

PFAS emissions during manufacturing of fluoropolymers (PTFE)

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Case study – PTFE emulsion polymerization

PFAS are used as raw materials for following 2 functions: Intermediates & Processing aids

Monomer (Tetrafluoroethylene)

- Intermediate substance that gets converted to PTFE. Unreacted TFE is recovered and reused in a continuous closed loop recycling process
- TFE according to OECD PFAS definition is not a PFAS
- Any accidental release of TFE leads to decomposition yielding carbonyl fluoride (COF₂) that is further hydrolyzed in the presence of atmospheric water to form hydrogen fluoride (HF) and carbon dioxide (CO₂)*
- Recycling is also important for manufacturers to improve the production-cost efficiency

Modifier (Perfluoropropylvinyl Ether, PPVE)

- PTFE is modified to impart special properties - reduced deformation under load, improved flexibility, lower porosity, lower permeability, good electrical and mechanical properties and better processing
- 25% of total commercially produced PTFE is chemically modified during polymerization; 0.05-0.1% of PPVE is incorporated in the PTFE polymer matrix; Approximately 1.5 times of PPVE is added to the reactor
- PPVE requirements for PTFE: $0.25 * 25000 \text{ tons} * 0.001 * 1.5 = 9.375 \text{ tons per annum}$
- Around 70% is recovered for reuse and remaining is captured and destroyed using abatement

* ECETOC JACC No. 42-Tetrafluoroethylene (CAS No. 116-14-3)

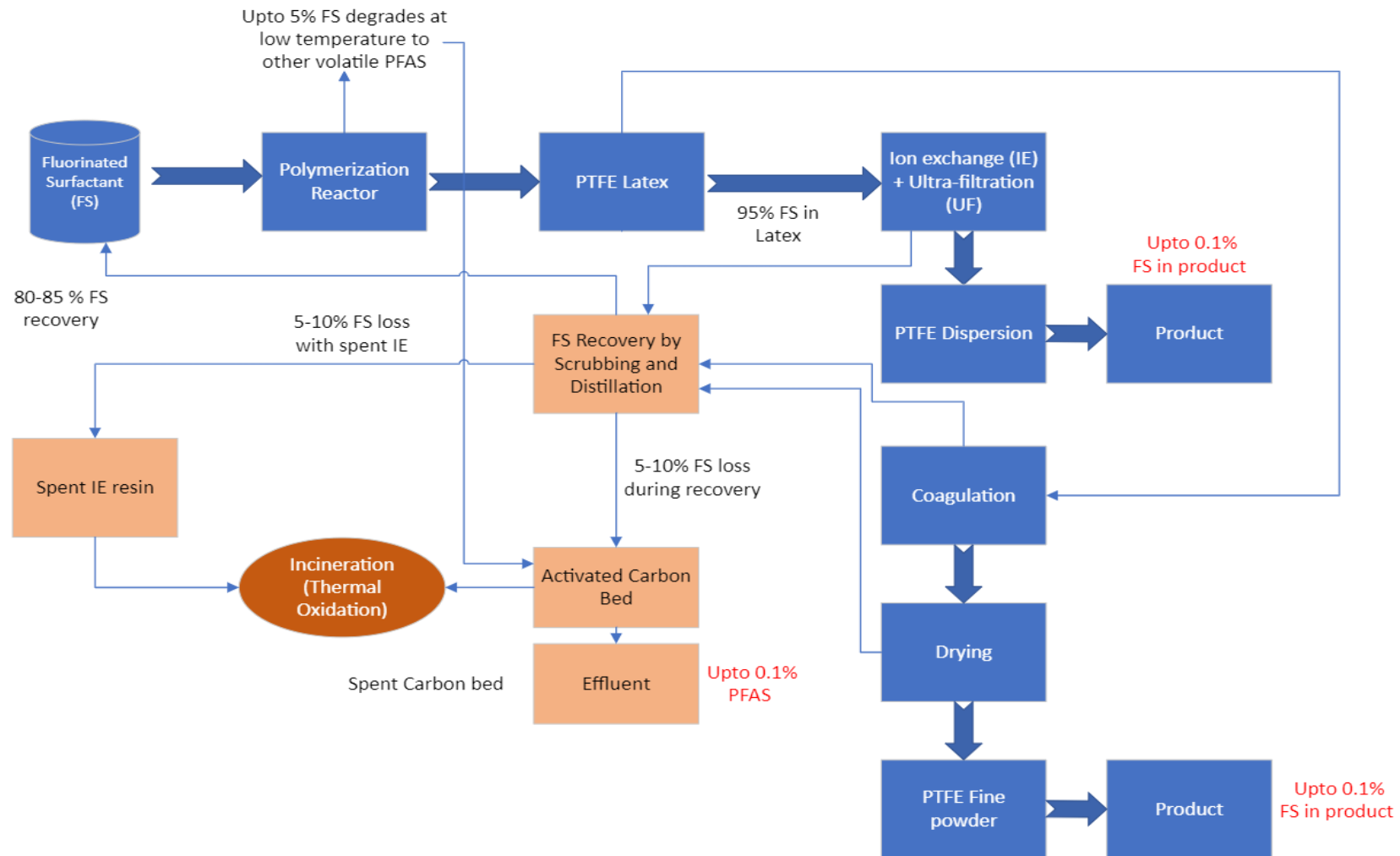
Case study – PTFE emulsion polymerization

