EU FOCUS

REACH Restriction Process on PFAS:

"What Way Forward For Fluoropolymers, Fluoromonomers & fluorinated Polymerization Aids?"

Scientific Thought Paper

June 2022

Introducing Chemours' 'ABC' approach

As part of the upcoming **PFAS** restriction process, a group of five EEA countries plan to submit, by January 2023, a REACH dossier to ECHA with the proposal to restrict the manufacture, placing on the market and use of all PFAS substances. PFAS are defined as "substances that contain at least one fully fluorinated methyl (CF3-) or methylene (-CF2-) carbon atom (without any H/Cl/Br/I atom attached to it)".

The basis of the restriction of such a broad group of compounds is the substances **hazard classification**. PFAS are highly persistent in the environment. Small molecular weight PFAS are highly mobile and have the potential to contaminate soil, surface and drinking water. In addition, it is argued that certain PFAS substances have the potential to bioaccumulate in living organisms. Finally, certain PFAS may to cause cancer or interfering with the hormonal system[1].

Fluoropolymers are a distinct class of PFAS. They are included in scope of restriction since their chemical structure includes at least 1 perfluorinated methyl (-CF3-) or methylene (-CF2) group. Likewise, substances specifically designed to manufacture fluoropolymers (e.g., monomers), are in scope of a possible PFAS restriction.

When discussing the **merits of a REACH restriction against fluoropolymers as class of PFAS**, it is critically important to provide, as first step, a workable approach to **grouping** of all substances necessary for the manufacture of fluoropolymers. As a second step, one needs to carefully examine each of the respective substances' hazard profile (non-polymers), exposure & risk **(RCR = risk characterisation ratio)** at the manufacturing, use and disposal phases. All PFAS used in the manufacturing of fluoropolymers are used in controlled industrial settings and show low to very low RCRs in the range of < 1 to 0.01 or even below 0.01. Independent of the low to very low RCRs it is important to note that exposure to PFAS used in polymerisation is very low.

This scientific thought paper constitutes the present state of scientific reflection on the grouping of all substances involved in the manufacturing of fluoropolymers, interpretation of legal obligations and options for a way forward under EU REACH Regulation. Significantly, based on a comprehensive fact-

[1] *According to ECHA*

checking and data-gathering exercise, it is important to draw a clear distinction between three groups of compounds:

GROUP A: **Fluoropolymers**

GROUP B: **Fluoromonomers used to manufacture Fluoropolymers**

GROUP C: **Fluorinated Polymerization aids used to manufacture Fluoropolymers**

Group A: Fluoropolymers

2) Grouping

In the polymeric PFAS category, one needs to distinguish between three distinct classes falling in the scope of the PFAS restriction:

1. Fluoropolymers (fluorinated carbon-only backbone)
2. Perfluoropolyether Polymers, PFPEs (fluorinated C and O backbone)
3. Side-chain fluorinated polymers (SCFP, non-fluorinated backbone with fluorinated sidechains)

Fluoropolymers are a class of PFAS. They appear mostly as solid in a granular or powder form but are also distributed as aqueous dispersions and films. Granulates are mainly used for moulding. Powders are used for paste extrusion (2^{nd} level in the value chain). The paste & mould are then used by 3^{rd} level value chain actors to manufacture final articles containing Fluoropolymers.

The three most common Fluoropolymers, PTFE, PVDF, and FEP, represent ~80 % of the total global fluoropolymer production.

3) Properties

While Fluoropolymers meet the broad structural definition of PFAS, they **present very different ecotoxicological, environmental fate and toxicological properties** when compared to other PFAS. For this reason, they should be considered separately from any regulatory initiative on PFAS.

The Fluoropolymer's **unique chemical property is their stability**; mechanical strength, inertness, thermal stability and resistance to chemical, biological and physical degradation are required. The bond between fluorine and carbon, C-F, is the strongest chemical bond in organic chemistry, characterized by its resistance to breaking when used, and are therefore, stable and durable.

