Fluoropolymers
Product Group of Plastics Europe

GUIDE FOR THE SAFE HANDLING OF FLUOROPOLYMER RESINS –

PTFE, ETFE, FEP, PFA, PVDF and ECTFE.

8 July 2025

FLUOROPOLYMERS PRODUCT GROUP OF PLASTICS EUROPE

Acknowledgement

This guide has been developed by the members of the Fluoropolymers Products Group (FPG) of Plastics Europe, the industry association representing European polymer producers. It operates in accordance with Plastics Europe governance, including Competition Compliance Rules. Plastics Europe covers the EU, plus the UK, Norway, Turkey and Switzerland.

Disclaimer

The information presented in this Guide is provided free of charge and submitted in good faith and is correct to the best of the Fluoropolymers Products Group present knowledge.

Following the Guide does not guarantee compliance with any regulation nor safe operation of any processing facilities. In particular, this Guide does not contain information for what end-uses materials can be used. Users are cautioned that the information upon which this guide is based is subject to change that may invalidate any or all of the comments contained herein.

The Fluoropolymers Products Group will be unable to accept responsibility or claims from any party, related to information presented in this brochure. Freedom under patents, copyright and registered designs cannot be assumed.

Table of Contents

Introduction

This update of the Safe Handling Guide covers the fluoropolymers PTFE, ETFE, FEP, PFA, PVDF and ECTFE. A further update will be made in due course to address fluoroelastomers and other specialty fluoropolymer substances.

The fluoropolymer resins covered by this guide are produced and sold by various manufacturers worldwide. Today, these fluoropolymers find application across a wide spectrum of technologies, industrial operations and daily uses, spanning from aviation and transportation, including electrical vehicles, hydrogen and chemical processing industries, architectural coatings, batteries, medical devices, energy generation, technical clothing and beyond. They are durable, chemically inert and mechanically strong in harsh conditions. This unique combination of characteristics of fluoropolymers makes them a critical material for a broad range of industries and sectors, playing a diverse and crucial role for society. Beyond their socio-economic value for European industry, their unique stability means that they are low-risk polymers for human health and the environment. The vast majority of fluoropolymers do not display any characteristics of high hazard polymers, which has been demonstrated by data in regulatory submissions and peer-reviewed literature [Henry, *et al*., 2018; Korzeniowski, *et al.,* 2023].

Due to the general inertness of the fluoropolymer resins, they are not classified as hazardous under the European Regulation (EC) No 1272/2008 on classification, labelling and packaging of substances and mixtures. Controlled incineration of fluoropolymers has been demonstrated to produce negligible levels of PFAS of concern evidencing mineralisation of fluoropolymers [Aleksandrov, *et al*., 2019; Gehrmann, *et al.,* 2024]. However, as with any natural or synthetic material, overheating or uncontrolled combustion of these resins can produce potentially toxic effluents. Additives used with fluoropolymers may also present certain hazards.

This guide provides information on safe handling during the processing of the materials identified in Chapter I. Although compounded fluoropolymers or resins in the form of micro-powders or lubricant powders will not be dealt with in detail, due to the variety and number of formulations, some general comments are provided. This guide includes additional information to address potential environmental risks, in addition to potential impacts for human health, that may arise from the processing of fluoropolymers and air and water treatment technologies to minimise this risk.

Chapter I

Fluoropolymer Resin Types and Properties

1. Resin types

The main resin types covered by this document are shown below. Some companies may offer other specialty fluoropolymers which are not included in this update of the guide. As mentioned in the Introduction, a further update of the guide will be made as a second step to cover fluoroelastomers and other specialty fluoropolymers. Reference should be made to the supplier for specific information on the handling of these specialty polymers.

PTFE:

PTFE is a polymer consisting of recurring tetrafluoroethylene monomer units whose formula is $[CF_2\text{-}CF_2]_n$. It can be modified with a small percentage of other comonomers. PTFE does not melt to form a liquid and cannot be melt extruded. On heating, the virgin resin forms a clear coalescent gel at 330°C+/-15°C. Once processed, the gel point (often referred to as the melting point) is 10°C lower than that of the virgin resin. PTFE is sold as a granular powder, an aqueous dispersion, fine powder (coagulated dispersion) and micropowder. Each is processed in a different manner.

FEP:

FEP fluorocarbon resin is a copolymer of tetrafluoroethylene and hexafluoropropylene with the formula $[(CF(CF_3)\text{-}CF_2)_x(CF_2\text{-}CF_2)_y]_n$. It can be modified with a small percentage of other comonomers. It has a melting point range of 250°-270°C and is melt processible. It is supplied in the form of translucent pellets, powder or as an aqueous dispersion.

PFA:

PFA fluorocarbon resin is generally a copolymer of tetrafluoroethylene and a perfluorinated vinyl ether having the formula $[\{CF(OR_f)\text{-}CF_2\}x(CF_2\text{-}CF_2)_y]_n$ where OR_f represents a perfluoroalkoxy group. PFA melts at 280°C minimum and is melt processible. Some grades are chemically stabilised. It is available in the form of translucent pellets, powder, and as an aqueous dispersion.

ETFE:

ETFE is a copolymer consisting mainly of ethylene and tetrafluoroethylene, having the formula $[(CF_2\text{-}CF_2)_x(CH_2\text{-}CH_2)_y]_n$ often modified with a small percentage of a third monomer. Depending on the molecular structure and grade the melting range is 180°C-280°C. ETFE is melt processible and is supplied in the form of pellets and powders

ECTFE:

ECTFE is a copolymer of ethylene and chlorotrifluoroethylene having the formula $[(CH_2\text{-}CH_2)_x(CFCl\text{-}CF_2)_y]_n$. It is often modified with a small percentage of a third monomer. Depending on the molecular structure, the melting range is 190°C-240°C. It is available in the form of translucent pellets and powder.

PVDF:

PVDF is a homopolymer of vinylidene fluoride having the formula $[CH_2\text{-}CF_2]_n$ There are several copolymers e.g. a copolymer of vinylidene fluoride and hexafluoropropylene having the formula $[\{CF(CF_3)\text{-}(CF_2\}_x(CH_2\text{-}CF_2)_y]_n$. PVDF homopolymers melt at 160°C-175°C, copolymers from 100°C-180°C, are melt processible, and are supplied in the form of powder, pellets, and aqueous dispersions.

The suppliers of the above materials and their addresses are listed in Appendix A. Many different grades or classes of each type of fluoropolymer resin are available. Individual suppliers should be contacted for specific product information.

2. Thermal properties

Although fluoropolymers are amongst the most thermally stable polymers known, they will start to decompose slowly when heated to elevated temperatures. Metal powders, particularly bronze and polymeric fillers like polyimide will reduce thermal stability.

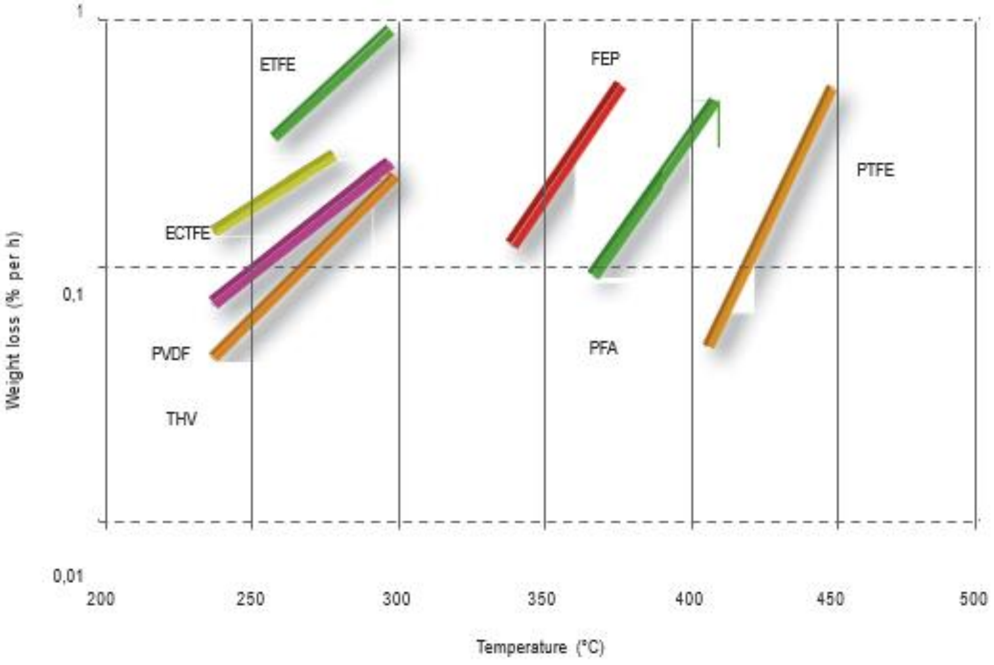
Although published literature is sometimes contradictory, especially around the decomposition temperature, significant decomposition occurs only above the recommended continuous service temperature for the polymer in question. The quantity of effluent evolved remains small until temperatures above the normal processing temperature for the polymer are reached.

