

# Guide to the Safe Handling of Fluoropolymer Resins

FIFTH ADDITION

**BP - 101**

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Consult the following information in fire emergencies and other emergencies. Be sure to review the details of proper handling and use of fluoropolymers in this Guide. Questions about proper use of fluoropolymer resins should be directed to the resin supplier. Questions about this Guide or the Fluoropolymers Division (FPD) should be directed to The Plastics Industry Association

## **IN CASE OF FIRE**

- Fluoropolymers do not burn without an external source of heat (See page 40.)
- The principle decomposition products in a fire are *hydrogen fluoride (HF)*, *carbonyl fluoride (COF<sub>2</sub>)*, and *carbon monoxide (CO)* and *low molecular weight fluoropolymers*. (See page 15.)
- Wear *self-contained breathing apparatus (SCBA)* to protect skin and eyes from contact with HF (See page 35.)
- Wear *full turnout gear or Level A equipment*, to protect skin, eyes and respiratory system from contact with HF (See page 35)
- Decontaminate personnel and equipment with water wash-down after fire and smoke exposure, as well as after salvage and overhaul. (See page 36.)
- See the National Fire Protection Association's publication, *Fire Protection Guide to Hazardous Materials*, 13th Edition and 29 CFR 1910.10 (k), "Hazardous waste operations and emergency response," for guidelines.

## **EMERGENCY RESPONSE**

- Hazardous fumes from PTFE may be produced at temperatures above 625°F (330°C). (See pages 14 and 19.)
- Toxic fumes from PTFE may be formed at 840°F (450°C) and above. (See pages 14 and 19.)
- Hazardous vapor and fumes will be liberated during a fire. (See page 40.)

**EMERGENCY RESPONSE NUMBERS** (see page 43 for additional information):

- Transportation Emergency for AGC Chemicals Americas, Arkema, Daikin America, CHEMOURS, and Solvay Solexis: (CHEMTREC) – (800) 424-9300
- For Dyneon/3M ONLY: (800) 364-3577

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**First Edition:           October 1992**  
**Second Edition:       October 1995**  
**Third Edition:           June 1998**  
**Fourth Edition:       November 2005**  
**Fifth Edition:           January 2019**

## **NOTE TO USERS**

This Guide was developed by the Fluoropolymers Division of The Plastics Industry Association, and is intended to provide information on general guidelines for safe handling of fluoropolymer resins in processing. The guidelines provided are based on the collective experience of members of the industry, but are not intended to be either exhaustive or inclusive of all pertinent requirements. The information provided in this guide is offered in good faith and believed to be reliable, but is made WITHOUT WARRANTY, EXPRESSED OR IMPLIED, AS TO THE MERCHANTABILITY, FITNESS FOR A PARTICULAR PURPOSE, OR ANY OTHER MATTER. The guidelines provided and the examples included are not intended to be directed to any particular product, nor are they claimed to satisfy all current legal requirements related to control of processing operations. Following the Guide does not guarantee compliance with any regulation nor safe operation of processing facilities. 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 Guide is not intended to provide specific advice, legal or otherwise, on particular products or processes. In designing and operating processing lines, users of the Guide should consult with their own legal and technical advisors, their suppliers, and other appropriate sources (including but not limited to product or package labels, technical bulletins, or sales literature) which contain information about known and reasonably foreseeable health and safety risks of their proprietary products and processes. Plastics Industry Association, its members and contributors do not assume any responsibility for the user's compliance with any applicable laws and regulations, nor for any persons relying on the information contained in this Guide.

The PLASTICS INDUSTRY ASSOCIATION, does not endorse the proprietary products or processes of any manufacturer or user of fluoropolymer resins or products. All information about an individual manufacturer's products contained herein has been provided by those manufacturers who are solely responsible for the accuracy and completeness of the data.

## INTRODUCTION

Fluoropolymers are produced and sold worldwide by several manufacturers and are essential to a variety of technologies and products that enhance human life and promote environmental improvements. Ranging from power generation to emission controls on vehicles, to semiconductor chip manufacturing and aerospace applications, fluoropolymers provide superior performance in products that contribute to increased safety in offices, homes, industry, and communities. Collectively this creates socio-economic value far beyond the direct impact of manufacturing and processing fluoropolymers, as demonstrated in the “Socio-economic Analysis of the European Fluoropolymer Industry”.

Fluoropolymers provide unique and critical performance properties in “system critical” applications that protect and benefit people and the environment. Fluoropolymers are among the few plastic materials that can withstand the temperatures inside ovens and the engine compartments of aircraft. Combined with chemical resistance and excellent dielectric stability, the heat resistance of fluoropolymers resins provides for an extremely versatile family of engineering materials. Fluoropolymers have high resistance to a broad range of fuels, solvents and corrosive chemicals. These unique properties provide critical performance characteristics needed to prevent fire, fluid emission, electrical overloading or similar emergencies in many high-performance applications. In addition, for virtually all of these applications, fluoropolymers are one of the very few materials that meet system performance needs in high temperature and harsh chemical environments.

Consistent with the principles of Responsible Care<sup>®</sup>, the intent of this guide is to provide processors and users of fluoropolymers with an overview of the safe handling and processing of fluoropolymers. Specifically, this Guide is intended to provide the necessary information to processors using fluoropolymers so they can meet their obligations under applicable Federal, state and local laws. This document includes the latest technical and research information currently available and may be updated in the future, but users are responsible for the interpretation and applicability of all information presented to their own operations.

Processors may also find the information in this guide useful in providing assistance to customers about the health, safety and environmental issues associated with using products made from or with fluoropolymers. Legal obligations require processors to pass along information about the hazards and safe handling of the products they make with fluoropolymers and to evaluate those products with respect to any changes in the nature or extent of the hazards due to the changes made by the processor in manufacturing its products. Good product stewardship requires that a seller of a product take steps to assure that customers receive appropriate information about its products. This guide may be helpful in doing so.

**CHAPTER 1 - FLUOROPOLYMER TYPES AND PROPERTIES**

The typical fluoropolymer types covered by this guide are discussed below. The information contained herein is taken from ASTM documents listed in Appendix A. Some companies may offer other specialty fluoropolymers that may not be included in this guide. Information on these fluoropolymers should be obtained from the manufacturer.

*A. Fluoropolymer Types*

- ECTFE** ECTFE is a copolymer of ethylene and chlorotrifluoroethylene having the formula  $[(CH_2-CH_2)_x-(CFCl-CF_2)_y]_n$ . ECTFE has a melting point range of 428o – 473oF (220o - 245oC) and is melt processable. It is available in the form of translucent pellets and as a fine powder.
- EFEP** EFEP is a copolymer of ethylene, tetrafluoroethylene, and hexafluoropropylene with the formula  $[(CH_2-CH_2)_x(CF_2-CF_2)_y(CF(CF_3)-CF_2)_z]_n$ . EFEP polymers melt at 311o – 392oF (155 – 200oC). It is melt processable and is supplied in pellet form.
- ETFE** ETFE is a copolymer of ethylene and tetrafluoroethylene of the formula  $[(CF_2-CF_2)_x-(CH_2-CH_2)_y]_n$ . Depending on various grades ETFE melts between 428oF – 518oF (220oC – 270oC). It is melt processable and is supplied in pellet and powder form.
- FEP** FEP resin is a copolymer of tetrafluoroethylene and hexafluoropropylene with the formula  $[(CF(CF_3)-CF_2)_x(CF_2-CF_2)_y]_n$ . It has a melting point range of 473o - 536oF (245o - 280oC) and is melt processable. It is supplied in the form of translucent pellets, powder, or as an aqueous dispersion.
- HTE** HTE is a copolymer of hexafluoropropylene, tetrafluoroethylene, and ethylene. HTE is melt processable with melting points from 310o to 420oF (155o to 215o C) depending on grade. It is available in pellet or agglomerate form.
- MFA** MFA is a copolymer of tetrafluoroethylene and perfluoromethylvinylether. It belongs to the generic class of PFA polymers. MFA melts at 536o– 554oF (280o- 290oC). It is available in the form of translucent pellets and aqueous dispersions.
- PCTFE** PCTFE is a polymer of chlorotrifluoroethylene with the formula  $[CF_2-CFCl]_n$ . It has a melting point range of 410o- 428oF (210o - 220oC) and is melt processable. It is available in pellet, granular and powder form.
- PFA** PFA resins are copolymers of TFE fluorocarbon monomers containing perfluoroalkoxy side chains. PFA melts at 536 oF (280oC) minimum and is melt processable. It is available in the form of pellets, powder, and as an aqueous dispersion.



- PTFE** PTFE is a polymer consisting of recurring tetrafluoroethylene monomer units whose formula is  $[\text{CF}_2\text{-CF}_2]_n$ . PTFE does not melt to form a liquid and cannot be melt extruded. On heating the virgin resin, it forms a clear, coalescable gel at  $626^\circ\text{F} \pm 18^\circ$  ( $330^\circ\text{C} \pm 15^\circ$ ). Once processed, the gel point (often referred to as the melting point) is  $18^\circ\text{F}$  ( $10^\circ\text{C}$ ) lower than that of the virgin resin. It is sold as a granular powder, a fine powder, or an aqueous dispersion. Each is processed in a different manner.
- PVDF** PVDF is a homopolymer of vinylidene fluoride having the formula  $[\text{CH}_2\text{-CF}_2]_n$  or a copolymer of vinylidene fluoride and hexafluoropropylene having the formula  $[\text{CF}(\text{CF}_3)\text{-CF}_2]_x[\text{CH}_2\text{-CF}_2]_y]_n$ . Copolymers of vinylidene fluoride are also produced with (1) chlorotrifluoroethylene, (2) tetrafluoroethylene, and (3) tetrafluoroethylene and hexafluoropropylene. These are all sold as PVDF copolymers. PVDF polymers/copolymers melt at  $194^\circ\text{-}352^\circ\text{F}$  ( $90^\circ\text{-}178^\circ\text{C}$ ), are melt processable, and are supplied in the form of powder, pellets, and dispersions.
- THV** THV is a copolymer containing tetrafluoroethylene, hexafluoropropylene and vinylidenefluoride. THV is melt-processable with melting points from  $240^\circ$  to  $455^\circ\text{F}$  ( $115^\circ$  to  $235^\circ\text{C}$ ) depending on grade. It is available in pellet, agglomerate or aqueous dispersions.

*B. Thermal Properties*

Although fluoropolymers are among the most stable polymers known, they will start to decompose slowly when heated to elevated temperatures. There is some contradiction in the published literature as to the exact temperature at which decomposition occurs, reflecting the difficulty in analyzing trace element emissions. However, significant decomposition occurs only when fluoropolymers are heated above their recommended processing temperatures. The quantity of effluent evolved remains small until temperatures in excess of the normal processing temperature for the polymer are reached.

The typical melting points, continuous use and processing temperatures for fluoropolymers are given in Table 1.

*Table 1 - Typical Melting Points, Continuous Use and Processing\* Temperatures of Fluoropolymers\*\**

Polymer	Typical Melting Point Temperature °F (°C)	Typical Continuous Use Temperature, °F (°C)	Typical Processing Temperature, °F (°C)
ECTFE	446 (230)	285 (140) – 300 (150)	540 (280) – 590 (310)
EFEP***	316 (158) - 383 (195)	212 (100) – 302 (150)	428 (220) – 500 (260)
ETFE***	428 (220) - 518 (270)	300 (150)	590 (310)
FEP	500 (260)	400 (205)	680 (360)
HTE***	320 (160) - 410 (210)	220 (105) – 300 (150)	390 (200) – 550 (290)
MFA	536 (280)	480 (249)	680 (360)
PCTFE	419 (215)	250 (120)	510 (265)
PFA	581 (305)	500 (260)	715 (380)
PTFE	626 (330)	500 (260)	715 (380)
PVDF	338 (170)	300 (150)	450 (232)
PVDF Copolymer***	239 (115) – 338 (170)	212 (100) – 300 (150)	450 (232) – 480 (249)
THV***	250 (120) - 446 (230)	158 (70) – 265 (130)	340 (171) – 590 (310)

\* Certain nonstick coating processes typically exceed these temperatures. See Chapter 3.

\*\* Note that the temperatures in this table are actual polymer temperatures — not oven or equipment temperatures, which may be significantly higher. Processing and Continuous Use Temperatures depend on use, environment and processing history. Consult your resin supplier for details.

\*\*\*Product families include different products with different continuous use temperatures and different processing temperatures.