From a **(eco-)toxicological standpoint**, Fluoropolymers do not pose a significant risk to human health or the environment in their intended use because of their unique characteristics. Fluoropolymers have thermal, chemical, photochemical, hydrolytic, oxidative, and biological stability. [2]:

[2] *Henry et al. A Critical Review of the Application of Polymer of Low Concern and Regulatory Criteria to Fluoropolymers in Integrated Environmental Assessment and Management — Volume 14, Number 3—pp. 316–334, 2018. http://dx.doi.org/10.1002/ieam.4035*

- **They are biologically stable and chemically inert** (in presence of virtually any chemical) and do not dissolve in water[3];
- **Fluoropolymers are practically insoluble in water and not subject to long-range transport**
-
- **Do *not* bioaccumulate (not B/vB)** as the molecules insoluble in water and octanol and are too big to enter cells[4].
- **Do *not* meet the criteria for being T (toxic)** as they are not classified to human health toxicology and ecotoxicology.
- **Do *not* meet the currently discussed criteria for mobile (M or vM)**.

From an **environmental fate standpoint**, this however translates into Fluoropolymers **meeting the criteria of very persistent (vP)** as defined by Annex XIII of the REACH Regulation[5], reason why they fall in scope of the upcoming PFAS restriction proposal. **Thus, any potential alternative will have to be persistent by definition to meet the same demanding technical requirements.**

4) Exposure

The Fluoropolymers are in conclusion of no concern regarding environmental fate, human health, and ecotoxicology. Thus, **exposure to the Fluoropolymers themselves does not pose a concern**. *Concerns may however be theoretically raised from residual monomers and polymerisation aids in the polymers.*

Studies show that the polymerisation is very complete resulting in high molecular weight polymers with very low to negligible content of oligomers (MW < 1000 Dalton) and unreacted monomers (typically below 1 ppm). In addition, in **leaching studies very low to negligible amounts of residual low molecular weight PFAS were detected** (Henry, 2018 and paper currently under preparation).

[3] https://fluoropolymers.plasticseurope.org/application/files/5116/3671/1909/Fluoropolymers_Safe_Hand_EN_2021.pdf

[4] *Idem and Henry et al. 2018.*

[5] *REACH Annex XIII, 1.1.1. A substance fulfils the persistence criterion (P) in any of the following situations: (a) the degradation half-life in marine water is higher than 60 days; (b) the degradation half-life in fresh or estuarine water is higher than 40 days; (c) the degradation half-life in marine sediment is higher than 180 days; (d) the degradation half-life in fresh or estuarine water sediment is higher than 120 days; (e) the degradation half-life in soil is higher than 120 days*

Just like monomers, while **potential residue of the polymerization aids like HFPO-DA (GenX compounds) cannot be excluded, estimated residual levels are low to negligible**. Exposure to end users and environment are therefore excluded or expected to be very low.

5) Degradation

Most, if not all Fluoropolymers, do not degrade. **PTFE** is a prominent example for Fluoropolymers. PTFE is chemically stable and inert and **degradation to smaller PFAS can be excluded based on the available data** (Henry, 2018).

A recent publication by leading FP manufacturers (not yet published) contains information on 14 additional Fluoropolymers (e.g., Polyvinylidene Fluoride – PVDF). All of them were shown to be stable to hydrolysis, light, oxidation, and biodegradation (aerobic and anaerobic). In addition, **most of the evaluated Fluoropolymers are thermally stable up to a minimum use temperature of 150°C.** Thermal decomposition starts at temperatures of 200°C and higher.

6) EXPOSURE: Fluoropolymers End-of-life & Disposal

If not reused or recycled, **Fluoropolymers typically end up in waste-to-energy incinerators (about 80% in Europe)**, of varying types, where they are thermally degraded into harmless substances together with other waste. At extreme temperatures of around 850-1100 °C, Fluoropolymers 'mineralise' (i.e., all C-F bonds break). This temperature range is also reflected in Article 50 of the Industrial Emissions Directive 2010/75/EU, where waste incineration must be designed (and operated) to ensure that flue gases reach the appropriate temperature. As a result, "*a good burnout of the combustion gases will be achieved"*[6].