As processing aids / surfactants

- Fluorosurfactants (FS) do not get consumed during polymerization
- Hundreds of tons of PFAS are intentionally used as polymerization aids leading to serious environmental pollution
 - FS usage per ton = 3-10 kgs: For 25000 tons of fluoropolymers produced by emulsion polymerization: 75-250 tons
- Manufacturing, Packaging, Storage and Transportation of FS are also contributing to PFAS emissions
 - Raw materials to manufacture FS are also PFAS
- FS break down to low temperature volatile PFAS that are difficult to abate
- FS can be partially recovered and reused: GFL has been recycling 80-85 % of FS for reuse
- Most fluoropolymers can now be produced without the use of FS
- Fluoropolymers should be exempted; instead, regulate fluorinated polymerization aids

PTFE emulsion polymerization process chart

Fluorinated Surfactant – Mass balance in PTFE aqueous dispersion / Fine powder



Development of Non-Fluorinated Polymerization Aid (NFPA)

Gujarat Fluorochemicals:

- GFL has developed NFPA technology to manufacture PTFE, PVDF, FKM, PFA
- GFL commits to completely stop the intentional use of PFAS as polymerization aids from 2024*

Solvay:

- Working towards the objective of manufacturing nearly 100% of fluoropolymers without the use of fluorosurfactants in Spinetta Marengo, Italy by 2026**
- Goal is to phase out the use of fluorosurfactants globally

Arkema:

- Voluntarily committed to manufacture its fluorinated polymers in Pierre-Bénite without the use of fluorosurfactants by the end of 2024, as well as its other production sites around the world***

Honeywell:

- Voluntarily committed to completely stop using fluorosurfactants in their manufacturing processes

* <https://www.gfl.co.in/upload/pages/a6132d2292fc0ad3a9a0751dad818450.pdf>

** <https://www.solvay.com/en/innovation/science-solutions/pfas>

*** <https://www.arkema.com/global/en/media/newslist/news/global/corporate/2023/20230221-arkema-position-on-european-proposal-to-restrict-pfas/>

Non-Fluorinated Polymerization Aid (NFPA)

- The NFPA used by GFL is an organic compound based on sulfonated hydrocarbon chemistry
- The specific NFPA substance is non-persistent, non-bioaccumulative, non-toxic and non-mobile
- It is EU REACH registered and is not listed under Substance of very High Concern (SvHC) and Toxic Release Inventory (TRI)
- NFPA based fluoropolymers exhibit equal or even better properties/specifications
- NFPA can be used to manufacture
 - High molecular weight fluoropolymers
 - Modified fluoropolymers
 - Copolymers and terpolymers
- A slight change in color may be noticed which is purely an aesthetic parameter and does not impact the performance

PFAS as byproducts using NFPA technology

- Compatibility in terms of non-reactivity of hydrocarbon surfactants with monomers is critical to prevent formation of PFAS byproducts
- EU has proposed PFAS concentration limits of 250 ppb as sum of targeted PFAS analysis
 - Fluoropolymers produced using GFL's NFPA have negligible PFASs measured using targeted analysis (LC-MS/MS)
 - There is no method or concentration limits defined for non-targeted PFAS analysis. GFL is confident to meet such requirements as and when they are notified
- By shifting to NFPA, annual EU PFAS exposure can be reduced to a maximum of
 $250 \text{ ppb} * 50,000 \text{ tons of fluoropolymers} = 12.5 \text{ kgs of PFAS}$

Thank you