*C. Product Information Sources*

Listed below are the addresses of resin manufacturer members of The Society of the Plastics Industry, Inc., Fluoropolymers Division, who contributed to this document:

**AGC Chemicals Americas Inc.**

55 East Uwchlan Ave. #201  
Exton, PA 19341  
Product Information: (800) 424-7833

**Arkema, Inc.**

Technical Polymers Department  
900 First Avenue  
King of Prussia, PA 19406-1308  
Product Information: (800) 722-9668  
(610) 205-7000

**Daikin America, Inc.**

20 Olympic Drive  
Orangeburg, NY 10962  
Product Information: (800) 365-9570

**The Chemours Company**

1007 Market Street  
Wilmington, DE 19899  
Product Information: (800) 441-7515  
(302) 773-1000

**Dyneon LLC, A 3M Company**

3M Center Building  
280-01W-03  
St. Paul, MN 55144  
Product Information: (800) 810-8499

**Solvay Specialty Polymers**

10 Leonard Lane  
West Deptford, NJ 08086  
Product Information: (856) 853-8119

## CHAPTER 2 - POTENTIAL HEALTH EFFECTS

### A. General Toxicology

Fluoropolymers are known for their excellent chemical stability and low reactivity. These polymers are not classified as hazardous substances according to GHS criteria (<https://www.ccohs.ca/oshanswers/chemicals/ghs.html>) and have been assessed to show that they “satisfy widely accepted assessment criteria to be considered as “polymers of low concern”.”.. The *Integrated Environmental Assessment and Management*, Vol. 14, No. 3, pp 316-334 indicates fluoropolymers have the following inherent toxicity:

- They have negligible residual monomer and oligomer content and low to no leachables.
- Fluoropolymers are practically insoluble in water and not subject to long-range transport.
- With a molecular weight well over 100,000 Da, fluoropolymers cannot cross the cell membrane.
- Fluoropolymers are not bioavailable or bioaccumulative, as evidenced by acute and subchronic systemic toxicity, irritation, sensitization, local toxicity on implantation, cytotoxicity, in vitro and in vivo genotoxicity, hemolysis, complement activation, and thrombogenicity studies on PTFE
- Clinical studies of patients receiving permanently implanted PTFE cardiovascular medical devices demonstrate no chronic toxicity or carcinogenicity and no reproductive, developmental, or endocrine toxicity.

New forms of fluoropolymers, such as nanoscale materials, may have unknown toxicological properties. As discussed below in section F of this Chapter, some fluoropolymers are formulated with additives such as fillers, pigments or surfactants, to provide improved processing or other characteristics. These additives may present other hazards in the use of the fluoropolymer resin. Consult the Safety Data Sheet (SDS) from the manufacturer for health information on the specific product you intend to process.

### B. Pellets, Powders and Nanoscale Materials

Routine handling and processing of fluoropolymer pellets and powders can produce exposure to dusts that are generally regarded as nonhazardous nuisance dusts. The U.S. Occupational Safety and Health Administration (OSHA) has established the following Permissible Exposure Limits (PELs) for Particulates Not Otherwise Regulated: Total dust, 15 mg/m<sup>3</sup>, Respirable fraction, 5 mg/m<sup>3</sup>. The TLV®-TWAs for Particulates

Not Otherwise Classified (PNOCs) are: Inhalable particulate, 10 mg/m<sup>3</sup>; Respirable particulate, 3 mg/m<sup>3</sup>. The use of engineering controls is recommended if the fluoropolymer is dispersed in air or if the fluoropolymer contains other hazardous

components. In the absence of adequate control of the contaminants, appropriate respiratory protection should be used. For typical handling tasks, air-purifying respirators with appropriate filters should be used. If dust exposures exceed the values cited above, selection of the appropriate respirator must follow current OSHA requirements.

New forms of fluoropolymers based on nanotechnology manufacturing techniques are finding their way into the marketplace, and such fluoropolymer materials may have different or unknown toxicological properties compared to the parent fluoropolymer. (Nanopowders are defined as particles which range in size from 1 to 100 nanometers (nm) ( $10^{-9}$  meter)). [Recent studies](http://www.cdc.gov/niosh) ([www.cdc.gov/niosh](http://www.cdc.gov/niosh)) suggest that nanoparticles may produce adverse effects in animals without apparent chemical effect. Some scientists are concerned that nanoparticles can penetrate the skin and translocate from the respiratory system to other organs. As different or unique procedures may be needed to handle and process nanomaterials safely, it is imperative that you consult with your supplier to obtain the SDS for the specific nano-fluoropolymer product you intend to handle and process.

### *C. Health Effects of Decomposition Products*

Although fluoropolymers are among the most thermally stable plastics, fluoropolymers will start to generate toxic air contaminants slightly above their recommended processing temperatures. This is why manufacturers recommend the use of local exhaust ventilation during processing operations. The rate of generation rises as temperatures increase and may cause sufficient degradation of the polymer to produce particulate fume as well as toxic gaseous by-products.

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. The four main types of products formed in the decomposition of fluoropolymers are fluoroalkenes, hydrogen fluoride, oxidation products, and low-molecular-weight fluoropolymer particulates. The presence of other monomers or additives in the fluoropolymer resin may change the nature of the decomposition products.

In the case of PTFE, numerous studies in the published literature 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 625°F (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 PTFE temperature increases to approximately 840°F (450°C) in air, carbonyl fluoride and hydrogen fluoride become the main decomposition products. Carbonyl fluoride hydrolyzes 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 chemical, perfluoroisobutylene, has been detected as a

minor product at temperatures above 890°F (475°C). When the temperature reaches approximately 1,470°F (800°C), tetrafluoromethane begins to form.

There is a similar decomposition pattern for other fluoropolymers. Decomposition products tend to form at lower temperatures and are dependent on the type and amount of copolymer in the fluoropolymer. Hazardous gases and vapors produced in fires involving fluoropolymers include hydrogen fluoride, carbonyl fluoride, carbon monoxide, and low molecular weight fluoropolymers.

#### *D. Polymer Fume Fever (Inhalation Fume Fever)*

The most common adverse effect associated with human exposure to fluoropolymer decomposition products is widely recognized as “polymer fume fever” (PFF). PFF is a temporary flu-like condition that lasts approximately 24 hours. PFF is similar to metal fume fever (foundry man’s fever) [Harris, D. K., Lancet 261, 1008, December, 1951] and other inhalation fevers. Symptoms include fever, chills and, sometimes, cough.

The article, “Characterization of Early Pulmonary Inflammatory Response Associated with PTFE Fume Exposure” [Toxicology and Applied Pharmacology, Article No. 0208, Academic Press, May 1996] found that overheating PTFE, 778°F (420°C), evolves fumes containing ultra-fine particles that can be highly toxic to the lung, causing pulmonary edema (excessive fluid in cells in the lungs) with hemorrhagic inflammation (severe irritation of the tissue with release of blood from small blood vessels). In animal experiments in which these particles were removed from the air, signs and symptoms similar to those of polymer fume fever did not develop in the animals. Unfiltered air produced the expected polymer fume fever response.

Inhalation of effluent products from overheated fluoropolymers or after smoking fluoropolymer-contaminated tobacco may also cause PFF. It is recommended that smoking and tobacco products be banned in work areas where fluoropolymer resins are processed. In addition, depending on the characteristics of the operation, local exhaust ventilation may be required.

#### *E. Other By-Products*

Depending upon the type of fluoropolymer and finished product manufacturing conditions, it is theoretically possible that small quantities of residual gases, including perfluoroisobutylene (PFIB), hexafluoropropylene (HFP), tetrafluoroethylene (TFE), and hydrogen fluoride (HF) may be trapped and slowly evolve from resins as well as finished products. Testing of some finished products has confirmed that PFIB and HFP can be found in the finished products, but the conditions under which these compounds form, and in what quantities, has not been investigated. This emphasizes the importance of

following manufacturer instructions in sintering and other finishing operations. These residual gases can accumulate in unventilated spaces (e.g., closed storage rooms, closed trucks, etc.) at levels that may be hazardous if the quantities of fluoropolymer materials and products stored are large. Therefore, it is important to ventilate these spaces before permitting personnel to enter.

Legal limits for occupational exposure to individual chemicals, called Permissible Exposure Limits (PELs), may be specified in the U.S. Code of Federal Regulations, Title 29, Part 1910, Section 1000 adopted by the US Department of Labor Occupational Safety and Health Administration (OSHA). Individual companies may establish their own limits for occupational exposure called Occupational Exposure Limits (OEL). Additional guidance regarding occupational exposure limits for individual chemicals may be available, from the American Conference of Governmental Industrial Hygienists (ACGIH) and The National Institute for Occupational Safety and Health (NIOSH). ACGIH publishes the below Threshold Limit Values (TLV) and NIOSH publishes Recommended Exposure Limits (REL). Additionally, individual companies may establish their own limits for occupational exposure called Occupational Exposure Limits (OELs).

Table 2. Fluoropolymer and monomer molecular weight and TLV data

Substance	CAS #	Molecular Weight	ACGIH TLV 8-h TWA
Monomer: TFE	116-14-3	100	2 ppm
Monomer: Ethylene	74-85-1	28	200 ppm
Monomer: HFP	116-15-4	150	0.1 ppm
Monomer: PPVE	1623-05-8	266	200 ppm (vendor limit)
Polymer: PTFE	9002-84-0	389,000-45,000,000	None
Polymer: ETFE	25038-71-5, 68258-85-5	530,000-1,200,000	None
Polymer:FEP	25067-11-2	241,000-575,000	None
Polymer:PFA	26655-00-5, 31784-04-0	200,000-450,000	None

Source: American Conference of Governmental Industrial Hygienists. 2010. TLVs and BEIs: Threshold limit values for chemical substances and physical agents and biological exposure indices. Cincinnati (OH): American Conference of Governmental Industrial Hygienists

The health hazards of the aforementioned decomposition products follow:

#### *Carbonyl Fluoride (COF<sub>2</sub>)*

The effects of overexposure to COF<sub>2</sub> may initially include: skin irritation with discomfort or rash; eye corrosion with corneal or conjunctival ulceration (destruction of the lens of the eye and surrounding tissues); irritation of the upper respiratory passages; or temporary lung irritation effects with cough, discomfort, difficulty breathing, or shortness of breath. It is important to note that the effects of exposure to carbonyl fluoride may be delayed for several hours. [Documentation of TLVs®, American Conference of Governmental Industrial Hygienists, Perfluoroisobutylene, 2004] If the effects observed include severe breathing difficulties, including congestion in the chest, seek immediate medical attention, including a period of observation. The TLV/TWA for COF<sub>2</sub> is 2 ppm and the short-term exposure limit (STEL) is 5 ppm.[American Conference of Governmental Industrial Hygienists (ACGIH), Threshold Limit Values (TLVs®) for Chemical Substances and Physical Agents and Biological Exposure Indices (BEIs®) 2005. All of the TLVs cited in this section are taken from this publication.]

*Carbon monoxide (CO)*

Carbon monoxide is an odorless 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. The TLV is 25 ppm.

*Hexafluoropropylene (HFP)*

Hexafluoropropylene is a colorless, odorless gas that is very poorly soluble in water. Hexafluoropropylene has a low toxicity after acute exposure. The genotoxicity of the compound was considered overall negative. When administered for a long period it may cause toxic effects primarily to the kidney. ACGIH has not established a TLV. Some producers have set internal OELs. Consult the fluoropolymer manufacturer's SDS for further information.

*Hydrogen Fluoride (HF)*

The odor threshold of HF is 0.036 ppm, which is less than the occupational exposure limit of 0.5 ppm TWA (time-weighted average) and a ceiling limit of 2 ppm [American Conference of Governmental Industrial Hygienists (ACGIH), Threshold Limit Values (TLVs®) for Chemical Substances and Physical Agents and Biological Exposure Indices (BEIs®) 2005. All of the TLVs® cited in this section are taken from this publication.] Inhalation of hydrogen fluoride at higher concentrations may cause: symptoms of choking, coughing, and severe eye, nose and throat irritation, possibly followed by fever, chills, difficulty in breathing, cyanosis, and pulmonary edema. Hydrogen fluoride is corrosive to the eyes, skin, and respiratory tract, and may be absorbed through the skin in toxic amounts. It can cause delayed burns that may not be immediately visible or painful. Acute or chronic overexposure to hydrogen fluoride can injure the liver and kidneys. If a person is overcome by exposure to hydrogen fluoride, seek immediate medical attention.

*Perfluorisobutylene (PFIB)*

The effects of inhalation exposure to PFIB have been studied in animals. Severe adverse effects occurred, including pulmonary edema, which can lead to death. Observed symptoms include wheezing, sneezing, difficulty breathing, and abnormally deep or rapid breathing. Animals that survive for 24 hours after exposure apparently recovered with no after-effects. Little human exposure data exists, but the ACGIH TLV-C is 0.01 ppm.

*Tetrafluoroethylene (TFE)*

TFE is a flammable, gaseous monomer that may cause acute effects when inhaled. Inhalation of TFE may cause irritation of the upper respiratory tract and eyes, mild central nervous system depression, nausea and vomiting, and dry cough. Massive inhalation of the gas may produce cardiac arrhythmia, cardiac arrest, and death. Chronic overexposure may cause toxic effects, primarily to the kidney.

*Other Considerations*

Individuals with preexisting diseases of the lungs may have increased susceptibility to the toxicity of excessive exposures from thermal decomposition products. Consult the



Safety Data Sheets (SDS) supplied by the resin manufacturer for additional information. While there are no known fatalities directly attributed to exposure to fumes generated by heating fluoropolymer resins in routine handling or processing, it continues to be important to require proper ventilation to prevent occupational illnesses or injuries. There has been one reported fatality that resulted from intentionally burning fluoropolymer-containing materials in equipment that was not properly equipped to handle the emissions. No cases of fatal injury are known when normal processing temperatures are not exceeded.

