even at an assumption of 100% uptake of PFOA, these extremely low levels will not be an essential intake route for humans. According to Horowitz, 98% of the PFOA intake is contributed to by food (Hororwitz, 2007).

Begley et al. (2005) analysed several consumer products for PFOA and concluded that fluorotelomer-based paper coating/additive formulations before application onto paper have the highest PFOA content, but during normal application rates this amount of PFOA will be diluted by about 300 times on the final paper product (see table 4). Therefore, the PFOA content in finished paper should be in the few hundred mg/kg range, which is consistent with the data in table 4.

| Concentration of PFOA (µg/kg) |
|--------------------------------------|
| 4–75 |
| 3 |
| 4 |
| 1 800 |
| nd |
| |
| 6–290 |
| nd |
| nd |
| nd |
| 88 000-160 000 |
| |

Table 4: Summary of PFOA analysis in product, (Begley et al. 2005).

nd = non detects

The residue content of PFOA in PTFE-products is directly related to the processing temperatures used to make the products. Cookware and dental products use a high temperature sintering process that should volatilize PFOA, while production of PTFE film used as e.g. sealant tape does not use that sintering process. Begley *et al.* (2005) conclude that fluoropolymer food-contact materials do not appear to be a significant source of human exposure to PFCs (e.g. PFOA). In particular, the coated cookware's tested did not appear to be a significant source of PFOA. Furthermore, an extreme heating test (abusive) of the cookware did not appear to increase the residual amount of PFOA in the cookware. Additional PFOA did not appear to be formed during the normal use or misuse of these products.

This result were in contrast to the results of a more recent study of Sinclair *et al.* (2007), where gas-phase release of PFOA, 6:2 FTOH, and 8:2 FTOH were measured from heating

non-stick frying pans and microwave popcorn bags. Gas-phase PFOA was measured in all four non-stick frying pan brands. PFOA was reported to vaporize at 189 °C and decompose at temperatures higher than 234 °C .

The authors suggest that residual PFOA is released from the PTFE coating to the gas phase under the normal cooking temperatures. Gas-phase concentration of PFOA varied depending on the frying pan brand, which suggests that the sintering conditions (temperature, pressure, and duration) used in the coating of fluoropolymers may have an influence on the release of PFOA. In addition, PFOA was detected in water boiled for 10 min. in three brands of non-stick frying pans (Table 5).

| Brand | Surface temperature | Area | PFOA | | 6:2 FTOH | | 8:2 FTOH | |
|--------------------|------------------------|-----------------|------|-------------------|----------|-------------------|----------|-------------------|
| | о С | cm ² | ng | µg/m ² | ng | g/cm ² | ng | µg/m ² |
| 1 | 180 | 640 | 12 | 19 | 16 | 25 | 73 | 114 |
| 2 | 229 | 477 | 32 | 67 | 97 | 204 | 298 | 625 |
| 3 | 190 | 670 | 192 | 287 | 36 | 54 | 28 | 42 |
| 4 | 205 | 659 | 40 | 61 | <10 | <15 | 40 | 61 |
| Stainless steel | 230 | 670 | <5 | <7 | <10 | <15 | <10 | <15 |

Table 5: Released amounts (ng) and concentrations ($\mu g/m^2$) of PFOA and FTOH from nonstick frying pans of 4 different brands (Sinclair et al. 2007).

In the same study, PFOA was found in the vapours produced by microwave heating of prepacked popcorn bags. Furthermore, mg quantities of both PFCAs and FTOHs were calculated to coat the entire surface of the package (Sinclair *et al.* 2007). The authors noted that they were not able to explain the origin of the FTOHs from the cookware, because FTOHs are not used to manufacture cookware, and no plausible way for FTOH to be formed from PTFE is known.

Table 6: *Released amount (ng) of PFOA of fluorotelomer alcohols at making popcorn in a bag of three different brands. (Sinclair et al. 2007)*

| Brand | PFOA | 6:2 FTOH | 8:2 FTOH |
|-------|------|----------|----------|
| 1 | 16 | 223 | 258 |
| 2 | 17 | <20 | <20 |
| 3 | <2,5 | <20 | <20 |

Eventually PFCAs can be present in consumer products treated with fluorinated compounds due to intentional application, in form of an unintended residues or due to degradation of precursor compounds like FTOHs. It is not always possible to distinguish between these cases, since recipes of technical applications are mostly confidential or the actual composition of the used mixture of active compounds confidential. Products intended for contact with food seem to contain small PFCA amounts, but since almost all available data origins from authors related to fluoropolymer manufacturing companies, the interpretation of these data should be

done carefully. The same is the case for research on metabolism of PFCAs in organisms. Data from independent research groups are needed in order to confirm these potentially prejudiced findings.

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