Rates of thermal decomposition for various fluoropolymers have been determined using a thermogravimetric analyser. Samples were heated in dry air flowing at a rate of 30 ml/minute. The temperature was increased at 20°C/minute from room temperature to the test temperature. The samples were then held at constant temperature for one hour and the weight loss during the hour was measured (isothermal weight loss).

The rate of weight loss was determined for each polymer at a series of three constant temperatures (four for PVDF). The test temperatures used were different for each fluoropolymer and were chosen according to the increasing thermal stability of the polymer.

The results are shown in figure 1

Figure 1: Typical weight loss of Fluoropolymers heated in air



It should be remembered that within any one polymer type, different grades will have different thermal stabilities according to properties such as molecular weight. The data presented in Figure 1 gives a general indication of the relative thermal stabilities of each polymer. Reference should be made to the polymer supplier if precise information is required on an individual polymer grade. Typical melting points, continuous use service temperatures and processing temperatures for the different fluoropolymers are given in Table 1.

Table 1: Typical melting points, continuous use and processing temperatures of Fluoropolymers

Polymer	Typical melting point (°C)	Typical maximum continuous use service temperature (°C)	Typical processing temperature (°C)*
PTFE	330-340**	260	380
FEP	250-270	205	360
PFA	280	225-260	360-380
ETFE	180-280	150	310
ECTFE	190-240	150	280
PVDF	160 – 175 (homopolymers) 100 – 180 (copolymers)	140	230

* Note that the processing temperatures in this table are actual polymer temperatures, not oven or equipment temperatures which may be significantly higher.

** Gel point.

Chapter II

Potential Health and Environmental Impacts

1. Polymer general toxicology

Fluoropolymer resins are known for their high chemical stability and low reactivity. These materials are of low toxicity, demonstrating little if any toxicological activity [Hintzer, *et al.*, 2014]. Where toxicological studies have been conducted on fluoropolymers, no findings of significance for human health hazard assessment have been reported [Radulovic and Wojcinski, 2014; Radulovic and Wojcinski, 2024].

Fluoropolymers have not been known to cause skin sensitivity or irritation in humans [Radulovic and Wojcinski, 2014; Johnson, *et al*, 2023]. Many resins are formulated with additives such as fillers, pigments or surfactants, to provide favourable processing, or other characteristics. These additives may present other hazards in the use of the resins. Some of the additives may have regulatory occupational exposure standards. The safe handling information provided by the resin suppliers should be consulted for specific health information on the additives used in their products.

2. TFE monomer toxicology- effect on fluoropolymer safety in use

Repeated exposure by inhalation of rats or mice to tetrafluoroethylene (TFE) for their lifetime led to increases in the incidence various types of tumours in kidney, liver and the haematopoietic system [National Research Council, 2015]. Studies comparing the metabolism of TFE in humans and animals, suggest that the risk for developing some of these tumours is lower for humans than for rats and mice [European Centre for Ecotoxicology and Toxicology of Chemicals, 2003]. A multicentre epidemiology study, involving cohorts from major producers of TFE, has investigated the carcinogenic impact of exposure of TFE in humans. No statistically significant increases in mortality were observed for any disease studied, including cancer [Consonni, *et al.*, 2013].

TFE is used as a building block in the manufacture of solid plastic materials such as PTFE and other fluoropolymers, which are normally sold as powders, granules or aqueous dispersions to specialist processors who convert these polymers into finished articles.

Tests on solid fluoropolymers sold by PTFE manufacturers to processors have failed to detect TFE.

Aqueous dispersions may contain traces (less than 1 ppm) of residual TFE. High temperature processing of fluoropolymers may generate low levels of TFE. However effective ventilation, which is currently required to prevent acute health problems such as polymer fume fever or exposure to hydrogen fluoride, is sufficient to prevent any potential exposure to TFE. Analysis of fabricated articles shows no detectable TFE; this applies to articles made from both solid fluoropolymers and aqueous dispersions processed under recommended conditions.

3. Health and environmental hazards during hot processing and toxicity of decomposition products

During the hot processing of fluoropolymer resins, some fumes will be generated, even at the temperatures reached during normal hot processing, and it is necessary to assume that the resulting fumes will present a potential health hazard. It is essential that adequate ventilation is provided to prevent exposure to the fumes in the workplace. (See Chapter IV). The potential consequence of overexposure to the fumes from fluoropolymers decomposing under these conditions is “polymer fume fever”. This is a temporary, influenza-like illness with fever, chills and sometimes a cough which lasts approximately 24 to 48 hours. The onset of symptoms may not be apparent for up to 24 hours. Acute exposure to higher levels of fumes may cause more serious symptoms such as breathing difficulties. As a precaution, any person thought to be suffering from polymer fume fever or who has been exposed to decomposition products should seek medical attention.

The illness is also associated with exposure to the decomposition products produced by smoking tobacco products, such as cigarettes, which have become contaminated by fluoropolymer resins, even by trace quantities. It is essential that smoking and tobacco products be banned in work areas where fluoropolymer resins are handled.

The four main types of product formed in the decomposition of fluoropolymers are fluoroalkenes, hydrogen fluoride, oxidation products and ultrafine fluoropolymer particulates.

The type of decomposition product depends on the conditions under which heating occurs. Temperature, availability of oxygen, the physical form of the article, and the residence time at elevated temperatures are among the factors that determine the ultimate nature of the decomposition products. In the case of PTFE there are many studies in the published literature, and these report a wide variety of results for the reasons outlined above. NIOSH suggested in its 1977 Criteria Document that the TFE monomer is the principle gaseous product at temperatures that just produce softening or melting of the polymer, probably near the gel point of a typical polymer 330°C. The TFE may be residual monomer that is trapped in the resin particles or evolved as the resin structure changes with temperature. As the temperature increases to around 450°C in the presence of air, carbonyl fluoride and hydrogen fluoride become the main products. Also, some carbon monoxide may be formed. Carbonyl fluoride hydrolyses rapidly in the presence of moist air to hydrogen fluoride and carbon dioxide. Small amounts of hexafluoropropylene may also be found at these temperatures. The highly toxic perfluoroisobutylene (PFIB) has been detected as a minor product at 475°C [Waritz, 1975]. When the temperature reaches 850°C, tetrafluoromethane begins to form [Williams, *et al.*, 1987].

Decomposition products tend to form at lower temperatures to a degree which depends on the type and amount of comonomer in the fluoropolymer. For example, studies indicate the formation of PFIB at temperatures from 360°C for some types of FEP.

Certain compounding ingredients may pose specific hazards, and manufacturers' or suppliers' recommendations should be followed.

Health and Environmental hazards of the most significant decomposition products are as follows (more detailed health, ecotoxicological, and environmental fate information is available via following link www.echa.eu):

HF (Hydrogen fluoride):

The odour threshold of hydrogen fluoride is significantly less than the indicative occupational exposure limit value (IOELV) (1.8 ppm v/v (8-hour TWA) – 2000/39/EC). Inhalation of hydrogen fluoride at higher concentrations will give rise to symptoms of choking, coughing and severe eye, nose and throat irritation. In severe cases, and possibly following a symptomless period, fever, chills, difficulty in breathing, cyanosis, and pulmonary oedema may develop, which may lead to death. Acute overexposure to hydrogen fluoride can also result in injury to the liver and kidneys.

Environmental exposure to hydrogen fluoride is expected to be minimal as it does not persist. Once released into the environment HF is unlikely to remain in its original form for very long.

In air, water and soil hydrogen fluoride is transformed to a variety of other fluorine compounds.