According to the 11<sup>th</sup> Report on Carcinogens, TFE is classified as reasonably anticipated to be a human carcinogen based on sufficient evidence of malignant tumor formation at multiple sites in multiple species of experimental animals [Report on Carcinogens, Eleventh Edition; U.S. Department of Health and Human Services, Public Health Service, National Toxicology Program.] The relationship of these effects to potential human response has not been established. The current TLV/TWA value is 2 ppm.

#### *F. Hazards of Compounds Containing Pigments and Fillers*

Filled and pigmented fluoropolymers are in widespread use. The normal precautions for handling fluoropolymers (i.e., ventilation, appropriate PPE) need to be observed. In addition, processors need to note any additional hazards associated with the fillers or pigments themselves as outlined on the product specific SDS.

Although many of the commonly used fillers and pigments have low toxicity, some are abrasive and may cause skin irritation. Avoid skin contact with filled or pigmented fluoropolymers or inhalation or ingestion of filled or pigmented fluoropolymer dust. When fluoropolymers containing cadmium pigments are handled, extra precautions may be necessary and compliance with OSHA standard 29 CFR 1910.1027 (Cadmium) is required. Contact your supplier prior to using filled and/or pigmented fluoropolymers for specific safety recommendations. When a processor adds pigments, fillers, or other materials to fluoropolymers, a hazard determination as required by the OSHA Hazard Communication Standard (HCS), 29 CFR 1910.1200 must be performed. Health and safety information must be obtained from the vendors of the additives, and the fluoropolymer processor must prepare MSDS for and affix appropriate hazard warning labels to containers of the filled resin. The processor who makes parts from the filled resins must determine, whether, in the normal circumstances of use, the part will release hazardous chemicals causing exposure of users. If so, an SDS and appropriate label must be provided.

**CHAPTER 3 - PROCESSING HAZARDS AND PRECAUTIONS***A. Heat Treating, Sintering, and Coalescence*

Heating fluoropolymers like PTFE to their melting point temperatures causes the polymer particles to melt and fuse together, eliminating voids that may result in weak points or flaws in the polymer structure. This process is termed heat treating, sintering or “coalescence” when applied to PTFE processing and is similar to the sintering process utilized in metallurgy. Other fluoropolymers are also heat-treated to achieve final polymer properties. The time and temperature profile of the sintering cycle determine the physical properties that the fluoropolymer will exhibit.

Because of the high temperatures required to sinter PTFE and melt other fluoropolymers, hazardous decomposition products form in processing ovens. Regardless of their design (batch, conveyor, chain-on-edge), ovens used to process or heat-treat fluoropolymers must have mechanical (forced) ventilation with sufficient airflow to remove hazardous compounds from them during their operation and to keep them from entering the work area. Oven exhausts are likely to be subject to local air pollution control requirements and may require controls to remove the decomposition products and other substances from the exhaust air stream. If the oven is a batch oven, oven doors must be properly adjusted and gaskets must be checked for serviceability to ensure that toxic gases do not leak into the workplace.

In addition to ensuring the level of ventilation is adequate, other safeguards should be employed to control potential exposure to hazardous decomposition products (please refer to Table 1 for typical processing temperatures). To ensure their safe operation, ovens should be equipped with an independent, high-temperature cut-off switch triggered by temperature increases that allows adequate control of the oven-set temperature, consistent with today's technology, to the level recommended by the fluoropolymer manufacturer. Allowable temperature increases should be no more than 50° to 60°F (28° to 33°C) higher than the recommended oven-set temperature. Both controls – the oven temperature controller and the high-temperature cut-off switch – should be calibrated frequently.

If a processing oven overheats and an inspection or repairs are needed, the oven must be cooled to ambient temperatures and purged of all fumes before entering the area or opening the door. Emergency or maintenance personnel must wear all appropriate Personal Protective Equipment (PPE), including eye protection, protective clothing and gloves, and appropriate respiratory protection. For emergencies and unknown concentrations, use self-contained breathing apparatus or a supplied-air respirator.

When opening, operating, or working in close proximity to processing ovens used to heat-treat fluoropolymers, appropriate PPE must be worn. Appropriate PPE may include protective clothing and gloves, protective eyewear and respiratory protection.

Certain nonstick coating processes for fluoropolymer dispersions may use processing temperatures as much as 100°F higher than those recommended in Table 1, to achieve certain technical effects. Ultra-high-temperature processing is defined as heat-treating at temperatures that exceed the typical processing temperatures listed in Table 1. Because the formation of hazardous decomposition products is accelerated during ultra-high-temperature processing, these operations must be conducted under carefully controlled conditions.

The appropriateness of engineering controls, work practices, and PPE (including eye protection, protective clothing and gloves, and appropriate respiratory protection) must be reviewed. Suitable actions must be taken prior to operations or trials to ensure employees are protected. Environmental releases of fumes, toxic chemical compounds and particulate matter to the environment must also be considered and if necessary controlled to comply with Federal, state, and local regulations. Potential residues of decomposition products in the coating should also be considered and managed as necessary.

Each fluoropolymer processor who contemplates ultra-high-temperature processing should consult the coatings supplier to ensure that the processor has complete knowledge and understanding of the equipment, processes, procedures, engineering controls, work practices, and safeguards necessary to safely process the anticipated volume of fluoropolymer products. The processor should also ensure that the ultra-high-temperature processing operations do not exceed the design limits of the equipment to be used for the ultra-high-temperature processing of fluoropolymer.

### *B. Melt Processing*

Precautions must be taken in the melt processing of any polymer to avoid the release of excessive levels of hazardous degradation products. Thermal decomposition of any polymer, halogenated or non-halogenated, leads to the release of toxins.

Melt processing of fluoropolymer resins in excess of recommended processing temperatures or exposing them to processing temperatures for extended times can cause rapid decomposition of the resins. Decomposition will produce gases at rates that can generate pressures in processing equipment sufficient to “blow back” through the feed port. If no exit path is available for these gases, as in some compression molding equipment, pressures can develop which may rupture metal parts, possibly with explosive force, and possibly cause injury to personnel near the processing equipment. It is considered an unsafe practice to stand in front of an extruder die face that is processing any thermoplastic, especially during start up.

To reduce the potential for accelerated decomposition of fluoropolymers, some manufacturers recommend the use of corrosion-resistant materials for processing equipment. Contact your material suppliers for specific product information.

If a fluoropolymer resin melt begins to darken, the color change is an indication that thermal degradation has begun. 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 vary less than plus or minus 10°F (6°C).

Melt extrusion of fluorinated polymers always leads to some degradation of the polymer. For FEP, for example, this degradation has two results:

- Lower molecular weight polymer (higher melt flow rate)
- Evolution of the toxic compound perfluoroisobutylene (PFIB) as well as other reactive by products.

PFIB may become trapped in the molten polymer and its slow evolution can present a hazard if substantial quantities of coated wires are stored in poorly ventilated areas.

Extrusion foaming processes are used to manufacture polymer insulation materials with superior electrical properties. Excessive temperatures and high shear rates should be avoided during such foaming processes.

With respect to FEP, research indicates that such anaerobic conditions can create potentially hazardous levels of hydrogen fluoride (HF) and perfluoroisobutylene (PFIB). Any extrusion foaming process that generates excessive temperatures and shear rates by its very design (e.g., the so-called "Free Foam" or "Free Flow" process), should be avoided because of the potential to release toxins at hazardous levels.

Plastics Industry Association has long recommended industrial hygiene practices designed to minimize safety hazards associated with melt extrusion, regardless of method. However, due to our assessment of the hazards associated with the "Free Foam" process and the availability of safer foaming methods, ***Plastics Industry has issued a notice to FEP and other polymer processors that foaming by the "Free Foam" process should not be done as the process creates potentially increased safety hazards.***

For FEP processing, the formation of PFIB in both solid and foamed wire constructions emphasizes the necessity for local exhaust ventilation above the extruder die, along the coating line, in storage areas where spools of coated wire may be stored or anywhere the gases can escape into the air of the facility. This would include the exhaust from the vacuum pump used to control the length of the melt cone in solid or in foamed

extrusions. It is also recommended that a minimum of six (6) air changes per hour be maintained in all areas.

Research has been conducted to understand the degradation products and support the recommendations given (See Appendix B).

### *C. Paste Extrusion*

Processing PTFE fine powder resins requires extrusion by a special process, commonly known as paste extrusion. This involves mixing the resin with a lubricant, usually a volatile petroleum solvent. The use of combustible and flammable liquids of relatively low flash point may create a significant potential fire and explosion hazard. In addition, solvents may cause health hazards due to inhalation and/or skin contact. Appropriate precautions must be taken for the safe use, storage, and handling of fluoropolymer resins containing solvent-based lubricants. Follow the recommendations of the solvent and PTFE suppliers and the information on the SDS.

Removal of the lubricant (solvent) after extrusion may take place in a separate batch drying oven or in a continuous oven fitted in-line with the extruder. Appropriate precautions need to be taken to minimize the risk of forming explosive mixtures of lubricant and air, and to prevent ignition. With an in-line operation, the drying operation is immediately followed by high temperature sintering, and there is the possibility that incorrect operation would cause flammable vapors to be carried into the sintering zone where it will almost certainly ignite if allowed to accumulate to sufficient concentrations. 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 entire 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 work place. Consult a fire protection engineer for specific design details.

### *D. Coating / Impregnation*

Even though fluoropolymer dispersions may not be classified as hazardous, they may contain small amounts of an ingredient used as a fluoropolymer polymerization aid (FPA). Additional information on FPAs may be found in [Appendix E](#). People working with dispersions should follow best practices to avoid exposure through skin contact, ingestion, or inhalation of dust or vapor from fluoropolymer dispersions.

Coating with fluoropolymer dispersions may involve the following processing steps: mixing of dispersions with other ingredients, applying the formulated dispersion onto surfaces, fabrics or yarns, by spraying or passing them through a dispersion bath, followed by drying, baking or sintering of the coated product.

The primary health and safety concerns for the mixing and the application steps are to avoid skin exposure by direct contact and splashing. There may be other hazards introduced by the use of other ingredients added to the dispersion not covered here (refer to the SDS).

Spraying of dispersions may generate a mist that might be an additional exposure route. Ventilation, personal hygiene and personal protective equipment (PPE) like gloves, goggles, face shields, lab clothing, protective footwear, etc. are commonly used to protect from these exposure sources.

Water and other volatile ingredients (or their degradation products) are removed from the coated products by drying, baking and sintering. These processes also have safety and health concerns such as burns from hot surfaces, and the inhalation of mists, vapors or fumes. Ventilation that is working properly and procedures that ensure proper ventilation of the oven prior to opening, as well as PPE (like heat protective gloves, etc.) are important safety measures.

Cleaning and maintenance of equipment that has been used to handle dispersions or vapors from hot processing of dispersions should always be performed under the assumption that the equipment is contaminated by FPA. FPAs may condense on surfaces, and so be present at higher concentrations than in the dispersion itself.

The health and safety issues are skin exposure by direct contact, splashing and inhalation of dust, mists and vapors. Personal protective equipment (such as protective clothing, gloves, goggles or face shield, respirator, etc.) should be used. The equipment should be vented and cooled before cleaning and maintenance. Risk assessments and work procedures that minimize the potential for exposure, particularly for unfamiliar tasks or unscheduled maintenance, are recommended.

#### *E. Grinding, Sawing and Machining Fluoropolymers and Fluoropolymer-Coated Articles*

Fluoropolymers and fluoropolymer-coated articles are routinely subjected to grinding, sawing, and machining operations. These operations may release and disperse small particles of dust, metal, and other contaminants into the air. These particles may be harmful if inhaled.

The presence of other materials either in the fluoropolymer resin or in a substrate may create hazardous dusts or particulate matter during these operations. Use engineering controls, including mechanical ventilation and local exhaust, to reduce airborne contaminants to below occupational exposure limits. For emergencies or unknown concentrations of dust, consult the manufacturer's SDS for specific respiratory recommendations.

The use of coolants during such operations is recommended. Coolants generally improve production rates and quality, reduce or eliminate the potential to generate

excessive heat and airborne particulate matter and may eliminate the need for special engineering controls like local ventilation.

Consult manufacturers' SDS for specific requirements and additional information.

#### *F. Using Cutting and Welding Torches on Fluoropolymer Articles*

Use appropriate techniques when welding fluoropolymers. Consult fluoropolymer resin suppliers for technical information. Excessive heat, including heat from cutting torches and welding operations, can quickly destroy the useful properties of fluoropolymer-based articles. For this reason, it is advisable to remove fluoropolymer parts from equipment that needs to be flame-cut or welded. Where removal of fluoropolymer parts is impractical or impossible, mechanical ventilation or respiratory protection must be provided to prevent exposure to toxic fumes.

As the products of thermal decomposition of fluoropolymers are difficult to measure, even under laboratory conditions, it may be difficult to determine if engineering controls are sufficient to reduce exposure levels to below occupational exposure limits. Because of these difficulties, it is prudent to require respiratory protection against fluoropolymer decomposition products during cutting torch and/or welding operations. Consult a certified industrial hygienist to review unique operations and identify the level of respiratory protection and other Personal Protective Equipment (PPE) that are appropriate for the situation.