The main decomposition products after incineration are HF and COF_2. COF_2 is rather unstable as it reacts readily with water and forms CO_2 and HF[7] (e.g., in stack scrubbers). Based on PTFE experience, RVIM concluded **that all fluorine-containing polymers thermally decompose to a very high degree** at similar temperatures.

As a next step, through various flue gas cleaning techniques, **emissions to the environment can be reduced by a factor of >99%.** Several studies pointed out that after incineration at temperatures of around 800 °C, no PFAS molecules could be detected, and it is therefore assumed that it fully degraded[8]. RVIM concluded that" the ***remaining PFASs are expected to be removed during the recovery of the carbon dioxide"***[9]. In a study by Alexandrov (2019) it was further concluded that no small molecular weight PFAS were created during incineration and that municipal incineration of PTFE using best available technologies (BAT) is not a significant source of PFAS and should be considered an acceptable form of waste treatment.

---

[6] *RIVM, Per- and polyfluorinated substances in waste incinerator flue gases, 2021.*

[7] *RIVM, Per- and polyfluorinated substances in waste incinerator flue gases, 2021.*

[8] *RIVM, Per- and polyfluorinated substances in waste incinerator flue gases, 2021.*

[9] *RIVM, Per- and polyfluorinated substances in waste incinerator flue gases, 2021.*

To a smaller extent, **fluoropolymers may be disposed in a landfill**. Fluoropolymers (e.g., PTFE) are stable and do not degrade under environmental relevant conditions. In addition, landfills in Europe are usually sealed of the environment with a HDPE liner, reducing any potential environmental exposure even further.

7) Polymers of Low Concern (PLC) and Polymers requiring registration (PRR)

Widely considered to be of low toxicological concern, Fluoropolymers meet **the polymer hazard assessment criteria to be considered polymers of low concern (PLC)** (Henry, 2018 and unpublished review). As per latest Draft EU PLC criteria discussed at the 3 December 2021 REACH Caracal meeting, **Fluoropolymers meet all PLC criteria <u>except for the elemental limitation criteria</u>[10].** End of 2021 the REACH Caracal seems to have largely agreed that only those fluoropolymers and perfluorinated polymers degrading into 'products of concern' should be exempt from PLC classification. In addition, several Member States flagged concerns that data on environmental fate are not available for many fluoropolymers.

Nevertheless, due to very broadly defined elemental limitation criteria most fluoropolymers are likely to be considered non-PLC, despite their overall very low risk profile.

<u>The following can therefore be concluded on GROUP A:</u>

- **Fluoropolymers are distinctly different from other polymeric and nonpolymeric PFAS and should be separated from them for hazard assessment or upcoming PFAS restriction. The same reasoning applies to chemically similar perfluoropolyethers**
- **Fluoropolymers are neither bio accumulative (B) nor toxic (T) nor mobile (M).**
- **They cannot accumulate in living organisms due to their high molecular weight**
- **Fluoropolymers are durable & resistant by nature, hence meeting REACH Annex XII persistency (P) criterion.**
- **They meet the OECD, and most of EU draft criteria of low concern (PLCs).**
- **Negligible levels of monomers, oligomers are expected to be present in Fluoropolymers, likely not to exceed 1 ppm (TBC).**
- **Fluoropolymers don't degrade under environmental conditions or in landfills, including into 'products of concern'**
- **Fluoropolymers thermally decompose to a very high degree >99% in waste-to energy incinerators, as confirmed by the Dutch RIVM.**

[10] *In addition to carbon, most Fluoropolymers do not contain hydrogen, nitrogen, oxygen, silicon or sulphur*

Group B: Fluoromonomers

1) Properties

Monomers[11] are the backbone of the European fluoropolymers production. Monomers meeting the PFAS definition are considered to be toxic. Examples include hexafluoropropene (HFP) or tetrafluoroethylene (TFE).