Special care should be taken with any liquid formed during processing as it may contain hydrogen fluoride which can be rapidly absorbed into the body causing severe systemic effects, some of which may be delayed up to 48 hours. Immediate treatment is therefore essential. Calcium gluconate gel (2.5%), antidote for hydrogen fluoride, should be applied to the skin.

Further information on hydrogen fluoride can be found via following link:
https://echa.europa.eu/brief-profile/-/briefprofile/100.028.759

Carbonyl fluoride:

Effects following inhalation, or skin or eye contact with carbonyl fluoride may initially include: skin irritation with discomfort or rash; eye corrosion with corneal or conjunctival ulceration; irritation of the upper respiratory passages; or temporary lung irritation effects with cough, discomfort, difficulty in breathing, or shortness of breath. Respiratory symptoms may be delayed for several hours. Some European countries apply an occupational exposure standard of 2 ppm v/v (8-hour TWA).

Carbonyl fluoride is expected to hydrolyse in water and in humid air into carbon dioxide and hydrogen fluoride. Small quantities of hydrogen fluoride will be neutralised by the natural alkalinity in aquatic systems. Larger quantities may lower the pH for extended periods of time. Fluorides are not expected to bioaccumulate.

Further information on carbonyl fluoride can be found via following link:
https://echa.europa.eu/brief-profile/-/briefprofile/100.005.941

Carbon monoxide:

An odourless flammable gas which reduces the oxygen carrying capacity of the blood, resulting in a decreased capacity for exertion, increased load on the heart and with severe exposure, unconsciousness and death. It is classified as 1A toxic for reproduction (may damage fertility and the unborn child) and causes damage to organs through prolonged or repeated exposure. Commission Directive (EU) 2017/164 specifies IOELV as 20 ppm v/v (8-hour TWA).

Carbon monoxide is not classified as hazardous to the environment. While not a directly greenhouse gas, it can react with other air pollutants to form ground-level ozone and can lead to formation of carbon dioxide.

Further information on carbon monoxide can be found via following link:
https://echa.europa.eu/brief-profile/-/briefprofile/100.010.118

HFP (hexafluoropropylene):

HFP is a colourless, odourless gas that is very poorly soluble in water. HFP is not considered to be genotoxic however it is classified as category 2 carcinogen. Repeated or prolonged inhalation exposure to HFP may cause damage to kidneys after repeated and single dose. Single dose inhalation exposure may cause respiratory irritation. The US ACGIH has established a TLV of 0.1 ppm v/v (8-hour TWA) for HFP.

In the environment HFP will distribute primarily to air and it will photolytically degrade. Due to its high vapour pressure, the environmental compartment of election is atmosphere. There is little to no potential for aqueous exposure to aquatic organisms. It is not a greenhouse gas and is expected to have a low global warming potential. HFP would readily volatilize into the atmosphere from soil. It should be noted that air exhaust from processing operations should be evaluated for environmental hazards.

Further information on HFP can be found via following link:
https://echa.europa.eu/brief-profile/-/briefprofile/100.003.753

PFIB (perfluoroisobutylene):

PFIB is highly toxic by acute inhalation, and any exposure can be fatal. The US ACGIH has ascribed a TLV – Ceiling level of 0.01 ppm to PFIB.

If released to air PFIB is likely to exist solely in the gas phase and is susceptible to hydrolysis in air. It is expected to volatilize from dry soil and volatilization from moist soil is expected to be attenuated by hydrolysis. If released into water, PFIB is expected to adsorb to suspended solids and sediment but rapidly decompose in water via hydrolysis.

Further information on PFIB can be found via following links:
https://echa.europa.eu/information-on-chemicals/cl-inventory-database/-/discli/details/12524
https://pubchem.ncbi.nlm.nih.gov/compound/octafluoroisobutylene
Perfluoroisobutylene | C4F8 | CID 61109 - PubChem

TFE (tetrafluoroethylene):

TFE is a colourless, odourless and flammable gas that is very poorly soluble in water. Tetrafluoroethylene has no cardiac sensitization potential nor genotoxic potential *in vitro* and *in vivo*. Exposure via inhalation may cause damage to kidneys. TFE has been found to be carcinogenic in animal studies and under the REACH regulation EC/1907/2006, TFE has been classified as a category 1B carcinogen. A multicentre epidemiology study, involving cohorts from major producers of TFE, has investigated the carcinogenic impact of exposure of TFE in humans. No statistically significant increases in mortality were observed for any disease studied, including cancer. The US ACGIH has established a TLV of 2.0 ppm v/v (8-hour TWA) for TFE.

Any TFE released into the environment is expected to partition almost entirely to the atmosphere where it degrades. The predicted toxic concentrations of TFE to either aquatic or terrestrial are higher than solubility of TFE in water. Therefore, it can be expected that TFE will not be toxic to the aquatic environment [European Centre for Ecotoxicology and Toxicology of Chemicals, 2003] due to its high vapour pressure (it is a gas) it stays in the atmosphere due to its high fugacity. TFE does not contribute directly to the greenhouse effect (global warming) but may enhance the formation of tropospheric ozone. Tetrafluoroethylene may volatilize from dry soil surfaces based upon its vapor pressure. If released into water, tetrafluoroethylene is not expected to adsorb to suspended solids and sediment and is expected to volatilize.

Further information on TFE can be found via following link:
https://echa.europa.eu/brief-profile/-/briefprofile/100.003.752

4. Specific hazards of compounds containing pigments and fillers

Filled and pigmented fluoropolymers are in widespread use. The normal precautions for handling fluoropolymers need to be observed. Users need to note any additional hazards arising from the fillers or pigments themselves. Although many of the commonly used fillers and pigments have low toxicity, some are abrasive, and may cause irritation in contact with the skin. Should therefore avoid skin contact with filled or pigmented fluoropolymers, or inhalation or ingestion of filled or pigmented fluoropolymer dust. More information in sections of fire and explosion protection and specific hazards with powdered materials. (Chapter V).

Contact your supplier prior to using filled and/or pigmented fluoropolymers for specific safety recommendations. Before a user mixes pigments, fillers or other materials with fluoropolymers, health and safety information must be obtained from the vendors of the added materials and the compatibility with the fluoropolymer must be checked.

Chapter III

Processing Hazards and Precautions

It is recommended that the appropriate risk evaluation is performed for each specific activity to identify the appropriate safety measures and Personal Protection Equipment (PPE). In addition, consult the resin suppliers' Safety Data Sheets (SDS) for information about the products in use and the precautions necessary to use the product safely. In any circumstance where exhaust gases may be generated and vented, see Chapter IV for occupational controls and Chapter VI for evaluation of environmental controls.

1. Transport

Fluoropolymers are generally not classified as hazardous materials under European transport regulations and other international guidelines. However, it is essential to follow specific regulations related to the transport of chemicals. Use appropriate packaging to prevent damage and contamination during transport. Ensure that containers are properly labelled and sealed. Have emergency procedures in place for spills, leaks, or other incidents during transport. This includes having material SDS readily available.

2. Loading / unloading

Ensure that all hoses, containers, and equipment are compatible with the fluoropolymers being handled. Make sure that all containers are properly sealed and secured to prevent leaks during transport. Be aware of the temperature and humidity levels, as extreme conditions can affect the stability/properties of fluoropolymers. Keep accurate records of the materials being loaded and unloaded, including any incidents or irregularities.

3. Manual handling (particularly when in powder form / dispersions)

When opening sealed fluoropolymers containers, ensure containers are opened in a well-ventilated area. "Well-ventilated" means that good general room ventilation is available (generally 6 times per hour), and the surrounding space is significantly larger in volume than the container being opened. After opening, these containers should be allowed to sit open for a 10-minute breathing period. Care must be taken when opening the container for the first time as traces of hydrogen fluoride may be present in the head space. In this case appropriate safety measures should be followed for hydrogen fluoride, e.g. wear protective eyewear, wear suitable gloves if prolonged skin contact is likely. Approved dust mask and goggles should be worn if exposure to high dust levels is likely.

Container type and quantity should be considered when identifying tools for opening. The equipment used should be bound and ground to prevent static discharge. It is advisable to provide comprehensive training for workers, including emergency procedures for spills and exposure incidents.

The handling hazards for fluoropolymer dispersions are mainly determined by the stabilising surfactant used in the product. Please refer to individual safety data sheets for specific handling information. In general, it is advisable to avoid skin and eye contact, breathing in spray and ingestion. Ensure adequate ventilation and that suitable PPE is worn.