#### *G. Cleaning and Maintenance of Process Equipment*

Cleaning processing equipment components (dies, screen packs, screws, etc.) may result in the pyrolysis of residual polymer remaining on the equipment. Care should be exercised to remove any residual fluoropolymer from equipment prior to burning off or pyrolysis operations. Failure to do so can result in the release of toxic and corrosive gases that can corrode some types of metals.

Due to their low surface tension fluoropolymers can often be effectively removed from metal surfaces by scraping or brushing with utensils made of soft metals such as brass. When this is not possible manufacturers often recommend purging equipment with a high viscosity purging compound or non-fluoropolymer which can be pyrolyzed cleanly and easily.

Appropriate ventilation and protective equipment should be designed to completely capture and remove the gases and particulate matter that are formed in the work environment. Please refer to the chapter on ventilation.

Processing vessels and ovens (equipment) can be defined as confined spaces under OSHA Standard 29 CFR 1910.146 Permit-Required Confined Spaces. Equipment that has been used to process fluoropolymers or fluoropolymer dispersion coatings often contains residual chemicals and decomposition products that may create a hazardous

atmosphere requiring compliance with the Standard. The Standard requires a comprehensive written program for protecting employees from permit-controlled confined space hazards and for regulating employee entry into permit-controlled confined spaces. Further, additional topics must be addressed including: acceptable work practices, pre-entry air monitoring, atmospheric hazard controls, perimeter controls, personal protective equipment and general-entry equipment provision, entry attendant, procedures for summoning rescue and emergency services, entry permit administration, contractor involvement, and an annual review of the program. Processors should review 29 CFR 1910.146 to ensure all requirements of the Standard are met prior to confined-space entry.

#### *H. Spills*

Fluoropolymers spilled during handling should be cleaned up immediately and appropriate measures taken to prevent the creation of a slippery surface. It is advisable that some form of anti-slip flooring or similar preventive measures be provided in areas where fluoropolymer resins are regularly handled. Slippery surfaces in walking and working areas pose increased accident risks. In case of a release or spill, liquids must be cleaned up promptly before the liquid carrier dries to prevent contamination of other surfaces in the area. Contain and absorb material onto sawdust, oil-dry or similar inert absorbent. Any remaining waste should be cleaned-up. Spilled materials should be placed into a covered container for disposal according to applicable local, state and federal regulations. Powder or pellets forms should be swept up immediately and properly disposed of according to applicable local, state and federal regulations. During clean up, caution must be exercised, as the spill area may be extremely slippery. Ventilation and appropriate Personal Protective Equipment (PPE) must be used when cleaning up a spill.

#### *I. Emissions from Resins and Manufactured Products*

Depending upon the material and finished product manufacturing conditions, it is theoretically possible that small quantities of residual gases, including PFIB, HFP, TFE, and HF may be trapped and slowly evolve from resins as well as finished products. According to *Integrated Environmental Assessment and Management (Vol. 14. No.3)*, the amount of residuals contained within select fluoropolymers are as follows:

Table 3: Fluoropolymer Residuals

Fluoropolymer	PTFE	ETFE	FEP	PFA
Residual Monomers Amount	<1ppm	<50ppb	<50ppb	<50ppb
Ratio of Residual Monomers to Molecular Weight	$\sim 10^{-13}$ to $10^{-15}$	$\sim 10^{-13}$ to $10^{-14}$	$\sim 10^{-13}$	$\sim 10^{-13}$



The residual gases can accumulate in unventilated spaces (e.g., closed storage rooms, closed trucks, etc.) at levels that may be hazardous if the quantities of fluoropolymer materials and products stored are large. Therefore, it is important to ventilate these spaces before permitting personnel to enter.

Packages that have been sealed may also contain significant concentrations of these gases; therefore, they should be opened in well-ventilated areas. Fluoropolymer processors should evaluate the potential for exposure to these gases in their operations, taking into account the type of resins they handle, the quantities involved, the tasks being performed, and the specific facilities in which the work is done.

#### *J. Incompatibility with Powdered Materials*

Fluoropolymer resins may react with specific powdered materials through a wide range of temperatures. Finely divided fluoropolymer resins can become extremely combustible in the presence of various metal fines. For example, metal fines (e.g., bronze, aluminum) mixed with powdered fluoropolymers when exposed to high temperatures (above typically recommended melt temperatures) may react violently producing fire and/or explosion. Exothermic reactions may occur even at sintering temperatures leading to fires. An example is the reaction of PVDF with glass fibers or powder at temperatures just slightly above normal melt processing temperatures. The decomposition can become violent.

Contact your materials supplier for specific information.

**CHAPTER 4 – INDUSTRIAL OCCUPATIONAL HYGIENE*****A. Ventilation***

In this section, methods, equipment and procedures to reduce and control exposures to monomer gases and effluent gases produced during processing of fluoropolymers are described. Processors should evaluate their operations in light of the quantities of resin processed, the type of processes used, and the physical plant in which the processing takes place to determine what, if any, of the controls described are appropriate or necessary. Good industrial hygiene practice as well as legal obligations under the Occupational Safety and Health Act (OSHA) may require processors to adopt one or more of the controls described and may require additional actions if air contaminants exceed occupational exposure limits. Following the methods described does not guarantee compliance or safety; however, the experience of processors and resin manufacturers over time suggests that the controls described are necessary in many, if not most, fluoropolymer processing operations.

If the processor does not employ knowledgeable individuals, consultants may be required to thoroughly assess the operations, evaluate the hazards, and assist in the design of appropriate controls. References for qualified consultants can be obtained from your resin supplier.

As with most polymers, minute quantities of residual gases may diffuse from the resins even at room temperature. Therefore, as a matter of good industrial practice, resin containers should be opened and used only in well-ventilated areas. Some resins may require the use of local exhaust ventilation to prevent exposure to hazardous gases that accumulate in the package during storage, shipping, and handling. Consult your resin supplier's SDS for specific recommendations.

All fluoropolymer resin processing (e.g., extrusion, molding, spray coating, and wire and cable coating) will release gases, vapors, or fumes that may be harmful to human health, if exposures are high. The typical continuous use and processing temperatures are noted on in Table 1.

The most effective way to control these emissions is to “capture” them at the point of release from equipment and remove them by exhaust ventilation before they are dispersed into the workplace. This “capture” technique is called local exhaust ventilation (LEV).

LEV is effective for the following reasons:

- only a relatively small amount of air is required to “capture” and remove the airborne chemicals released from fluoropolymer resins compared to the very large volumes required to try and change the air in an entire area or building, and
- the proper capture of contaminants at the source can significantly reduce any exposure to chemicals by workers.

NOTE: The use of fans, ceiling exhaust or open windows is generally not effective because contaminants are allowed to mix with room air. In some cases, they may actually interfere with LEV by creating cross-drafts.

*Principles to Follow In Using LEV*

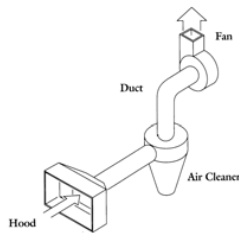
1. The parts of an LEV system are: 1) an exhaust fan (to pull air and any contaminants), 2) connected to a duct and 3) an exhaust “hood” (located close to the source of release of contaminants [see illustration of exhaust systems in Figures 1, 2 and 3]) [Proper Use of Local Exhaust Ventilation During Hot Processing of Plastics, DuPont Company Bulletin L-10954, 8/20/11.]
2. Room air will be exhausted by the LEV system and the discharge can be treated in various ways to remove contaminants or can be exhausted to the outdoors in accordance with any applicable laws or permits. Make-up air, tempered in some regions, will be required to replace the exhausted air.
3. The hood should be shaped to cover and enclose the source as far as is practical yet still allow access to the equipment for normal operation. The hood should be removable or be an adjustable duct that can be moved aside for maintenance or troubleshooting. Adjustable ductwork of this type is commercially available.
4. The hood is the most critical part of the LEV system. The hood should be as close to the source as is practical. Tests have shown that the capture effectiveness diminishes rapidly as the distance from the hood opening increased (see Figure 4).
5. If the contaminants contain dusts, mists or fumes, the air velocity in the duct must be high enough to prevent these materials from settling out in the ductwork.

The capture effectiveness of a hood can be improved by placing flanges around the hood opening to restrict airflow from above and from the side of the hood. The airflow around the area where the contaminants are generated is sensitive to crosscurrents, which can actually push the gases back towards you unless you use an enclosure (e.g., curtains) to help your LEV.

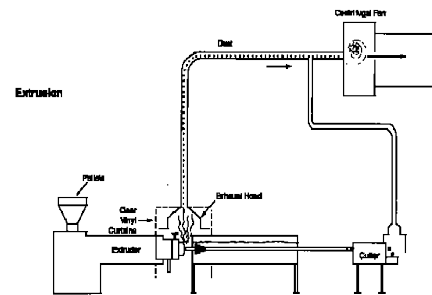
### Proper Design of Exhaust Systems

Properly designed exhaust hoods should be installed to remove all emissions released during processing operations including all vacuum parts, pumps, and vents on process equipment. For this purpose, a number of hood designs are shown in **Figure 5**.

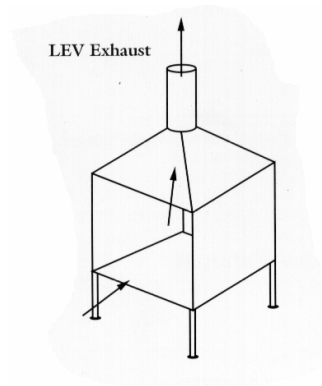
[American Conference of Governmental Industrial Hygienists, *Industrial Ventilation: A Manual of Recommended Practice*.] These designs present several alternatives to allow adequate exhaust volumes for effective capture and removal of emissions. Situations frequently encountered and the capture velocities (generation of air flow sufficient to remove contaminated air issuing from the source and causing it to flow into an exhaust hood) needed to exhaust all the gases from the vicinity of hot polymer are summarized in **Table 2**. Proper design may require the assistance of professional engineering experts, preferably those having industrial exhaust experience.



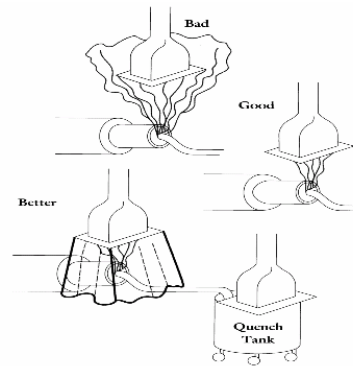
**Figure 1** Exhaust Systems



**Figure 2** Typical Exhaust Setup



**Figure 3** Hood



**Figure 4** Extruder Die Hood

The work situation is selected from **Figure 2** and the centerline velocity required to capture all gases is then used to calculate the volumetric rate of airflow required for the hood design selected from **Figure 5**. For example, in the extrusion coating of wire, we may assume a minimum capture velocity of 200 fpm (1 m/s) is needed. To illustrate how the table is used, consider the following. Assume that a plain opening hood (line 3 in Figure 5) is used, the hood is located 0.5 feet from the wire as it exits the extruder, and (3) it has an opening of 1 ft x 0.5 ft, giving an area of 0.5 f<sup>2</sup>. The volume of air required is given by the equation:

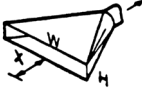
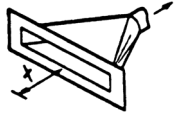
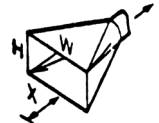
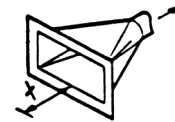
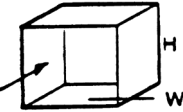
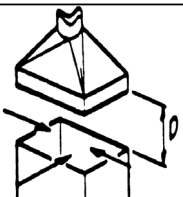
$$Q = V (10X^2 + A)$$

Plugging in the values above gives the following result:

$$\begin{aligned} Q &= 200 (10 (0.5)^2 + 0.5) \\ &= 200 (10 (0.25) + 0.5) \\ &= 200 (2.5+0.5) \\ &= 200 (3) \\ &= 600 \text{ cubic feet per minute (cfm).} \end{aligned}$$

Figure 5: Hood Design

(Reprinted by permission of American Conference of Governmental Industrial Hygienists, Inc.)

Hood Types	Description	Aspect Ratio, H/W	Air Rate**
	Slot	0.2 or less	$Q = 3.7 WVX$
	Flanged slot*	0.2 or less	$Q = 2.8 WVX$
	Plain opening	0.2 or greater and	$Q = V (10X^2 + A)$
	Flanged opening*	0.2 or greater and	$Q = 0.75V (10X^2 + A)$
	Booth	To suit work	$Q = VA = VWH$
	Canopy	To suit work	$Q = 1.4 PDV$

Wherever possible, flanges should be provided to eliminate air flow from ineffective zones where no contaminant exists. Increasing the hood effectiveness in this manner will usually reduce air requirements by 25%. For most applications the flange width can be equal to the hood diameter or side but need not exceed 6 in/15 cm.