During polymerization, chemical properties or reactivity of the monomer get lost, resulting in much stabler, non-toxic, non-mobile, non-bioaccumulative polymers. The polymerisation reaction is a very complete reaction resulting in very high molecular Fluoropolymers with low to negligible residual monomer and oligomer content.

2) Usage as intermediates & emissions at manufacturing stage

All monomers used in the manufactures of fluoropolymers meet REACH criteria for intermediates. They are intermediates[12] by technical function, as they are transformed into a new substance during synthesis, namely a polymer (or in our case, a fluoropolymer).

From a legal standpoint, to be considered as an **intermediate**, a substance must fulfil three cumulative conditions: (i) the intended purpose of the substance consists in transforming that substance into another different substance; (ii) the transformation needs to take place by synthesis; (iii) the use of the substance remains confined to a controlled environment, which may be either the equipment within which synthesis takes place, or the site in which the manufacturing and synthesis takes place or to which that substance is transported[13].

The REACH regulation distinguishes two types of intermediates, with resulting REACH Annex XVII implications:

- **On-site isolated intermediates** are substances used for chemical processing to be transformed into another substance on one specific "site". These are unconditionally exempt from REACH restriction (REACH art. 68(1)).

- **Transported isolated intermediates** are substances that are first isolated before being "used for" chemical processing to be transformed into another substance and then transported between sites. Transported isolated intermediates are exempt from REACH restriction only if they are used under strictly controlled conditions, *i.e.* if all of the conditions set out in Article

[11] *Monomers are defined as a substance which can form covalent bonds with a sequence of additional like or unlike molecules under the conditions of the relevant polymer-forming reaction used for the particular process*

[12] *For monomers that are used as on-site isolated intermediates or transported isolated intermediates, Articles 17 and 18 (registration) shall not apply*

[13] *Regulation (EC) N° 1907/2006 of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), OJ L 396, 30.12.2006, p. 1*

18(4) of REACH[14] are respected. In that case, they are treated the same as on-site isolated intermediates.

ECHA RAC **explicitly recognized** the exemption of transported isolated intermediates manufactured/used under strictly controlled condition from the scope of REACH restriction **in two dossiers**:

- **Restriction on the manufacturing and placing on the market of PFOA, its salts and any related substances.** More precisely, the Committee stated that the restriction would not apply to "*a substance that is to be used, or is used as a transported isolated intermediate, provided that the conditions in points (a) to (f) of Article 18(4) of this Regulation are met*".[15] The Commission, ultimately, endorsed the RAC position in its Regulation[16].
- **Restriction on the manufacturing and placing on the market of PFHxA, its salts and related substances**[17]. Both BAUA (Dossier Submitter) and RAC agreed to include a derogation on the use of the substance as this specific transported isolated intermediate, provided that the conditions set out in Article 18(4)(a) to (f) of REACH are met. That derogation was based on the estimated very low release of PFHxA and its related substances.

In conclusion, since monomers used to manufacture Fluoropolymers are used as intermediates, only negligible emissions of monomers in the environment during manufacture are, therefore, expected.

The following can therefore be concluded on GROUP B:

- **All monomers used to manufacture Fluoropolymers are used as intermediates: on site isolated or transported isolated ones used under strictly controlled conditions.**
- **Either type of intermediate is exempt from REACH restriction or treated equivalently.**
- **The above legal provision was recognized by ECHA RAC in at least two REACH restriction cases involving fluorinated chemicals.**
- **Negligible levels of monomers are expected to be present in Fluoropolymers, likely not to exceed 1 ppm. (TBC)**

[14] *Past precedents: restrictions on PFOA, its salts and related substances, as well as PFHxA, its salts and related Substance. In the restriction proposal for PFHxA, transported intermediates were exempted if used under strictly controlled conditions.*

[15] *Commission Regulation (EU) 2017/1000 of 13 June 2017 amending Annex XVII to Regulation (EC) No 1907/2006 of the European Parliament and of the Council concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) as regards perfluorooctanoic acid (PFOA), its salts and PFOA-related substances, OJ L 150, 14.6.2017, p. 14–18. As PFOA, its salts and any related substance are now included in Annex I to Regulation (EU) 2019/1021, the PFOA entry has been removed from Annex XVII to REACH*