When processing dispersions refer to the Chapters II and III on thermal decomposition of fluoropolymers. Do not discharge dispersions to lakes, streams or waterways. Disposal to water will produce a milky appearance. The fluoropolymer component is not toxic. The stabilising surfactants have varying ecotoxicity profiles and users should contact their supplier for more detailed ecotoxicological information on their particular product.

4. Mixing (when in powders / liquids)

Verify that all substances being mixed are compatible to avoid hazardous reactions. When mixing fluoropolymers into solvents, be aware degradation materials may become present in the headspace. Ensure proper ventilation in the workspace to prevent the accumulation of toxic fumes. Use local exhaust ventilation systems to capture fumes at the source. Wear appropriate PPE, including gloves, safety goggles, and respiratory protection. Have procedures in place for managing spills of fluoropolymer powders or liquids. Clean up spills promptly using appropriate methods to prevent dust generation.

5. Dust control

It is commonly recommended that occupational exposure limits of 10 mg/m^3 total dust, 5 mg/m^3 respirable dust be used. However, machining products manufactured from resins which contain fillers, pigments, or other additives may produce hazardous dusts due to the presence of fillers and other additives. Consult the additive supplier or SDS for further information on additives.

6. Sintering

Sintering operations require the use of high temperature ovens in which various amounts of decomposition products are formed. Ovens must be designed to incorporate adequate ventilation, including sufficient air flow and capture capability, to ensure process gases do not enter the work area during oven operation and when the door is opened. Ovens must be regularly maintained and gases from the oven must be kept from leaking into the work area. Exhaust from processes should be vented to a safe location and evaluated for environmental impact. See Chapter VI for environmental controls discussion.

Temperatures in excess of the normal sintering range must be avoided. To assist in this, ovens should be equipped with an independent high temperature cut-off, triggered by an increase of approximately 5% of the desired sintering temperature, in addition to the normal control system. Both systems need to be calibrated at regular intervals. It is important that an interlock is provided which cuts off the heating if the forced ventilation is interrupted. If the oven temperature exceeds the high temperature cut-off setting, the heaters must be switched off and the oven must be cooled to ambient temperature and properly vented before the door is opened. Compounds containing fillers may be more sensitive to decomposition than PTFE alone and may require the use of lower temperatures. When opening sintering ovens after overheating, appropriate personal protection is recommended. Some examples of appropriate personal protective equipment are protective clothing, a self-contained breathing apparatus, thermally insulating gloves, safety gloves, but these are not exhaustive.

7. Melt processing / extrusion

Melt processing of fluoropolymer resins at excessively high temperatures or exposing them for extended times at processing temperatures can cause decomposition. Such decomposition may produce gases and generate pressures in processing equipment sufficient to “blow back” through the feed port. If no vent is available for these gases, as in some compression moulding equipment, pressures can develop which may rupture metal parts and possibly cause injury to personnel near the processing equipment. For example, for ETFE, at normal moulding temperatures, thermal decomposition does not occur. However, even around 300°C, if maintained for a long period of time, weight loss due to decomposition occurs. In such a situation, the gas generated by decomposition consists mostly of hydrogen fluoride. (https://agcce.com/wp-content/uploads/2023/10/FluonETFE.pdf)

It is considered bad practice to stand in front of an extruder without appropriate PPE. The exhaust from the vacuum pump used to control the length of the melt cone during extrusion is likely to contain decomposition products from the fluoropolymer that should be discharged outside the workplace. Extruders should be equipped with local ventilation extract at the die or a vent port to remove any gases. As in other cases, exhaust gases should be evaluated.

Considering the reactivity of high-temperature molten resin, process equipment must be made of corrosion-resistant materials (e.g. high-nickel, low-iron alloys) or materials that do not contain substances that promote the decomposition of fluoropolymer resin (e.g. copper, aluminium). Contact the manufacturer for specific machine information.

If fluoropolymer resin melt begins to darken, the colour change may be an indication that thermal degradation has begun. Bubbling and white off-gassing may also indicate thermal degradation. If an operator believes that thermal degradation is occurring, zone temperatures should be lowered and the fluoropolymer resin purged from the equipment. Fluoropolymer resins should be processed on equipment having accurate, reproducible temperature control. Temperature cycling should be less than +/- 5°C.

8. Paste extrusion

Processing PTFE coagulated dispersion/fine powder resins requires extrusion by a special process, commonly known as paste extrusion. This involves mixing the resin with a lubricant, usually volatile petroleum fraction. The use of combustible and flammable liquids of relatively low flashpoint is a significant potential fire and explosion hazard and presents the potential for gas emissions. Electrically conductive containers must be used for the solvents and equipment should be grounded to reduce ignition sources. In addition, solvents often have health hazards due to inhalation and/or skin contact associated with their use.

Appropriate precautions must be taken for the safe use, storage and handling of fluoropolymer resins containing solvent-based lubricants. Follow the recommendations of the lubricant supplier. Removal of the lubricant after extrusion may take place in a separate batch drying oven, or in a continuous oven in-line with the extruder. Appropriate precautions need to be taken to minimise the risk of forming explosive mixtures of lubricant and air, and to prevent ignition. With inline operation, the drying oven is immediately followed by a high temperature sintering oven, and there is the possibility that incorrect operation would cause flammable vapour to be carried into the sintering zone, where it would almost certainly ignite. It is essential to have fire extinguishing equipment available. For small fires, portable carbon dioxide extinguishers are usually adequate, but a permanent installation, which can rapidly fill the complete oven with carbon dioxide in the event of a large fire is advisable. Ventilation of the drying and sintering operations requires the same precautions as described earlier in this section for operation of sintering ovens in the workplace, including evaluation of exhaust gases.

9. Etching

Articles of fluoropolymers can be etched to allow the article to be bonded to another surface. Etching chemically alters the surface of PTFE by the process of defluorination. Etching is usually performed by either chemical methods or by plasma treatment.

In the chemical etching process, PTFE is brought into contact with alkaline metal solutions by either dipping the PTFE into a tank or applying the etchant to the surface of the PTFE.

Plasma etching is a process performed in low-pressure plasma with hydrogen as a process gas. Here, the hydrogen radicals react with the fluorine in the PTFE to form hydrogen fluoride, leaving unsaturated carbon bonds which are good bonding spots for the attachment of the molecules of liquids.

Safety precautions must be taken due to generation of hydrogen fluoride, see Chapter II on safety precautions for hydrogen fluoride. For both methods, great care is needed and requires careful consideration of materials and byproducts. Appropriate safety data sheets should be consulted for advice on handling raw materials used.

The etched surface of PTFE is susceptible to degradation over time, particularly when exposed to UV light, and only has a shelf life of a few months. For this reason, etched PTFE should be stored in a dark place or in UV-blocking bags. Etched PTFE should also be kept away from air and moisture as much as possible prior to bonding it.

10. Coating / impregnation

The processing of fluoropolymer aqueous dispersions normally requires a heating process to remove water and surfactant prior to sintering the fluoropolymer. Some surfactants and their degradation products are flammable and may have specific irritant or other adverse effects on health. The oven used to remove these products must be provided with forced ventilation to prevent a hazardous build-up of vapour. Ventilation of gases should be evaluated for air emissions to the environment and whether there is a need to install abatement technology. Where the aqueous dispersion uses a surfactant, this removal step should contain and/or destroy any surfactant-containing gas emissions – ventilated gases should not be emitted directly to the environment. Furthermore, there may be significant build-up of decomposition products in the ovens. Protective equipment should be worn when removing such deposits. Contact your dispersion supplier for specific information.

Some coating systems may contain organic solvents in addition to the fluoropolymer resins. These solvents may be combustible and flammable liquids of relatively low flashpoint and therefore present a potential fire and explosion hazard. In addition, the solvents often have health hazards due to inhalation and/or skin contact associated with their use. Appropriate precautions must be taken for the safe use, storage and handling of fluoropolymer resins containing dispersion medium or additives, following the recommendations of the supplier.

Fluoropolymer dispersions are made using fluoropolymer processing aids. In most cases the levels of fluoropolymer processing aids have been reduced to trace amounts, however any emissions or waste generated from the use of these products should be evaluated for proper handling.