## Nomenclature

V = Centerline velocity at "X" distance from face of hood, fpm (m/s) (use recommended capture velocity from Table 1)

X = Distance from source to face of hood, ft (m)

Q = Air volume, cfm (m<sup>3</sup>/s)

A = Area at face of hood, sq ft (m<sup>2</sup>)

P = Perimeter of work, lin ft (lin m)

D = Height above work, ft (m)

H = Height of hood, ft (m)

W = Width of hood, ft (m)

Table 3: *Capture Velocities Recommended in Various Work Situations*

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<b>Dispersions of Contaminants into Air</b>	<b>Examples</b>	<b>Capture Velocity, fpm (m/s)</b>
Released with practically no velocity into quiet air.	Drying of fluorocarbon resins—granular, powder, cubes, evaporation of solvents, water, etc. from powders and dispersions	50-100 (0.25-0.50)
Released at low velocity into moderately still air.	Spray coating fluorocarbon dispersions or powders. Normal blending of fluorocarbon cubes or powders. Molding and sintering of fluorocarbon resins into large billets.	100-200 (0.50-1.0)
Active generation into zone of rapid air motion.	Melt extrusion of fluorocarbon resins on wire and into tubing. Paste extrusion and sintering of fluorocarbon resins on wire and tubing. Injection and transfer molding of melt-processible resins.	200-500 (1.0-2.5)
Released at high initial velocity into zone of very rapid air motion.	Grinding and machining of parts from fluorocarbon resins. High-speed mixing of fluorocarbon powders in turbulent mode.	500-2000 (2.5-10.0)

In each category above, a range of capture velocities is shown. The proper choice of values depends on several factors:

<b>Lower End of Range</b>	<b>Upper End of Range</b>
<ol style="list-style-type: none"> <li>1. Room air currents minimal or favorable to capture.</li> <li>2. Contaminants of low toxicity.</li> <li>3. Intermittent, low production.</li> <li>4. Large hood—large air mass in motion.</li> </ol>	<ol style="list-style-type: none"> <li>1. Disturbing room air currents.</li> <li>2. Contaminants of high toxicity.</li> <li>3. High production, heavy use.</li> <li>4. Small hood—local control only.</li> </ol>

The importance of locating the hood opening close to the hot polymer is indicated by the fact the “X” dimension (the distance from the face of the hood opening to the point at which fumes are formed) is exponential in the above equation. Thus, if this distance were doubled in the above example, the volumetric rate of air flow required would increase to 200 ( $10 \times 1^2 + 0.5$ ) = 2100

#### *Resin Package Opening and Manual Transfer of Materials*

Fluoropolymer resins may contain residues of gases used to manufacture the resins that are released slowly over time. The quantities of gases in the closed packages may be significant. Opening packages of resin may require the use of local exhaust ventilation to control employee exposure to residual gases. Controls for work stations vary depending on a number of factors, including: whether bags or drums are opened; whether the product is liquid or solid (powder); the number of packages to be opened at a

single time; whether smaller quantities are to be removed from the package and the package resealed for future use; and the presence of other activities in the immediate vicinity of the package opening station. Typical bag opening and weighing station are shown in Figures 6 and 7.

Local exhaust for drum opening is not normally used if there is a pump or other closed method of transfer (such as a self-closing valve). In these cases, employees must be trained to follow procedures designed to minimize exposure. These include, among others: transferring resins only in a well-ventilated area; using a hand pump to transfer resin to another container; and transferring resin directly into the process vessel.

Studies by the National Institute of Occupational Safety and Health (NIOSH) indicate that significant exposure occurs when workers lean over into partially empty drums of solid materials to obtain

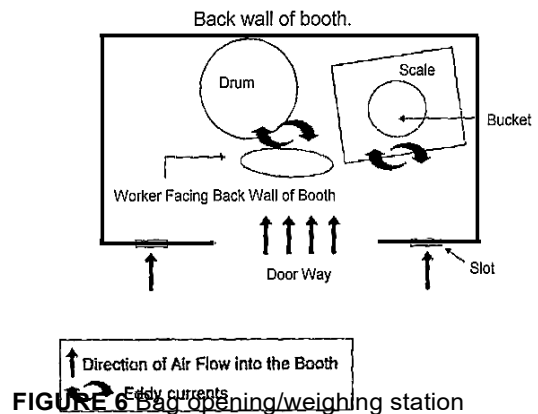


FIGURE 6 Bag opening/weighing station

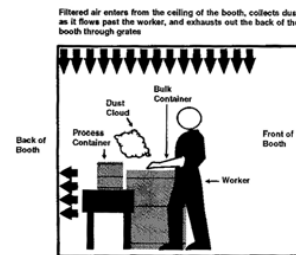


FIGURE 7 Weighing Station



less than a full-package quantity. Stations designed to control these exposures can similarly be used to prevent overexposure in opening packages.

Whatever methods are used, the processor must be aware of the potential presence of residual monomer gases and their potential hazards and assure that its employees take the steps designed to reduce or eliminate the exposure. In some cases, the use of personal protective equipment, such as face shields, aprons, gloves, and even respirators may be required. Consult the resin suppliers' SDS for information about the products in use and the precautions necessary to use the product safely.

#### *Methods of Checking and Measuring Airflow*

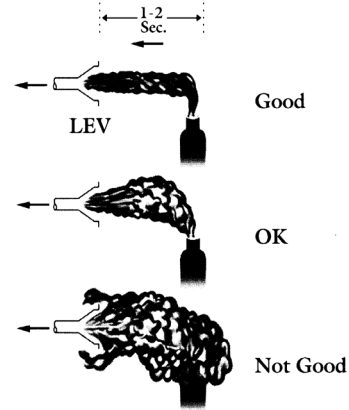
The airflow in a ventilation system duct can vary depending on your equipment, fan size, etc. A simple way to monitor the performance of the system, once it is working properly, is to install a gauge to measure the static pressure in the exhaust duct. Changes in this pressure — in either direction — mean that the airflow has changed and, therefore, a maintenance check of the fan and/or duct is needed. This “transport” velocity can be measured with a special flow meter.

A simple check of the LEV system's effectiveness can be made by using a ventilation “smoke tube” (NOTE: this smoke is *not* from a fire) to produce a stream of dense white smoke at the location where the hot plastic will release contaminants. If the “transport” velocity is high enough, the smoke should be rapidly captured (within 1—2 seconds) by the exhaust air and swept into the hood (see Figure 7). If smoke escapes the hood and moves into the surrounding air, then some adjustment of the hood location and/or air velocity will be needed. Installing additional enclosures, e.g., heavy plastic curtains to surround the operation or source of the gases should be considered.

If the processor does not employ individuals knowledgeable in ventilation, consultants may be required to thoroughly assess the operations, evaluate the hazards, and assist in the design of appropriate controls. References for qualified consultants can be obtained from your resin supplier.

*Equipment and Test Devices*

1. Ventilation Smoke Tubes: to visually check the air currents around an exhaust hood (Figure 8).<sup>16</sup>
2. Air Velocity Meters: to measure airflow and “capture” velocity
3. Static Pressure Gauges
4. Portable LEV units
5. Adjustable Duct Systems.

**FIGURE 8** Use of Smoke Tubes*B. Personal Protective Equipment*

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

If dust cannot be avoided when handling fluoropolymer resin powders, appropriate NIOSH-approved respiratory protection should be worn. While processing and handling filled compounds, respirators must be selected based on the potential hazards of the other chemicals in the resins, and goggles and protective gloves should be worn as recommended on the supplier's SDS. Resins containing solvent may require the use of NIOSH-approved organic vapor cartridges fitted with appropriate dust/mist filters.

[Consult your resin supplier for guidance.]

Fluoropolymer dispersions contain residues of additives that should not come into contact with the skin. Review the product-specific SDS before handling the material. It is necessary to wear protective gloves, goggles, face shields or other protective clothing to prevent contact when handling these products. Appropriate ventilation is required to avoid inhalation of dust, vapors or fumes.

The spray application of all coatings, including fluoropolymer coatings, must be performed in suitably equipped spray booths. Operators should wear personal protective clothing and equipment as appropriate. It is recommended that the spray

booth be equipped with a water bath to precipitate and remove the spray mist from the air being exhausted.

### *C. Personal Hygiene*

When training personnel it is important to emphasize that tobacco products should not be carried or used in work areas. Smoking tobacco contaminated with even very small amounts of fluoropolymer resin can cause “polymer fume fever” (described in Chapter 2, Section D. Polymer Fume Fever) by inhalation of the effluents. After smoking contaminated tobacco, the person may suffer shivering attacks (known appropriately as the “shakes”) and other flu-like symptoms. The symptoms invariably subside within 24 to 48 hours. For these reasons it is recommended smoking and tobacco products be banned in work areas where fluoropolymer resins are processed.

To prevent traces of fluoropolymer resin powders being carried out of the work area on clothing, personnel should be given the opportunity to store their work clothing separate from their street clothing (double locker or separate change rooms). Employees should be provided with adequate washing facilities and be encouraged to use them regularly.

Additional personal hygiene procedures should be followed when using fluoropolymer dispersion. It is important to keep clothing dry, and to change contaminated clothing immediately. Contaminated clothing should be stored separately from clean items. This includes personal protective equipment like gloves, goggles etc. Contaminated gloves should not be kept in the pockets of clothing or protective wear. Splashes should also be cleaned off of footwear right away.

Operators should wash their hands after any contact with dispersions and when leaving processing areas. Food and drinks should be kept out of processing areas.

Solvents and other additives to the fluoropolymer dispersions might trigger the need for additional hygiene procedures – please consult the SDS sheet for your specific product or consult your supplier.

### *D. First Aid*

#### *Inhalation*

### **Fluoropolymer Fumes**

Fumes evolved during the processing of fluoropolymer resins may contain oxides of carbon, potentially toxic, corrosive, fluorine compounds (hydrogen fluoride [HF], carbonyl fluoride [COF<sub>2</sub>], perfluoroisobutylene [PFIB], tetrafluoroethylene [TFE]) and ultra-fine, low-molecular-weight fluoropolymer particles. The fumes are acutely very toxic and may be immediately harmful if inhaled in sufficient amounts. See page 13 for further discussion of these chemicals.

Inhalation of ultra-fine, low-molecular-weight fluoropolymer particles may cause an influenza-like condition called "polymer fume fever." The symptoms of polymer fume fever are chills (shakes), fever, chest pains, shortness of breath, and coughing. The symptoms do not normally occur at the time of exposure, but develop over a period of several hours after exposure ends. The symptoms usually subside in twenty-four (24) to forty-eight (48) hours. No permanent effect from the condition is known.

If an individual does inhale fluoropolymer fumes and is affected by them, the individual should be immediately removed to fresh air and medical assistance should be provided for irritation or other symptoms. HF is acutely very toxic and may be immediately harmful if inhaled in sufficient amounts. The OSHA PEL is 3 ppm; the ACGIH TWA is 0.5 ppm; and there is a ceiling limit of 2 ppm. Because overexposure to HF requires specific medical treatment, the treating physician must be informed that the individual may have been exposed to HF.

If an individual has been overcome by fumes, is unconscious, or is otherwise incapacitated, do not enter the contaminated area until it is established that the area can be entered safely. For emergencies or unknown concentrations, emergency responders must use positive-pressure, self-contained breathing apparatus (SCBA) respiratory protection. If evacuation of personnel is necessary (as in the case of a fire), evacuate them to an upwind area.

HF is also extremely corrosive and can cause severe burns. If skin or eye contact with HF is suspected, immediately flush the skin and eyes with copious amounts of water. Seek immediate medical attention. Emergency Responders must wear full turnout gear or Level A equipment to protect skin and eyes from exposure to HF. In any emergency involving exposure to chemicals, copies of SDS for chemicals the person was using should be provided to the treating physician.

### **Fluoropolymer Dispersion Coatings**

Fluoropolymer dispersion coatings, whether aqueous, waterborne (a blend of water and solvents), or solvent borne, may contain organic solvents and/or additives which may be harmful if inhaled. Consult product-specific SDS for safe handling instructions. If overcome by vapor, mists, or processing fumes, remove the individual from exposure. If breathing is irregular or stopped, start resuscitation and administer oxygen. Seek immediate medical attention.

*Eye Contact***Fluoropolymer Pellets and Powders**

The primary hazard associated with eye contact is mechanical irritation. In case of eye contact, remove contact lenses if worn, then flush the eyes with water for several minutes. If irritation persists or if other symptoms develop, seek medical attention. In any emergency involving exposure to chemicals, copies of SDS for chemicals the person was using should be provided to the treating physician.

**Fluoropolymer Dispersion Coatings**

Fluoropolymer dispersion coatings may contain organic solvents and/or additives which may be harmful. In case of eye contact, remove contact lenses if worn, and then flush the eyes with water for several minutes. If irritation persists or if other symptoms develop, seek medical attention. In any emergency involving exposure to chemicals, copies of SDS for chemicals the person was using should be provided to the treating physician.

*Skin Contact***Fluoropolymer Pellets and Powders**

Fluoropolymer pellets and powders are not likely to be hazardous by skin contact. In case of skin contact, remove contaminated clothing, and then wash the skin with soap and water. If molten polymer contacts and bonds to the skin, immediately flush the affected area with copious amounts of cold water. Do not attempt to remove the solidified polymer from the skin. Seek immediate medical attention. In any emergency involving exposure to chemicals, copies of SDS for chemicals the person was using should be provided to the treating physician.