[16] *See RAC Opinion, available at https://echa.europa.eu/documents/10162/d825ec25-8be6-80cc-ed05-95346dfa008e*

[17] *See Annex XIV dossier, available at: https://echa.europa.eu/documents/10162/c4e04484-c989-733d-33ed-0f023e2a200e*

Group C – Fluorinated Polymerization aids

1. Identity

Another small, yet vital subgroup of compounds used in the manufacturing of Fluoropolymers are substances called **polymerization aids.** Their primally function is to assist the polymerization of individual monomer units. As they are only part of the technological process, but not part of the chemical function, the intention is not having them consumed in the process. Therefore, once they have fulfilled their function, they are extracted from the produced FP and can be reused or recycled. High-grade (thus with higher molecular weight and lower bioavailability) Fluoropolymers such as PTFE, depend in their production on Polymerization aids.

Polymerization aids are specifically required and are essential to produce high-grade Fluoropolymers.

One historically used polymerisation aid is PFOA. Due to its bioaccumulation potential, the use of PFOA in Europe was ceased in 2012. New polymerisation aids with a more favourable toxicological profile, such as HFPO-DA (GenX compounds), came to replace PFOA. **HFPO-DA is registered by The Chemours Company under REACH in a tonnage band of 10-100 t/a**. For 2022 a total tonnage of 50 t/a was assessed in the Chemical Safety Report.

2. Properties

Most of polymerization aid compounds are toxic (T), persistent (P), mobile (M) but *not* bio-accumulative (B). HFPO-DA – one of the replacement polymerization aid compounds – is however ***not* classified for human health toxicity** (T). Despite not classified as CMR, HFPO-DA was nevertheless included, on 27 June 2019, in the REACH Candidate list on ground of 'equivalent concern' due to "its very high persistence, mobility in water, potential for long-range transport", among others.

3. EXPOSURE: Fluoropolymers Production Phase

Occupational exposure

Exposure to industrial workers and the general population to polymerization aids is regularly controlled. To this effect, all relevant engineering and administrative controls are observed[18]. This includes additional measures such as workers wearing PPE, spill management and emergency response. This results in low to negligible exposure as documented in the Chemical Safety Reports (CSRs)submitted to ECHA as part of the REACH registration dossiers.

The results are documented through the Risk Characterization Ratios (RCRs), as advised by ECHA and are already clearly under 0.1 for human health and 0.01 for the environment. As a reminder, if the RCR is under 1, risks are adequately controlled according to ECHA[19].

[18] https://echa.europa.eu/documents/10162/17224/information_requirements_part_e_en.pdf/1da6cadd-895a-46f0-884b-00307c0438fd

[19] *ECHA, Guidance on Information Requirements and Chemical Safety Assessment. Part E: Risk Characterisation, 2016.*

$$\text{RCR} = \frac{\text{Exposure}}{\text{DNEL}^{20}}$$

Chemours investments in the operation health and safety at Dordrecht have been acknowledged by authorities such as the Dutch National Institute for Public Health and Environment who concluded that there is "*no health risk is expected for people living in the vicinity of the Chemours Dordrecht plant due to exposure*"[21]. Chemours is investing in new technologies and techniques to lower the exposure even further.

In conclusion, **no or negligible occupational exposure** from polymerisation aids is expected, as proven for HPFO-DA by a chemical operators' blood tests at Chemours Dordrecht Works in the Netherlands.

3. *Environmental Exposure*

For technical reasons, **some direct or diffuse emissions of processing aids into the environment (air and water), cannot however be excluded**. The risks of direct and indirect emissions can be reduced and have largely improved over the recent decades.