11. Machining

Grinding, sawing, and machining fabricated shapes of fluoropolymers are performed routinely in fabricators' shops. All normal high-speed machining techniques can be used provided the tools have sharp cutting edges. Coolants are recommended to improve production rates and quality, and they will serve to control any tendency toward overheating, eliminating the need for special ventilation. Dust will be generated by machining products manufactured from fluoropolymer resins and as such appropriate PPE equipment should be used and appropriate ventilation of the facility is required.

12. Welding

Special precautions are necessary when welding fluoropolymer parts to one another because hydrogen fluoride is generated in significant quantities by the process. (Consult applicable national occupational exposure limits) (IFA, 2021. GESTIS International Limit Values. Hydrofluoric acid ILV). Complete skin and eye protection is necessary as well as the appropriate respiratory protection which may include the use of self-contained breathing apparatus.

13. Soldering, welding and melt Stripping of metals coated with fluoropolymers

Major uses for fluoropolymers are in electrical insulation. In many cases, soldering or use of a heated element to remove insulation or the coating from a metal substrate are routine operations. The combined effects of temperature, quantity of resin, exposure time, and ventilation conditions are important factors for worker comfort and safety. The use of local fume hoods as described in the ventilation section is strongly recommended.

Direct application of welding arcs and torches using temperatures above 400°C can quickly destroy the usefulness of parts made from fluoropolymers. During such treatment, toxic fumes are liberated, and it is advised to remove all fluoropolymer parts before such treatment. Where removal is not possible, such as in welding or cutting coated parts, mechanical ventilation should be provided to prevent exposure to fumes and personnel protection should be worn.

14. Cleaning and maintenance of process equipment

Cleaning and maintaining process equipment components (dies, screen packs, screws, etc.) may involve pyrolysis of residual polymer. As much polymer as possible should be removed (e.g. with a brass brush) before finally burning off. Appropriate hoods should be designed to completely exhaust the gases and particulates that are formed. See Chapter IV for additional information on ventilation.

Processing vessels and ovens can be considered as confined spaces and special procedures may be required before allowing personnel access for cleaning.

15. Spillage

Fluoropolymers spilled during handling should be cleaned up immediately and appropriate measures should be taken to prevent the creation of a slippery surface. It is advisable that some sort of anti-slip flooring and steps should be provided in areas where fluoropolymer resins are regularly handled. Slippery surfaces in walking and working areas pose an increased accident risk.

To mitigate the issue of pellet loss as a form of spillage, Plastics Europe introduced the Operation Clean Sweep (OCS) program. This industry-led initiative is an international programme designed to prevent the loss of plastic granules (pellets, flakes and powders) during handling by the various entities in the plastics value chain and their release into the environment. By adhering to established best practices and guidelines, OCS strives to safeguard water quality, protect the environment, and enhance worker safety across the entire plastics supply chain. www.opcleansweep.eu

Chapter IV

Occupational Hygiene

1. Ventilation

As with most polymers, minute quantities of residual gases may diffuse from the resins, even at room temperature. Therefore, as a matter of good occupational hygiene practice, resin containers should be opened and used only in well-ventilated areas. Personnel should be instructed to minimise exposure whilst opening and closing containers.

For hot processing operations where fumes may be released, such as drying, extrusion or sintering, ventilation is required. In addition, it may also be required in "cold" operations such as spray coating, blending and high-speed grinding or machining to remove aerosols, mists or particulates.

Appropriate exhaust ventilation should be selected dependent on the nature of the process involved and local conditions. Proprietary systems may be available for specific activities, e.g., spray booths or fume cupboards and these should comply with relevant standards. In other cases, local extract ventilation may have to be specifically designed for the process concerned. In either case, ventilation systems should always be designed or supplied by competent ventilation specialists.

The design of the extraction hood, ducting system and fan should be based on a good understanding of the fumes and other exhaust materials involved. This may include environmental and process conditions which could affect the captured materials. It will be necessary to specify the required capture velocity at the point of the formation sufficient to ensure adequate control. This is related to the velocity of the materials and any associated air movements or currents. Good design and use of a hood (e.g., slots, rim ventilation, annular extraction, booths and cabinets) is important for efficient capture of off-gases. It should be designed taking into account all the material characteristics. The most effective hoods are those which enclose or contain the exhaust materials. More air is required as the level of containment decreases. The required extraction volume to give an adequate velocity at the point of formation should be determined. The ducting, fan and air cleaner can then be correctly designed to match the extraction volume requirements. Further ideas on design and information can be obtained from your resin supplier.

Even with the precautions during processing described in Chapter III, processors are advised to allow sufficient degassing of the product prior to further handling of the finished article. For treatment of the exhausted air see Chapter VI.

2. Personal Protective Equipment (PPE)

At processing temperatures fluoropolymer melt can cause severe burns; therefore, appropriate protective measures including safety glasses, gloves, and arm protection (gauntlets) are recommended during processing. Jewellery should not be worn.

If dust cannot be avoided when handling fluoropolymer resin powders or during machining operations, respirators or dust masks should be worn. Refer to your supplier's Safety Data Sheet for specific guidance. While processing and handling filled compounds, in addition to the dust masks, eye protection and protective gloves may be required.

Fluoropolymer dispersions contain wetting agents which should not come in contact with the skin. It is necessary to wear protective gloves and other protective clothing to prevent skin contact when handling these products. The spray application of coatings must be performed in suitably equipped spray booths. Depending on the efficiency of this system, operators may also be required to wear safety glasses, respirators and gloves. It is recommended that the spray booth be equipped with a water bath to precipitate the spray mist. A risk assessment should be performed of the area to determine the proper PPE. See Chapter VI for disposal guidance.

3. Personal hygiene

In regular training of personnel, it is important to emphasise that tobacco products must not be carried or used in work areas. Smoking tobacco contaminated with even very small amounts of fluoropolymer resin can cause “polymer fume fever” by inhalation of the effluents (see “Health hazards during hot processing” in Chapter II). To prevent traces of fluoropolymer resin powders from being carried out of the work area on clothing, it is advised that personnel should store their work clothing separately from their normal clothing (double locker or separate changing rooms). Personnel should be provided with adequate washing facilities and required to use these regularly.

Chapter V

Fire and Explosion Hazard

1. Ignition characteristics

The self-ignition temperatures (SIT) of solid PTFE products measured in accordance with ASTM D 1929 are in the range of 500°C-560°C, for PVDF it is higher than 400°C and hence far above those of materials capable of sustaining combustion when the ignition source is removed. For comparison, the SIT of cellulose containing materials such as wood, paper, board etc. is 240°C-245°C.

All fire and flammability tests show that fluoropolymers are amongst the most difficult plastics to set on fire. If a flame is applied to the surface of these polymers it will ignite because of the formation of gaseous decomposition products. However, if the flame is removed combustion ceases. During the combustion of fluoropolymers little or no smoke is produced. Care should be taken however to avoid the inhalation of smoke generated by all combusting materials, including fluoropolymers. The exceptionally low flammability of the fully fluorinated fluoropolymers is also indicated by their limiting oxygen index (LOI) measured in accordance with ASTM D 2863. The oxygen index is the minimum concentration of oxygen in a mixture of oxygen and nitrogen that will just support flaming combustion of a material. The LOI for fully fluorinated polymers such as PTFE, PFA and FEP is greater than 95%. For polymers which are not fully fluorinated, the LOI is between 30% and 60% depending on the molecular structure. This compares with values of around 20% for cellulose products. PTFE does not form flammable dust clouds under normal factory conditions. PTFE and other fluoropolymer powders fall into dust explosion class St 0.

2. Fire and combustion products toxicity

Fluoropolymers are normally a minor component of most structures. They have a very high ignition temperature in comparison with most other organic materials and it is difficult to sustain a flame. This means that it is unlikely that fluoropolymers will be involved in a fire on their own. It is important to take account of the properties of all materials present in fires when assessing the potential health consequences of exposure to the combustion products evolved.

If fluoropolymers are involved in a fire, the hazardous gases and vapours produced include hydrogen fluoride, carbonyl fluoride, carbon monoxide, low molecular weight fluorinated substances and ultrafine fluoropolymer particulates. The four main types of product formed in the decomposition of fluoropolymers are fluoroalkenes, hydrogen fluoride, oxidation products and ultrafine fluoropolymer particulates. The toxicology of the combustion products have been investigated extensively, and it has been shown that particulates have potential, under certain laboratory conditions, to be extremely toxic. A more detailed assessment of the combustion toxicology of fluoropolymers is given in Appendix B. In a fire, the previously discussed thermal degradation products (e.g., hydrogen fluoride, carbonyl fluoride) are expected to be present. See the firefighting section 4.