As noted above under inhalation, HF may be a component of fumes evolved during high-temperature processing of fluoropolymer materials. HF is extremely corrosive and can cause severe burns to skin and eyes.

If contact with HF is suspected, immediately flush the skin and eyes with copious amounts of water. Seek immediate medical attention. In any emergency involving exposure to chemicals, copies of SDS for chemicals the person was using should be provided to the treating physician.

**Fluoropolymer Dispersion Coatings**

Fluoropolymer dispersion coatings may contain organic solvents and/or additives which may be harmful. Many hazardous chemicals can be absorbed through the skin and may cause, for example, narcotic effects. In case of skin contact, remove contaminated clothing, then flush the affected area with water. If irritation or other symptoms develop, seek immediate medical attention.

*Ingestion***Fluoropolymer Pellets and Powders**

Unfilled fluoropolymers are generally regarded as non-hazardous if ingested. If irritation persists or if other symptoms develop, seek medical attention. In any emergency involving exposure to chemicals, copies of SDS for chemicals the person was using should be provided to the treating physician.

**Fluoropolymer Dispersion Coatings**

Fluoropolymer dispersion coatings may contain organic solvents and/or additives that may be harmful if ingested. In case of ingestion, seek immediate medical attention. If vomiting occurs spontaneously, keep the individual's head below the hips to prevent aspiration of vomitus into the lungs. In any emergency involving exposure to chemicals, copies of SDS for chemicals the person was using should be provided to the treating physician.

**CHAPTER 5: FIRE AND EXPLOSION HAZARDS***A. Ignition Characteristics*

All fire and flammability tests show that fluoropolymers are among the most difficult plastics to ignite. For example, the self-ignition temperatures (SIT) of solid PTFE products measured in accordance with ASTM D 1929 are in the range of 500°C to 560°C and hence are 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 to 245°C.

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 fluoropolymer, little or no smoke is produced. Care should be taken however to avoid the inhalation of smoke generated by all combusting materials, including fluoropolymers.

Fluorinated polymers are very hard to burn as indicated by their Limiting Oxygen Index (LOI) measured in accordance with ASTM D 2863. The oxygen index is the minimum concentration of oxygen of 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 unfilled polymers that are not fully fluorinated, the LOI is between 30 and 60 depending on the molecular structure but some of these can be formulated to have an LOI of 95%. 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.

*B. Extinguishing Agents*

All extinguishing agents such as water, carbon dioxide, dry powder, and foam are suitable for fires involving fluoropolymers. Extinguishing agents that 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.

*C. Fire, Explosion, and Toxicity Information*

Fluoropolymers are "self-extinguishing," i.e., they will not support combustion unless there are external sources of oxygen and ignition. There is no evidence that fluoropolymers form flammable or explosive dust clouds.

Although fluoropolymers do not support combustion, they will thermally decompose if exposed to flames or other sources of extreme heat. The fumes may contain oxides of

carbon, potentially toxic, corrosive, fluorine compounds (such as HF, COF<sub>2</sub>, PFIB, TFE), and ultra-fine, low-molecular-weight fluoropolymer particles. Fumes containing these chemicals are acutely very toxic and may be immediately harmful if inhaled in sufficient amounts.

#### *D. Fire-Fighting Precautions and Extinguishing Agents*

Fire fighters, hazardous materials (HazMat) team members, and emergency responders (fire fighters) must wear full turnout gear or Level A equipment and self-contained breathing apparatus (SCBA) to protect their skin, eyes, and respiratory system from contact with HF and other toxic fumes which may be present in any fire involving fluoropolymers.

Because fluoropolymers, in essence, do not burn, firefighters should fight fires with fire-fighting techniques and extinguishing agents which are appropriate for the materials that are providing fuel for the fire. All commonly-used ABC, BC, and D fire extinguishing agents, i.e., carbon dioxide (CO<sub>2</sub>), “alcohol” foam, dry chemical, and water spray / water fog extinguishers may be used if fluoropolymers are being burned in fires fueled by other substances. Consult the manufacturer’s SDS for the preferred extinguishing agent for mature fires.

It is imperative that firefighters and their equipment are thoroughly decontaminated with a water wash-down after fire and smoke exposure. Machinery and equipment that was involved in a fire must also be decontaminated prior to commencing repair or salvage operation.



**CHAPTER 6: FOOD CONTACT AND MEDICAL DEVICE APPLICATIONS**

Under the Federal Food, Drug and Cosmetic Act, substances can be used in food-contact applications if they are: (1) not reasonably expected to become a component of food under the intended conditions of use; (2) the subject of an applicable Food Additive Regulation, Threshold of Regulation exemption letter, issued by the Food and Drug Administration, or an effective Food Contact Notification (FCN) accepted by the Food and Drug Administration; (3) the subject of a “prior sanction” or approval issued by the FDA or the United States Department of Agriculture (USDA) prior to 1958; or (4) deemed generally recognized as safe (GRAS) by qualified experts. The FDA has cleared many fluoropolymers for use in contact with food. The primary regulations governing fluorocarbon resins are 21 CFR §177.1380 §177.1550, and §177.2510 as listed in Appendix A. Other fluoropolymers have been the subject of various FCNs found at <http://www.cfsan.fda.gov/~dms/opa-fcn.html>; these FCN listings, unlike Food Additive Regulations, are only applicable to the notifiers who obtained them and their customers. Further, stabilizers, antioxidants, colorants, and other adjuvants that are not an essential part of the polymerization process must also be cleared by one of the methods described above. Most FDA regulations for antioxidants, stabilizers, and other adjuvants appear in 21 CFR Part 178.

Processors wishing to use fluoropolymers in food contact applications must make their own decision concerning the suitability of the individual fluoropolymer for the specific intended use. Processors wishing to use fluoropolymers in food contact applications should consult with their suppliers to determine whether the supplier has a policy governing such uses and with individuals experienced in making such assessments. In any event, consultation with legal counsel experienced in food additive and clearance requirements is essential.

Some fluoropolymers have been used to manufacture medical devices, which are regulated by the FDA. The manufacturers and sellers of finished medical devices are responsible for obtaining any required clearance or approval for their device(s). FDA does not “approve” individual components of medical devices, such as fluoropolymer resins. Furthermore, Congress has enacted legislation intended to protect suppliers of individual raw materials and component parts of implanted medical devices from product liability lawsuits. The Biomaterials Access Assurance Act of 1998, codified at 21 U.S.C. §1601 – 1606, is intended to provide an incentive to suppliers who might have been deterred by potential liability concerns to continue to supply implanted medical device manufacturers with necessary raw materials, thus ensuring the supply of critical medical devices. PIA has not sought or received approval from any regulatory authority concerning the use of fluoropolymers in medical devices. Device manufacturers wishing to use fluoropolymers in such applications should consult with their suppliers to determine whether they have a policy governing such uses, and with regulatory counsel experienced in FDA medical device matters. Processors who are asked to provide such assurances should consult the fluoropolymer supplier and regulatory counsel as well.

**CHAPTER 7: EMERGENCY TELEPHONE NUMBERS**

AGC Chemicals Americas, Inc.

**Medical Emergency:****(800) 420-8479**

Product Information:

(800) 424-7833

Transport Emergency:

(800) 424-9300 (CHEMTREC)

Arkema, Inc.

**Medical Emergency:****(866) 767-5089**

Product Information:

(800) 722-9668

(610) 205-7000

Transport Emergency:

(800) 424-9300 (CHEMTREC)

Dyneon LLC, A 3M Company

**Medical Emergency:****(800) 364-3577**

Product Information:

(800) 723-9127

Transport Emergency:

(800) 364-3577

Daikin America, Inc.

**Medical Emergency:****(845) 365-9500**

Product Information:

(800) 365-9570

Transport Emergency:

(800) 424-9300 (CHEMTREC)

The Chemours Company

**Medical Emergency:****1-866-595-1473 (outside US  
1-302-773-2000)**

Product Information:

(302) 773-1000

Transport Emergency:

(800) 424-9300 (CHEMTREC)

Outside US 1-703-527-3887

Solvay Solexis, Inc.

**Medical Emergency:****(856) 853-8119**

Product Information:

(800) 323-2874

Transport Emergency:

(800) 424-9300 (CHEMTREC)

## APPENDIX A: BIBLIOGRAPHY

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ASTM D1430 "Standard Classification System for Polychlorotrifluoroethylene (PCTFE) Plastics."

ASTM D2116 "Standard Specification for FEP - Fluorocarbon Molding and Extrusion Materials."

ASTM D2863 "Standard Test Method for Measuring the Minimum Oxygen Concentration to Support Candle-Like Combustion of Plastics (Oxygen Index)"

ASTM D3159 "Standard Specification for Modified ETFE - Fluoropolymer Molding and Extrusion Materials."

ASTM D3222 "Specification for Unmodified Poly (Vinylidene Fluoride) (PVDF) Molding, Extrusion and Coating Materials."

ASTM D3275 "Standard Classification for ECTFE - Fluoroplastic Molding, Extrusion and Coating Materials."

ASTM D3307 "Standard Specification for Perfluoroalkoxy (PFA) - Fluorocarbon Molding and Extrusion Materials."

ASTM D4441 "Standard Specification for Aqueous Dispersions of Polytetrafluoroethylene."

ASTM D4745 "Standard Specification for Filled Compounds of Polytetrafluoroethylene (PTFE) Molding and Extrusion Materials."

ASTM D4894 "Standard Specification for Polytetrafluoroethylene (PTFE) Granular Molding and Ram Extrusion Materials."

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IRE HSE

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## **APPENDIX B: “GUIDE TO THE SAFE HANDLING OF FLUOROPOLYMER DISPERSIONS”**

### **NOTE TO USERS**

This Guide was developed by Plastics Industry Association, and is intended to provide information on general guidelines for safe handling of fluoropolymer dispersions. The guidelines provided are based on the collective experience of members of the industry but are not intended to be either exhaustive or inclusive of all pertinent requirements. The information provided in this guide is offered in good faith and believed to be reliable, but is made **WITHOUT WARRANTY, EXPRESSED OR IMPLIED, AS TO THE MERCHANTABILITY, FITNESS FOR A PARTICULAR PURPOSE, OR ANY OTHER MATTER**. The guidelines provided, and the examples included are not intended to be directed to any particular product, nor are they claimed to satisfy all current legal requirements related to control of processing operations. Following the Guide does not guarantee compliance with any regulation nor safe operation of processing facilities. Users are cautioned that the information upon which this guide is based is subject to change which may invalidate any or all of the comments contained herein.

The Guide is not intended to provide specific advice, legal or otherwise, on particular products or processes. In designing and operating processing lines, users of the Guide should consult with their own legal and technical advisors, their suppliers, and other appropriate sources (including but not limited to product or package labels, technical bulletins, or sales literature) which contain information about known and reasonably foreseeable health and safety risks of their proprietary products and processes. PLASTICS, its members and contributors do not assume any responsibility for the user's compliance with any applicable laws and regulations, nor for any persons relying on the information contained in this Guide.

PLASTICS does not endorse the proprietary products or processes of any manufacturer or user of fluoropolymer resins or products. All information about an individual manufacturer's products contained herein has been provided by those manufacturers who are solely responsible for the accuracy and completeness of the data.

## **HANDLING AND STORAGE / EXPOSURE CONTROL**

It is important to handle fluoropolymer dispersion according to guidelines given in the product-specific SDS. Fluoropolymer dispersions usually contain fluorinated polymerization aids (FPAs) at very low levels. FPAs are released when dispersions are dried or heated. The primary exposure routes of FPAs when processing dispersions are through the skin (dermal), ingestion (e.g., by transference from hand to mouth), and via inhalation. For FPA specific hazard information, contact your dispersion supplier.

Based on the high vapor pressure of some of these FPAs, it is important to clean up spills and overspray before they dry and allow the FPA to potentially sublime. Dispersion containing waste should also be disposed of in closed containers. The vapor pressures are high enough that under conditions of poor ventilation these sources of FPA may result in exposures that exceed the ACGIH TLV. See Chapter 3 for more detail.

Use of engineering controls, good hygienic practices and personal protection equipment (PPE) are critical in reducing employee exposure to dispersions and FPAs when working with these chemicals. Alone, each of these control methods cannot eliminate potentially hazardous work conditions, but a combination of these methods, employee involvement, and company support can control exposure.

Wear appropriate gloves and protective eyewear when handling this material. In addition, use one or more of the following personal protection items as necessary to prevent skin contact: head covering, coveralls, and aprons.

Do not allow smoking and/or eating in areas where FPAs or fluoropolymers are used. Wash hands and exposed skin after use, and before handling food or applying cosmetics. There are other health and safety hazards associated with handling, use, and processing of fluoropolymers, including dispersions. Smoking cigarettes or tobacco contaminated with dust from fluoropolymer products is associated with "Polymer Fume Fever."

The major health hazard associated with handling fluoropolymers is the inhalation of decomposition products. In addition, when handling fluoropolymer dispersions, FPAs are released when coatings are dried or heated. Provide sufficient ventilation to maintain exposures below recommended limits. If exhaust ventilation is not adequate, use appropriate respiratory protection.