As part of its **Corporate Responsibility Commitment (CRC) targets**, Chemours implemented wide measures to address emission of polymerization aids to air and water:

- Air and water process emissions of fluorinated organic chemicals are to be reduced by 99% or more compared to the 2018 emission levels by 2030.
- By 2024, the company's Dordrecht Works (NL) plant will have achieved 80% of this goal.
- The Belgian blending plant in Mechelen has already achieved this target for emissions to wastewater.

These achievements are also reflected by the updated **national permits**, which are mostly at the limits of what is technically feasible through BAT. At Dordrecht Works in the Netherlands, where the majority of Chemours' processing aids are used, **there are permitted level of emissions of GenX compounds. The actual emissions fluctuate depending on year and production load but stay within the permitted levels.**

- **In the air:** permitted 450 kg/year, released around 30 kgs in 2021 vs 8000 kgs in 2013.
- **In water:** permitted 7 kg/year, released significantly less (1.2 kg in 2020)

[20] *DNEL = Derived no-effect level*

[21] *National Institute for Public Health and the Environment, Ministry of Health, Welfare and Sport, Evaluation of substances used in the GenX technology by Chemours, Dordrecht, 2016.*

<u>The following can therefore be concluded on GROUP C:</u>

- **Polymerization aids play a vital role during polymerization process for high-grade Fluoropolymers. <u>No high-grade Fluoropolymers are possible without polymerization aids</u>.**
- **Only minor volumes are used during production phase, extracted at end of the phase & reused (10-100 t/a).**
- **Occupational exposure to polymerization aids is proven to be negligible at Chemours Dordrecht works.**
- **Minor emissions are expected into the air and water, yet in line with the industrial permits. Chemours is nevertheless working hard to reduce the emissions even further as part of its CRC targets by 2030.**
- **Negligible residues of polymerization aid are expected to be present in Fluoropolymers. The concentrations are estimated to be at the level of 1 ppm. (TBC)**
- **Waste-to-energy incinerators thermally decompose minor residues of polymerization aids to a very high degree >99%, as confirmed by the Dutch RIVM.**

Conclusion & Considerations

In conclusion, the **'ABC' approach** provides a structured, logical approach to grouping the various compounds which are part of the fluoropolymers value chain. Having carefully examined each of the groups, several conclusions could be made.

Firstly, Fluoropolymers (GROUP A) are not substances of concern as part of the upcoming PFAS restriction process due to their overall low hazard profile. They lack toxic, mobile, bio accumulative and bioavailability potential. Even if containing potential negligible residues of monomers and polymerization aids, they do not degrade under environmental conditions such as landfills. They can be thermally destroyed in high energy incinerators.

Fluoropolymers' persistency (= stability and durability) is their key assets Reason why they are widely used in critical applications where durability is the main technical requirements. However, as explained above, this does not weaken the argument around the safety of fluoropolymers towards humans and the environment given their stability and low-degradation potential.

Reason why Fluoropolymers should be excluded from the upcoming PFAS restriction.

Fluoromonomers (GROUP B) and fluorinated polymerisation aids (GROUP C) require however a more careful examination.

In terms of industrial emissions, many of the monomers are hazardous, unstable substances. Yet these used exclusively either as on-site intermediates (i) or transported isolated intermediates under strictly controlled conditions (ii). Hence, they should be out of scope of the upcoming PFAS restriction, as per REACH provisions confirmed in two REACH restrictions dossiers by ECHA RAC and the European Commission. Polymerization aids are, however, used in small annual volumes, and Chemours is working hard to reduce small emissions in the water & air, in line and beyond the industrial permits.

As for residues in the final product, negligible level of compounds of either group cannot be excluded in Fluoropolymers, but the concentrations pose a negligible risk to human health & environment, given the stability of Fluoropolymers during use and at end-of-life phase. No detectable amounts of by-products are traced when Fluoropolymers are incinerated, as confirmed by RIVM.

Polymerisation aids are vital in the manufacturing of high-grade Fluoropolymers. No high-grade polymers are possible without polymerization aids.

Substances from these Groups (B &C) should therefore be exempted from restriction when used in closed systems and comply with stringent technical measures to control emissions & industrial emissions permits.