3. Extinguishing agents

All extinguishing agents such as water, carbon dioxide, dry powder, foam are suitable for fires involving fluoropolymers. Extinguishing agents which are most appropriate to the surrounding materials, location of the fire and the stage of fire development should be used. For established fires water is the preferred extinguishing agent.

4. Fire fighting

Fluoropolymers are difficult to ignite and will not themselves sustain a flame so under normal circumstances will make no contribution to the start or spread of fires. However, if they are involved in a fire they can decompose and may contribute to the toxicity of the fire gases formed. Chapter II and Appendix B provide more information. It is therefore important to take normal industrial fire precautions in factories processing fluoropolymers to reduce the risk of a fire. Since the possibility of a fire starting and spreading can never be completely ruled out the relevant local authorities should be advised of the chemical nature of the fire gases.

In the event of a fire, the fire service should be warned of the possibility of the presence of toxic and corrosive gases. Self-contained breathing apparatus must always be worn when extinguishing fires or when conducting cleaning up operations in the presence of fire effluent. Suitable measures should be taken to prevent the exposure of members of the public. If individuals are exposed, treatment may be required for inhalation of hydrogen fluoride or the other decomposition products or for skin contact with hydrogen fluoride. If exposed, individuals should seek medical help. Hydrogen fluoride is rapidly absorbed into the body causing severe systemic effects, some of which may be delayed up to 48 hours. Immediate treatment is therefore essential. Calcium gluconate gel (2.5%), antidote for hydrogen fluoride, should be applied to the skin. It is imperative that firefighters and their equipment are thoroughly decontaminated with a water wash down after fire and smoke exposure.

5. Explosion protection

In the paste extrusion process flammable lubricants are normally used. The possible risk of fire or explosion through the formation of flammable vapour/air mixtures should also be taken into account.

Similarly with fluoropolymers powder compounds containing carbon and metal powders, measures to prevent static charge accumulation should be taken if dust/air mixtures are likely to occur in operations such as mixing.

6. Specific hazards of fluoropolymers with powdered materials

A hazard identified with the handling of fluoropolymer pellets or components is the potential for static electricity build-up. There have been reports of electrostatic shocks when handling pellets or proximity to a production line (e.g., tubing extrusion). Potential static discharge points should be identified, and grounding or other static control measures should be evaluated and appropriate for the environment. Where fluoropolymer components or waste are being collected, consider the potential for static charge build-up in process hazard reviews.

Finely divided fluoropolymer resins can become extremely combustible in the presence of various metal fines. For example, metal fines (e.g., bronze, aluminium) mixed with powdered fluoropolymers when exposed to high temperatures (above about 370°C) may react violently producing fire and/or explosion. Exothermic reactions may occur even at sintering temperatures leading to fires.

Other fluoropolymer materials may react at higher or lower temperatures. In addition, other materials known to catalyse these reactions include silica, silicon carbide, titanium dioxide, metallic compounds and glass fibres or beads. Some extrusion purging agents use finely dispersed metal particles. These extrusion purging agents with finely dispersed metal particles should not be used to clean extruders where fluoropolymers were last used. Contact your materials suppliers for specific information.

Chapter VI

Waste and Emissions

1. Recycling

Recycling options are available for fluoropolymers [Ameduri and Hisao, 2023]. Polymer scrap resulting from the processing of fluoropolymer resins should be recycled where possible. This can be done by the processor themself or on a large scale mainly by specialist multinational recycling companies. At present compounds containing fillers such as glass fibre, carbon or bronze are recyclable to a more limited extent than unfilled fluoropolymers but outlets for recycled compounds are being developed. The presence of fluoropolymers is not necessarily a barrier to recycling the main component. For example, steel components containing small amounts of a fluoropolymer article may be re-smelted and the metal recovered.

Recycling of fluoropolymers with example of PTFE

The recycling of PTFE can be divided into primary recycling, secondary recycling and tertiary recycling (up-cycling).

In primary recycling, the PTFE waste is ground into a powder. This powder can be further processed in various ways, but the properties of this regeneration differ fundamentally from those of virgin PTFE.

Secondary recycling differs from primary recycling in a way that the PTFE powder is obtained using thermomechanical processes or radiation. When radiation is used, emissions should be evaluated for degradation products. The PTFE micro-powder obtained in this way can be used as an additive for a wide range of applications.

Tertiary recycling (up-cycling) can be performed by pyrolysis which converts PTFE under an inert atmosphere into corresponding monomers TFE and HFP which can then be reused in polymerisation.

Others such as melt processible fluoropolymers (e.g., ETFE, FEP, PFA, PVDF) can also be recycled. When extruding film for example, trimming waste can be directly refed into the extruder. It is also possible to reprocess the material from shutdowns and startups. In the case of PVDF, material is fully mechanically recyclable without impacting key performance of the material. However, final properties of the product may be affected and therefore resulting material not suitable for all applications.

2. Disposal

The preferred option for disposal of fluoropolymer aqueous dispersions is to separate solids from liquid by precipitation and decanting or filtering. The preferred option for disposal of the solids, including other fluoropolymer-containing wastes is incineration.

The liquid filtrate may be discharged to a wastewater system in accordance with local regulations or permits. However, the liquid filtrate should be evaluated for any residuals of additives or fluoropolymer processing aids and pre-treated as necessary prior to discharge to a wastewater system in accordance with local regulations or permits. Industrial fluoropolymer waste containing additives such as solvents, primers or thinners must be regarded as special waste. Companies should contact their local waste disposal authorities for details of the relevant waste disposal regulations. Fluoropolymers can be incinerated in industrial waste incinerators, with sufficient temperature and residence time [Aleksandrov, *et al.*, 2019, Gehrmann, *et al*., 2024]. Control measures, such as wet scrubbing with alkaline solutions, may be necessary to maintain the emission of hydrogen fluoride below that specified by national or local regulation.

Several studies have been conducted to determine if substances of concern are emitted when fluoropolymers are incinerated at a municipal waste disposal facility. One study concluded that: “The results confirm that fluoropolymers at their end of life when incinerated under representative European municipal incinerators conditions do not generate any measurable levels of PFAS emissions and therefore pose no risk to human health and the environment.” [Gerhmann, *et al*., 2024]. Furthermore, the German Environment Agency has recently published its own study investigating PFAS in waste streams that concludes “these conditions [minimum temperature of 850°C and a dwell time of at least 2 seconds] are sufficient to largely destroy PFAS during incineration” [Meermann, *et al*., 2024]. If industrial fluoropolymer waste is to be landfilled the site must be a lined landfill in accordance with local regulations.

3. Air Treatment Technologies

For fluoropolymer particles in captured air which may occur when processing by grinding, sawing, and machining conventional air pollution control (APC) equipment for particle capture i.e. bag houses and similar units utilize filter media with smaller pore openings than the targeted particles can be applied. Dust particles can also be removed by washing the flue gas with water or another liquid, solution or mixture, also known as a scrubber. This option may be considered if, in addition to removal of dust, gaseous components need to be removed.

More complex is the treatment of airborne vapours due to degradation products from fluoropolymers. The following three main technologies have been proven efficient for treatment of some of the degradation products:

Thermal oxidation: Thermal oxidizers achieve destruction through high-temperature thermal oxidation - a process that employs a combination of temperature, residence time, turbulence, and oxygen to convert pollutants into carbon dioxide, corresponding halogen acid gases and water vapor.

Wet scrubbing: The removal of gaseous or particulate pollutants from a waste gas stream via mass transfer to water or an aqueous solution. It may involve a chemical reaction (e.g. in an acid or alkaline scrubber). Water stream from scrubbing could be treated in an appropriate wastewater treatment facility.

Activated carbon adsorption (fixed bed): can be used for the removal of specific PFAS from waste gases,

Exhaust gases that may be formed from the processing of fluoropolymers, as described in Chapter III, should be evaluated against local regulatory requirements. Use of thermal oxidation technology on fluorine-containing emissions will generate HF, which if generated in regulated amounts will require additional treatment via caustic scrubbing.