Engineering controls are the first line of defense to control exposure. Examples of engineering controls include both general plant ventilation and local exhaust ventilation for specific, potentially high exposure tasks. A spray paint booth is an example of a local exhaust system (see the Safe Handling Guide for a description of local exhaust systems used in fluoropolymer processing). Enclosing processes is an additional type of engineering controls; automation is another way to limit exposure. Lastly, all heated processing equipment requires a ventilation system to prevent inhalation exposures.

A hazard assessment of job tasks will help determine what types of PPE are appropriate and necessary. Using PPE properly is important. For example, significant exposure can occur from clothing contaminated by improper storage or disposal of gloves, such as

putting them in pockets of work clothes between uses. In addition, thorough and frequent washing of hands and any exposed skin will reduce potential exposure.

Care should be taken to prevent the spread of material by contaminated clothing and shoes. Contaminated clothing and shoes should be thoroughly cleaned before re-use. Employees should not remove contaminated clothing from the workplace. Finally, good housekeeping practices also help reduce potential exposure.

### ***ECOTOXICOLOGICAL INFORMATION***

Do not discharge dispersions, or wastes containing them, to lakes, streams or waterways. See discussion below for disposal considerations. Disposal to water may produce a milky appearance.

The fluoropolymer component is not toxic. The stabilizing surfactants have varying ecotoxicity profiles, and users should contact their supplier for more detailed ecotox information for their particular product.

FPA's are persistent in the environment.

### ***DISPOSAL CONSIDERATIONS***

Fluoropolymer dispersions typically have the following waste disposal considerations. Consult your supplier for information on their particular product.

Preferred options for disposal are: (1) Separate solids from liquid by precipitation and decanting or filtering. Dispose of dry solids in a landfill that is permitted, licensed or registered to manage industrial solid waste. Consult your local regulations for discharge of liquid filtrate to a wastewater treatment system (2) Incinerate only if incinerator is capable of scrubbing out hydrogen fluoride and other acidic combustion products.

RCRA/US EPA WASTE INFORMATION: Discarded product is not typically a hazardous waste under RCRA 40 CFR 261. Dispose in an authorized landfill site or incinerate under approved controlled conditions. This product may be incinerated above 800° C (1472° F) using a scrubber to remove hydrogen fluoride.

EMPTY CONTAINER: Empty containers should be punctured or otherwise destroyed before disposal. Empty containers must not be used for home or personal uses.

ALL DISPOSAL METHODS: Treatment, storage, transportation, and disposal of this product and/or container must be in accordance with applicable federal, state/provincial, and local regulations.



## APPENDIX C: TFE IN FLUOROPOLYMERS

At the Fluoropolymer Division Fall 1996 Conference, a series of presentations was made discussing the results of the National Toxicology Program's (NTP) animal study of the effects of exposure to tetrafluoroethylene (TFE) gas. This brief written summary is based on the presentations given at that meeting.

As noted in Chapter 1, TFE is a monomer used to make certain fluoropolymers. Even though it is a gas, a minute quantity of TFE may remain in the resin. There is also the potential that some TFE may be formed during heat processing or overheating of fluoropolymers of all kinds. Tests performed by resin manufacturers show that small amounts TFE may be evolved during processing of fluoropolymer resins.

The Formation of TFE from heating PTFE has been studied. Experimental data on the formation of TFE during the decomposition of PTFE at temperatures from about 500-752°F (260-400°C) are shown in FIGURE 1. PTFE was heated in a stream of air or inert gas (helium) and the TFE was trapped out and then analyzed. The data plotted in Figure 1 suggest that TFE is formed at a rate of about 1-30 ppm (microgram TFE/gram polymer processed)/hour. Ventilation of processing operations to prevent exposure to TFE other acute toxicants as described in Chapter 3 is required.

TABLE 1 shows that TFE has not been found in articles, manufactured using standard recommended processing conditions. The method of analysis had detection limits generally down to about 0.01 ppm weight/weight.

<b>TABLE 1 - TFE CONCENTRATION IN POLYMER</b>				
<b>Data Source</b>		<b>Powder</b>	<b>Aqueous</b>	<b>Sintered</b>
		<b>ppm (w/w)</b>	<b>ppm (w/w)</b>	<b>ppm (w/w)</b>
TNO 1979	value Lod	nd 0.01		nd 0.01
PIRA 1987	value Lod	nd 0.01		nd 0.01
TNO 1994	value Lod	nd 0.3	0.24	
Producers 1996	Value Lod	nd 0.01-1.00	0.2-0.7	nd 0.01
Lod = Limit of Detection nd = Not Detected				

TFE formation in processing PTFE has been studied at and above the maximum continuous recommended service temperature of 500°F (260°C). TFE is first detectable

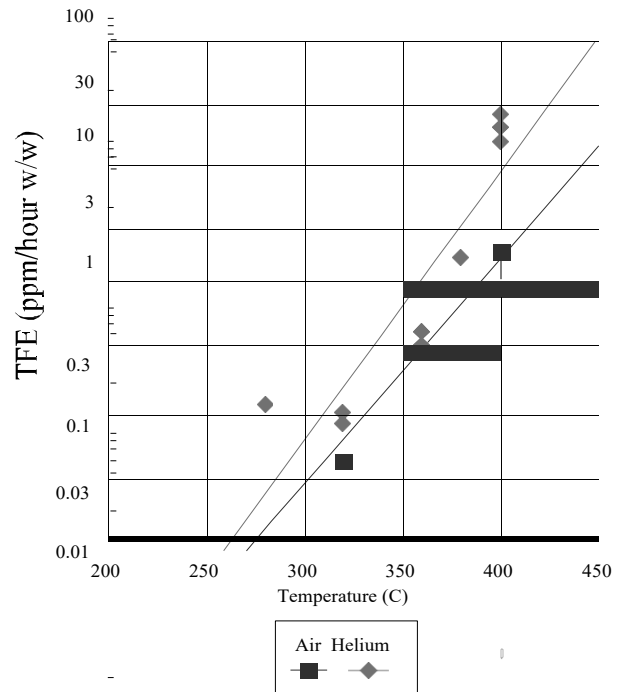
at temperatures of 608°F (320°C) when PTFE was heated in air, being found in one of two runs at that temperature.

TFE monomer was tested for its carcinogenicity by researchers at the National Toxicology Program using standard techniques for the types of animal studies performed. The study results were interpreted by the NTP peer reviewers as showing "clear evidence of carcinogenic activity" in both rats and mice.

Levels of TFE monomer in resins are low; resin manufacturers can provide information on sampling techniques and laboratory methods of analysis to allow measurement of occupational exposure in processing.

The TLV<sup>®</sup> is 2 parts per million (ppm) of TFE based on an eight-hour time weighted average.

Figure 1 - TFE FORMATION FROM PTFE



Processors should evaluate their operations to determine if their employees have the potential for exposure to TFE, as well as other chemicals that may be encountered in processing fluoropolymers and, if so, to provide training under the Occupational Safety and Health Administration (OSHA) Hazard Communication Standard (HCS).

Exposure to TFE should not be confused with the exposure to the degradation products that cause polymer fume fever (PFF). PFF is a condition that sometimes results when persons are exposed to the fumes that are generated when PTFE and other fluoropolymer resins are overheated or “burned off.” Although it is theoretically possible that some TFE may be produced in the effluent generated, other substances, including hydrogen fluoride, perfluoroisobutylene, fine particulates, and carbonyl fluoride, are known to be produced and are present in quantities that may be hazardous. Current data suggests that PFF may be attributable to heated ultra-fine particles of polymers. There is no known relationship between PFF and the carcinogenic response in rodents exposed to TFE. Processors should review the information about PFF in Chapter 2 - Potential Health Effects and Chapter 4 – Industrial Occupational Hygiene with their employees and make sure they use appropriate controls, such as enclosures and ventilation, to limit potential employee exposure.

TFE is listed under the California “The Safe Drinking Water and Toxic Enforcement Act of 1986 (Proposition 65)” as a chemical known to the State to cause cancer.

## **APPENDIX D: POTENTIALLY APPLICABLE REGULATORY INFORMATION**

### **Introduction:**

Regulations exist that may apply to the manufacture and processing of fluoropolymers. A list of the potentially applicable regulations and a brief summary of each is listed below. New regulations are announced on a regular basis and each processor is encouraged to check current information with their Federal, State and Local agencies. The fluoropolymer manufacturer can also supply information. Manufacturers' addresses are listed in Chapter 1, Section C.

Because the regulations change regularly and interpretations and case law also affect responsibilities and rights under the law, users of this Guide must consult competent legal counsel and environmental (EHS) consultants to be sure that all applicable regulations are known and followed. This list may not be complete and new regulations may be adopted at any time. See disclaimer, NOTE TO USERS, page 6.

### **A. Safety and Health Considerations**

Title 29 Code of Federal Regulations is the Occupational Safety and Health Administration (OSHA). OSHA's mission is to assure the safety and health of America's workers by setting and enforcing standards; providing training, outreach, and education; establishing partnerships; and encouraging continual improvement in workplace safety and health. ([www.osha.gov](http://www.osha.gov)) The following OSHA Standards are likely to apply to a fluoropolymer processor facility:

Part 1904 — Recording and Reporting Occupational Injuries and Illnesses

Part 1910 — Occupational Safety and Health Standards

1910.147 The control of hazardous energy (lockout/tagout).

1910.1200 Hazard Communication

Machinery and Machine Guarding

1910.216 Mills and calendars in the rubber and plastics industries.

1910.241-244 Hand and portable powered tools; Guarding; Other portable tools and equipment.

Electrical

1910.176 Materials Handling — general.

1910.178 Powered industrial trucks.

1910.151 Medical services and first aid.

Personal Protective Equipment

1910.145 Specifications for accident prevention signs and tags.

1910.146 Permit-required confined spaces.

Welding, Cutting and Brazing

1910.1000 Air-contaminants (Permissible Exposure Limits).

1910.134 Respiratory protection.

Emergency Preparedness

1910.37 Means of egress, general.

1910.38 Employee emergency plans and fire prevention plans.

1910.120 Hazardous waste operations and emergency response (HAZWOPER).

1910.157 Portable fire extinguishers.

In addition, the following standards affect fluoropolymer coaters operations as well:

Bulk Storage

1910.106 Flammable and combustible liquids.

Ventilation

1910.94 Ventilation.

1910.107 Spray finishing using flammable and combustible materials.

1910.119 Process safety management of highly hazardous chemicals.

1910.1450 Occupational exposure to hazardous chemicals in laboratories.

## **B. Environmental Considerations**

Most environmental considerations are regulated by the Federal Environmental Protection Agency (EPA). The mission of the EPA is to protect human health and the environment. Since 1970, EPA has been working for a cleaner, healthier environment for the American people. There are also State and Local regulations in addition to the Federal regulations that may apply to fluoropolymer processing facilities. The EPA website is [www.epa.gov](http://www.epa.gov).

The following EPA regulations could potentially apply to fluoropolymer processing facilities:

- a) **Clean Air Act (CAA)** - 40 CFR Chapter I, Subchapter C – “The US Clean Air Act is the main Federal statute governing ambient air quality and permitting emissions to air. The main purpose of the act is to protect public health, prevent adverse effects and assure good visibility by establishing ambient air quality standards.”

Sections that may apply to fluoropolymer processors are:

- i) 40 CFR 60 – New Source Performance Standards (NSPS)
  - ii) 40 CFR 61 and 63 – National Emission Standards for Hazardous Air Pollutants (NESHAPS)
  - iii) 40 CFR 51, 52, 62, and 81 – State Plans
  - iv) 40 CFR 70 and 71 – Operating Permits
  - v) 40 CFR 68 – Accidental Release Prevention
  - vi) 40 CFR 82 – Stratospheric Ozone Protection (Montreal Protocol)
- Neither fluoropolymers nor any of their decomposition products pose any threat to the ozone layer.

Hydrochlorofluorocarbon 22 (HCFC22) is used as feedstock in the manufacture of the principal monomer used in fluoropolymers. The Montreal Protocol (which deals with the control of ozone-depleting substances) recognizes that substances used as chemical feedstocks and

transformed in the process are thus removed from the environment. When used this way, their ozone-depleting potential is zero. For this reason, the Protocol specifically excludes these substances from its regulation.

- b) **Clean Water Act (CWA)** – 40 CFR Chapter I, Subparts D, N and O. The main purpose of the Clean Water Act is to control water pollution and maintain water quality in US waters.

Sections that may apply to fluoropolymer processors are:

- i) 40 CFR 110 – Discharges of Oil

Certain lubricants used by fluoropolymer processors may be regulated as oils. An oil is defined in 40 CFR 311 (a) (1) as any kind or any form, including but not limited to, petroleum, fuel oil, sludge, oil refuse and mixed with wastes other than dredged spoil.”

- ii) 40 CFR 112 – Oil Pollution Prevention

- iii) 40 CFR 122 – National Pollutant Discharge Elimination System (NPDES)

This part of the regulation could apply if the processor has any direct water discharges to waters of the United States

- iv) 40 CFR 122.26 – Storm Water Permits

If a fluoropolymer processor utilizes any materials that could potentially enter a water stream through a rainfall event, by storing any material containers outdoors for any length of time, the processor may be regulated under a Stormwater permit. Stormwater permits may be issued by the State or by the local authorities

- v) 40 CFR 403 – National Pretreatment Standard

These standards apply if a processor is discharging any water, other than sanitary, to a Publicly Owned Treatment Works (POTW).