4. Water Treatment Technologies

Water treatment technologies are needed when there is a possibility that degradation products and other non-polymeric PFAS could be present in water from processing of fluoropolymers.

A large proportion of water treatment techniques are sensitive to suspended solids like for instance fluoropolymer particles. To effectively remove non polymeric PFAS from waste streams it is important that, as an initial step, suspended solids are removed to improve efficiency and protect the operation of the technique. If too high concentrations of suspended solids are present in the influent of the water treatment techniques, this will ultimately have a negative effect on the removal efficiency of PFAS.

Suspended solids can be removed by applying one or a combination of the following techniques:

- Gravitational settling/decantation
- Sand filtration
- Coagulation/flocculation;
- Dissolved air flotation;
- Diaphragm based techniques (microfiltration/utrafiltration)

It should always be considered that the resulting residue or filtrate from any of these techniques, as well as things like filter cloth will be contaminated with the PFAS. They may well require special treatment/disposal methods of their own.

The effectiveness of the technique(s) applied generally depend on the size or size ranges of the solid particles and applying these techniques in a series (abatement train) should be considered.

Further treatment of wastewater containing non polymeric PFAS will generally depend on a number of factors. The main are:

- Type and concentration of PFAS
- Corresponding technology effectiveness
- Cost considerations
- Environmental considerations

The following techniques are most commonly used:

- Adsorption by activated carbon
- Adsorption by ion exchange resins
- Reverse osmosis
- Nanofiltration

Many other technologies are available or under development. The Flemish Institute for Technological Research VITO has developed a detailed (albeit Dutch language) Best Available Techniques document [VITO 2023] for treatment of industrial and drainage water contaminated with PFAS, providing information on available techniques (including their technology readiness levels) and provides information on measuring PFAS in waste water and guidance on selection of techniques. If the processing of fluoropolymers is done in an installation that is subject to the IPPC Directive (chemical industry), the Best Available Techniques (BAT) Reference Document for Common Waste Water and Waste Gas Treatment/Management Systems in the Chemical Sector [JRC 2016].

Appendix A

Members of the Fluoropolymers Products Group

AGC CHEMICAL EUROPE, LIMITED
Hillhouse Int., Fleetwood Road North,
Thornton Cleveleys Lancashire
FY5 4QD, United Kingdom
Tel: +44 1253 209600
Web: www.agcce.com

ARKEMA
51 esplanade du Général de gaulle
Immeuble Lightwell
92000 Puteaux, France
Tel: +33 1) 49 00 80 80
Web: www.arkema.com

Chemours International S.a.r.l.
Route du Nant-D’Avril 150
1217 Meyrin
Geneva, Switzerland
Tel: +41 22 719 1500
Web: www.chemours.com

DAIKIN CHEMICAL EUROPE GmbH
Am Wehrhahn 50,
40211 Düsseldorf, Germany
Tel: +49 211 179 22 50
Web: www.daikinchem.de www.daikin.com

DuPont
Chestnut Run Plaza
974 Centre Rd
Wilmington, DE 19805
https://www.dupont.com/

W.L. GORE & ASSOCIATES GMBH
Hermann-Oberth-Str. 26
85640 Putzbrunn, Germany
Tel: +49 89 46 12 0
Web: www.gore.de

Gujarat Fluorochemicals GmbH
Esplanada 40, 9. Stock
20354, Hamburg, Germany
Tel: +49 40 5582 395-80
Web: www.gfl-europe.com

Honeywell NV
Hermeslaan 1H
1831 Diegem, Belgium
Tel: +32 2 728 27 11
www.honeywell.com

KUREHA Corporation
3-3-2, Nihonbashi-Hamacho, Chuo-ku,
Tokyo 103-8552, Japan
Tel: +81 3 3249 4666
Web: www.kureha.co.jp/en/

SYENSQO
Rue de la Fusée 98
1130 Brussels, Belgium
Tel: +32 2 264 19 00
Web: www.syensqo.com

Appendix B

The inhalation toxicity of combustion products of PTFE and similar fluoropolymers

A considerable number of studies have been conducted to investigate the toxicity of the combustion/thermal degradation products of PTFE.

Prior to 1982 it was considered that the major products, including hydrogen fluoride and carbonyl fluoride, were responsible for the toxic effects seen in rats exposed to the evolved combustion products of PTFE, toxicity being approximately ten times greater than for the combustion products of wood. However, in [Levin *et al*., 1982], using the newly developed National Bureau of Standards small-scale test method for assessing the toxicology of combustion products, reported an unexpectedly high toxicity when testing PTFE. They found an LC50 of 0.045mg/l for PTFE products as compared with 20-40 mg/l for a standard sample of wood (Douglas Fir). This unexpected result could not be explained in terms of the expected combustion products and led to an extensive investigation of this phenomenon by several laboratories.

A number of reviews of these studies were presented at the Interflam '90 conference [Purser, 1990, Fardell, 1990; Clarke van Kuijk, *et al*., 1990a; Clake, Seidel, *et al*., 1990b] which, together with several other publications [Warheit *et al*., 1990; Lee and Seidel, 1991], provide an interesting explanation for the extreme toxicity associated exclusively with thermal degradation products of PTFE or similar perfluoropolymers. In brief, there are a few critical parameters essential for expression of extreme toxicity. Thermal degradation must occur under non-flaming conditions. Experimental design must allow for recirculation of evolved fume through the combustion area, as in the NBS apparatus, or for rapid exposure to freshly generated fumes, as described by [Warheit *et al*., 1990].

The particulate phase of the degradation products is clearly responsible, specifically with regard to the size of the particles evolved. When fumes are generated in a temperature range of approximately 450°C-800°C the particles generated are extremely fine, typically less than 0,05 microns and in an apparatus such as the NBS chamber, will be confined to a relatively small volume. They will rapidly undergo thermal coagulation producing fume particles of greater size and lower number concentration and which will spread throughout the 200-litre exposure chamber. As they recirculate through the furnace they may undergo de-aggregation and dispersal, stabilising at the ultrafine particle size and producing extreme toxicity. In a dynamic system such as that described by [Warheit *et al*., 1990], if exposure is affected before coagulation occurs extreme toxicity is also seen but if coagulation is allowed to occur initially the toxicity is reduced considerably. It has been suggested that the specific requirement for fresh or recycled fume to induce extreme toxicity may also relate to free radical production during pyrolysis and indeed relatively stable alkylfluoroperoxy radicals are reported to have been detected [Fardell, 1990].

Nonetheless, the most critical factor appears to be the size of the particles when inhaled. This dictates the proportion that will deposit in the alveolar region where damage is seen, but possibly more importantly, the interaction of the particle with the epithelial cells. There is increasing evidence that ultrafine particles of sizes less than approximately 0,05 microns of even highly inert materials such as titanium dioxide are substantially more toxic to the lung compared with larger particles [Oberdorster 1990, Johnston 1996] due to direct penetration into or reaction with the epithelial cells. The extreme toxicity of PTFE pyrolysis products is consistent with this picture. The toxicity of PTFE pyrolysis products is influencing decisions by regulators on many potential uses of PTFE due to direct extrapolation to real, large scale fire scenarios where humans may be exposed to combustion products.

However, caution must be exercised in such extrapolations. The only time that extreme toxicity has been demonstrated has been under closely controlled experimental conditions. It is not inconceivable that such conditions could be reproduced in a real fire, but other factors must also be taken into consideration. Firstly, experimental studies have shown effects only when using PTFE or fluoropolymers alone. Several studies have been conducted on “mixed” materials, for example where PTFE was combusted with wood [Purser, 1990], and extreme toxicity was not observed. This is more appropriate to real fires which generally involve mixtures of materials, the smoke particles from which will be larger in size and will tend to scavenge and hence detoxify fine PTFE particles. Secondly, in full scale fire tests using a number of potential ignition sources for perfluoropolymer-insulated cables [Clarke, van Kuijk, *et al*., 1990b], the toxicity reported in rats exposed to the combustion products was consistent with that expected of the principal toxic agents carbon monoxide, hydrogen fluoride and carbonyl fluoride with no indications of extreme toxicity. Therefore, it is more likely in a real fire situation that any fluoropolymers present will contribute to the toxicity by virtue of normally expected thermal degradation products but will not dominate the toxicity due to production of extremely toxic products.

References

Aleksandrow, K, Gehrmann, H-J, Hauser, M., Matzing, H., Pigeon, D., Stapf, D., and Wexler, M., (2019) Waste incineration of Polytetrafluoroethylene (PTFE) to evaluate potential formation of per- and Poly-Fluorinated Alkyl Substances (PFAS) in flue gas, Chemosphere, 2019, 226, 898-906

Améduri, B. and Hisao, H. (2023). Recycling and the end-of-life assessment of fluoropolymers: recent developments, challenges and future trends. Chem. Soc. Rev., 52, 4208-4247. https://doi.org/10.1039/D2CS00763K

Clarke, F B, van Kuijk, H, Valentine, R, Mokovec, G T, Seidel, W C, Baker, B B, Kasprazak, D, Marovec, G J, Bonesteel, J K , Janssens, M and Herpol, C H (1990). The inhalation toxicity of smoke from fires involving perfluoropolymers: full scale fires, proceedings of Interflam ’90, 287-295.

Clarke, F B , Seidel,W C, SchererV Jnr, Clins D Jnr, Olsen, A and Bonesteel, J. (1990). Formation, identity and coagulation of fluoropolymer-derived smoke aerosols. The relationship between aerosol behaviour and observed toxicity of fluoropolymer smoke. Proceedings of Interflam ’90, 297-304.

Consonni, D., Straif, K., Symons, J.M, Tomenson, J. A., van Amelsvoort, L.G.P.M., Sleeuwenhoek, A., Cherrie, J.W., Bonetti, P., Colombo, I., Farrar, D.G., Bertazzi, P.A. (2013). Cancer Risk Among Tetrafluoroethylene Synthesis and Polymerization Workers, American Journal of Epidemiology, Volume 178, Issue 3, Pages 350–358, https://doi.org/10.1093/aje/kws588

Ellis DA, Mabury SA, Martin JW, Muir DC. (2001) Thermolysis of fluoropolymers as a potential source of halogenated organic acids in the environment. Nature. 2001 Jul 19;412(6844):321-4. https://doi.org/10.1038/35085548 . PMID: 11460160.

European Centre for Ecotoxicology and Toxicology of Chemicals, (2003). Joint Assessment of Commodity Chemicals (JACC) Report no 42. Tetrafluoroethylene.

Fardell, P. (1990). UK studies of the toxic potency of PTFE in fire. Proceedings in Interflam ’90, 257-271.

Gehrmann, H.-J., Taylor, P., Aleksandrov, K., Bergdolt, P., Bologa, A., Blye, D., Dalal, P., Gunasekar, P., Herremanns, S., Kapoor, D., Michell, M., Nuredin, V., Schlipf, M., Stapf, D. (2024). Mineralization of fluoropolymers from combustion in a pilot plant under representative European municipal and hazardous waste combustor conditions, Chemosphere, Volume 365, 143403. https://doi.org/10.1016/j.chemosphere.2024.143403

Henry, B.J., Carlin, J.P., Hammerschmidt, J.A., Buck, R.C., Buxton, L.W., Fiedler, H., Seed, J. and Hernandez, O. (2018), A critical review of the application of polymer of low concern and regulatory criteria to fluoropolymers. Integr Environ Assess Manag, 14: 316-334. https://doi.org/10.1002/ieam.4035

Hintzer, K., Zipplies, T., Carlson, D.P. and Schmiegel, W. (2014). Fluoropolymers, Organic. In Ullmann's Encyclopedia of Industrial Chemistry, (Ed.) https://doi.org/10.1002/14356007.a11_393.pub2

Johnston C J, Finkelstein J N, Gelein R and Oberdorster G (1996). Characterization of early pulmonary inflammatory response associated with PTFE fume exposure. Toxicology and applied pharmacology, article 0208, academic press, May 1996.

Johnson, W. Jr, Bergfeld W.F., Belsito, D.V, Hill, R.A., Klaassen, C.D., Liebler, D.C., Marks, J.G. Jr, Shank, R.C., Slaga, T.J., Snyder, P.W, Fiume, M., Heldreth, B. (2023). Safety Assessment of Polyfluorinated Polymers as Used in Cosmetics. International Journal of Toxicology;42(3_suppl):144S-161S. doi: 10.1177/10915818231208647. PMID: 37978581.

Joint Research Centre (JRC) (2016) Best Available Techniques (BAT) Reference Document for Common Waste Water and Waste Gas Treatment/Management Systems in the Chemical Sector

Korzeniowski, S.H., Buck, R.C., Newkold, R.M., kassmi, A.E., Laganis, E., Matsuoka, Y., Dinelli, B., Beauchet, S., Adamsky, F., Weilandt, K., Soni, V.K., Kapoor, D., Gunasekar, P., Malvasi, M., Brinati, G. and Musio, S. (2023), A critical review of the application of polymer of low concern regulatory criteria to fluoropolymers II: Fluoroplastics and fluoroelastomers. Integr Environ Assess Manag, 19: 326-354. https://doi.org/10.1002/ieam.4646

Lee, K P and Seidel, W C. (1991). Pulmonary response of rats exposed to polytetrafluoroethylene and tetrafluoro- ethylene hexafluoropropylene copolymer fume and isolated particles. Inhalation Toxicology, 3, 237-264.

Levin, B.C., Fowell, A.J., Birky, M.M, Paabo, M., Stolte, A., Malek, D. (1982). Further Development of a Test Method for the Assessment of Acute Inhalation Toxicity of Combustion Products. National Bureau of Standards (US), NBSIR 82-2532

Meermann, B., von der Au, M., Potrykus, A., Schramm, B., Obajdin, K., de Bruijne, E. A., F., Zotz, Broneder, C. (2024) Investigation of the occurrence of PFAS (per- and polyfluorinated alkyl compounds) in waste streams. Publisher: German Environment Agency TEXTE 86/2024.
https://www.umweltbundesamt.de/sites/default/files/medien/11850/publikationen/86_2024_texte_pfas_in_waste_streams_0.pdf

National Research Council. (2015). Acute Exposure Guideline Levels for Selected Airborne Chemicals: Volume 19. Washington, DC: The National Academies Press.
https://doi.org/10.17226/21701 .

Oberdorster, G, Ferin, J, Finkelstein, J, Soderholm, S. and Gelein R. (1990). Ultrafine TiO22 particles as a model for studying overload related mechanisms. J. Aerosol Med. 3, 79.

Purser, D A. (1990). Recent developments in under- standing of the toxicity of PTFE thermal degradation products. Proceedings of Interflam ’90, 273-286.

Radulovic, L.L., Wojcinski, Z.W. (2014). PTFE (Polytetrafluoroethylene; Teflon®), Editor(s): Philip Wexler, Encyclopedia of Toxicology (Third Edition), Academic Press, Pages 1133-1136.

Radulovic, L.L., Wojcinski, Z.W. (2024), PTFE (polytetrafluoroethylene; Teflon®), Editor(s): Philip Wexler, Encyclopedia of Toxicology (Fourth Edition), Academic Press, Pages 1001-1006. https://doi.org/10.1016/B978-0-12-824315-2.00270-0.

Vlaams Kenniscentrum voor Beste Beschikbare Technieken (VITO), (2023) BBT-studie voor de zuivering van met PFAS belast bedrijfsafvalwater en bemalingswater

Warheit, D B, Seidel, W C, Carakostas, M C and Hartsky, M. (1990). Attenuation of perfluoropolymer fume pulmonary toxicity: effects of filters, combustion methods. and aerosol age. Exp. Mol. Path. 52, 309-329.

Waritz, R. S., (1975) "An industrial approach to evaluation of pyrolysis and combustion hazards," *Environ Health Perspect,* vol. 11, pp. 197-202, Jun 1975, doi: https://doi.org/10.1289/ehp.7511197.

Williams, S. J., Baker, B. B., and Lee, K. P., (1987) "Formation of acute pulmonary toxicants following thermal degradation of perfluorinated polymers: Evidence for a critical atmospheric reaction," *Food and Chemical Toxicology,* vol. 25, no. 2, pp. 177-185, 1987/02/01/ 1987, doi: https://doi.org/10.1016/0278-6915(87)90152-9.

Fluoropolymers

Product Group of Plastics Europe

FPG - Fluoropolymers Product Group, https://fluoropolymers.eu/
Plastics Europe AISBL, Rue Belliard 40, box 16, 1040 Brussels, Belgium
Transparency Register: 454264611835 56