- (1) 40 CFR 400-471 – Effluent Guidelines and Standards

These standards are applicable for specific types of industry. Some that may apply to fluoropolymer processors are:

410 – Textile Mills Point Source Category

446 – Paint Source Point Source Category

463- Plastics, Molding, and Forming Point Source Category

469- Electrical and Electronic Components Point Source Category

- c) **Waste Disposal** – Disposal of fluoropolymer containing wastes must follow applicable federal, state and local regulations. Waste must not be mixed with domestic or industrial waste that will be incinerated unless the facilities are equipped and permitted to handle acidic combustion products. Preferred options for disposal of resins, fine powders, and granular are recycling and landfill. Incinerate only if the incinerator is fitted and permitted to scrub out hydrogen fluoride and other acidic combustion gases.

The preferred option for disposal of fluoropolymer aqueous dispersions is to separate solids from liquid by precipitation and decanting or filtering. Dispose of dry solids in a landfill that is permitted, licensed, or registered by a state to

manage industrial solid waste. Liquid filtrate/waste may contain fluorinated polymerization aids. Check your local regulations for discharges to a wastewater treatment system. Specify incineration only if the incinerator is equipped to scrub out hydrogen fluoride and other acidic combustion gases.

Pigmented, filled, and solvent-laden waste will require special disposal practices in accordance with Federal, state, and local regulations. Suitable compliance strategies must be observed when storing, handling, and transporting hazardous wastes.

- i) **Resource Conservation and Recovery Act (RCRA)** – 40 CFR Chapter I, Subpart I. Wastes are regulated under various regulations. The RCRA regulations are to assure that certain hazardous wastes are contained and managed to prevent release to the environment and to eliminate hazards to people working with the wastes. State and local waste regulations may also apply to fluoropolymer processors.

Sections of RCRA that may apply to fluoropolymer processors are:

- (1) 40 CFR 260- Hazardous Waste General Information and Definitions
- (2) 40 CFR 261- Identification of Hazardous Wastes
- (3) 40 CFR 262 – Hazardous Waste Generator Standards
- (4) 40 CFR 263 – Hazardous Waste Transporter Standards
- (5) 40 CFR 264-270 – Hazardous Waste Treatment, Storage and Disposal Facilities
- (6) 40 CFR 268- Land Disposal Restrictions
- (7) 40 CFR 271- State Hazardous Waste Programs
- (8) 40 CFR 273- Universal Wastes
- (9) 40 CFR 279- Used Oil Regulations
- ii) Packaging  
Appendix G provides information for the fluoropolymer industry on how to dispose of packaging used to transport PTFE resin.

d) **Emergency Response –**

- i. **Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) and Emergency Planning And Community Right- to- Know Act (EPCRA) - 40 CFR Chapter I, Subpart J.** The main purposes of CERCLA and EPCRA are to allow for reporting of accidental hazardous substance releases and assess liability for cleanup damages, and to allow the public to know what hazardous substances inventories exist on site and are released. Sections that may apply to fluoropolymer processors include:
  - (1) 40 CFR 300 – National Contingency Plan
  - (2) 40 CFR 302 – Hazardous Substance Designation, Reportable Quantities and Notifications
  - (3) 40 CFR 355 – Emergency Planning and Notification
    - . 355.30 Emergency planning.
    - . 355.40 Emergency release notification.

Appendices A and B to Part 355 — The List of Extremely Hazardous Substances and Their Threshold Planning Quantities

(4) 40 CFR 370- Hazardous Chemical Inventory Reporting (Also known as SARA 311, 312)

(a) Subpart D – Inventory Forms

(5) 40 CFR 372- Toxic Release Reporting (also known as SARA Form R)

. Subpart D — Specific Toxic Chemical Listings

. Subpart E — Forms and Instructions

e) **Toxic Substances Control Act (TSCA) – 40 CFR Chapter I, Subpart R –**

TSCA regulations were enacted to acquire information about chemicals with potentially toxic effects and to establish management controls on particular toxic substances. The two major sections of TSCA involve chemical reporting and chemical management. Sections of TSCA that may apply to fluoropolymer processors are:

i) 40 CFR 704 – Specific Chemical Reporting

(1) Substances and mixtures that apply identified in 40 CFR 704 Subpart B

iii) 40 CFR 707- Chemical Imports and Exports

(1) Certification requirements

iv) 40 CFR 710 – TSCA Inventory List – all chemicals used must be present on list

v) 40 CFR 716- Health and Safety Data Reporting

vi) 40 CFR 717- Reports of Allegations – must collect and keep records for a chemical that causes a “reaction that may indicate a substantial impairment of normal activities or long-lasting or irreversible damage to health or the environment.” (40 CFR 717.3)

vii) 40 CFR 720- Premanufacture Notice (PMN) – applies to any new chemical substance

viii) 40 CFR 721- Significant New Use Reporting (SNUR) – definition in Subpart B, specific chemicals listed in Subpart E

**C. Transportation Considerations – Department of Transportation (DOT)**

([www.dot.gov](http://www.dot.gov))

The regulations found under 49 CFR regulate the transportation of hazardous materials. The following sections may apply to fluoropolymer processors:

i) 49 CFR 171 – General Information, Regulations, Definitions

(1) 171.15 Immediate notice of certain hazardous materials incidents.

(2) 171.16 Detailed hazardous materials incident reports.

ii) Part 172 — Hazardous Materials Table, Special Provisions, Hazardous Materials Communications, Emergency Response Information, and Training Requirements

(1) 172.101 Purpose and use of hazardous materials table.

iii) Part 173 — Shippers — General Requirements For Shipments and Packaging

iv) Part 177 — Carriage By Public Highway

(1) 177.816 Driver training.

(2) 177.817 Shipping papers



- (3) 177.834 General requirements.
- (4) 177.837 Class 3 (flammable liquid) materials.
- v) Part 397 — Transportation of Hazardous Materials; Driving and Parking Rules.

#### **D. Prop 65 Considerations**

In November 1986, California voters overwhelmingly approved an initiative to address growing concerns about exposures to toxic chemicals. That initiative became *The Safe Drinking Water and Toxic Enforcement Act of 1986*, better known by its original name: Proposition 65.

Proposition 65 requires the Governor to publish a list of chemicals that are known to the State of California to cause cancer, birth defects, or other reproductive harm. Agents that cause cancer are called *carcinogens*; those that cause birth defects or other reproductive harm are called *developmental and reproductive toxicants* (DART). The current list of chemicals listed can be obtained at: <https://oehha.ca.gov/proposition-65/proposition-65-list>.

Proposition 65 imposes certain controls that apply to chemicals that appear on the lists. These controls are designed to protect California's drinking water sources from contamination by these chemicals, to allow California consumers to make informed choices about the products they purchase, and to enable residents or workers to take whatever action they deem appropriate to protect themselves from exposures to these potentially harmful chemicals.

For further information, contact the Office of Environmental Health Hazard Assessment's (OEHHA) Proposition 65 Implementation Office at 916.445.6900 or <http://www.calepa.ca.gov/oehha/>.

On May 1, 1997, OEHHA listed tetrafluoroethylene (TFE) as a chemical known to the state to cause cancer based on the work performed by the National Toxicology Program. In accordance with the requirements of Proposition 65, manufacturers of products using fluoropolymer resins are required to determine if the use of their product could cause exposure of the user to TFE. Consult Appendix A for more information on TFE and fluoropolymer processing and contact your fluoropolymer resin supplier for detailed information on products you use.

On November 10, 2017, OEHHA listed Perfluorooctanoic acid (PFOA) as a chemical known to the state of California to cause reproductive toxicity. For years PFOA has been used in the manufacturing of certain fluoropolymers as a polymerization aid. Several manufacturers of fluoropolymers eliminated the use and emissions of PFOA from plant sites and products in 2015 as part of EPA's 2010/2015 Voluntary PFOA Stewardship program.

## APPENDIX E: GLOSSARY

**A3 rating:** ACGIH<sup>®</sup> animal carcinogen rating. Confirmed animal carcinogen with unknown relevance to humans: The agent is carcinogenic in experimental animals at a relatively high dose, by routes of administration at sites, of histologic types, or by mechanisms that may not be relevant to worker exposure. Available epidemiologic studies do not confirm an increased risk of cancer to exposed humans. Available evidence does not suggest that the agent is likely to cause cancer in humans except under uncommon or unlikely routes or levels of exposure.

Source: current edition, ACGIH Threshold Limit Values (TLV<sup>®</sup>s) for Chemical Substances and Physical Agents and Biological Exposure Indices (BEI<sup>®</sup>s).

**American Conference of Governmental Industrial Hygienists (ACGIH):** A professional organization devoted to the administrative and technical aspects of occupational and environmental health. ACGIH is not a government entity. For additional information refer to the current ACGIH TLVs<sup>®</sup> and BEIs<sup>®</sup> book or see [www.acgih.org](http://www.acgih.org).

**APME:** Association of Plastics Manufacturers in Europe. Now known as Plastics Europe (PE)

**Fluorinated Ethylene Propylene (FEP):** FEP resin is a polymer of tetrafluoroethylene and hexafluoropropylene with the formula  $[(CF(CF_3)-CF_2)_x(CF_2-CF_2)_y]_n$ . It has a melting point range of 473°-563°F (245- 280°C) and is melt processible. It is supplied in the form of translucent pellets, powder, or as an aqueous dispersion.

**Fluoropolymer dispersions:** Fluoropolymer dispersions are an aqueous form of fluoropolymer consisting of finely divided fluoropolymer particles suspended in water. They are frequently used as ingredients for coating compositions applied to metal surfaces or fiberglass cloth to create durable, nonstick surfaces.

**Fluoropolymer Polymerization Aid (FPA):** FPAs are members of a class of commercially available perfluoroalkyl carboxylate surfactants. FPAs are used to suspend and emulsify some fluoropolymers during manufacture or industrial use and are typically used in concentrations less than 0.5%.

**Freon<sup>®</sup>** is a registered trademark of The CHEMOURS Company

**Nanopowders:** Nanopowders consist of particles which range in size from 1 to 100 nanometers (nm) ( $10^{-9}$  meter). Particles this small are also known as ultrafine particles.

**NIOSH:** The National Institute for Occupational Safety and Health is a federal agency. It conducts research on health and safety concerns, tests, certifies respirators, and trains occupational health and safety professionals

**OSHA:** U. S. Occupational Safety and Health Administration.

**Permissible Exposure Limit (PEL):** A term used by OSHA. Unless noted otherwise,

OSHA PELs are TWA concentrations that must not be exceeded during any eight-hour work shift of a forty-hour workweek. These PELs are expressed as eight-hour TWA. Additional information can be found on the OSHA web site, [www.osha.gov](http://www.osha.gov).

*Personal Protective Equipment (PPE):* PPE is used to reduce exposures to hazards when engineering and administrative controls are not feasible or effective in reducing these exposures to acceptable levels.

*Perfluoroalkoxy Resin (PFA):* PFA resin is a polymer of tetrafluoroethylene and a perfluorinated vinyl ether having the formula  $[(CF(OR_f)-CF_2)_x(CF_2-CF_2)_y]_n$  where  $OR_f$  represents a perfluoroalkoxy group. PFA melts at 572°F (300°C) minimum and is melt processible. It is available in the form of pellets, powder, and as an aqueous dispersion.

*Polymer Fume Fever:* A type of inhalation fever associated with the inhalation of fluoropolymer decomposition products (exhaust effluents, fumes, and gases). It is characterized by temporary flu-like symptoms, which may include fever, chills, and / or, cough. Symptoms may be delayed approximately 4-24 hours following exposure. The severity of effects depends on the extent of overheating and the quantity inhaled. Decomposition products may produce progressive breathing difficulty and later develop into severe pulmonary edema. Edema may be delayed and unlike polymer fume fever, requires medical intervention.

*Polytetrafluoroethylene (PTFE):* PTFE is a polymer consisting of recurring Tetrafluoroethylene monomer units whose formula is  $[CF_2-CF_2]_n$ . PTFE does not melt to form a liquid and cannot be melt extruded. On heating the virgin resin, it forms a clear coalescable gel at 630°F±20° (332°C±10°). Once processed, the gel point (often referred to as the melting point) is 20°F (10°C) lower than that of the virgin resin. It is sold as a granular powder, a fine powder, or an aqueous dispersion.

*Polyvinylidene Fluoride (PVDF):* PVDF is a homopolymer of vinylidene fluoride having the formula  $[CH_2-CF_2]_n$  or a copolymer of vinylidene fluoride and hexafluoropropene having the formula  $[(CF(CF_3)-CF_2)_x(CH_2-CF_2)_y]_n$  or a copolymer of vinylidene fluoride and chlorotrifluoro ethylene having the formula  $[(CFClCF_2)_x(CH_2-CF_2)_y]_n$  PVDF polymers melt at 273 - 352°F (134 - 178°C) is melt processible, and is supplied in the form of powder, pellets, or as an aqueous dispersion.

*RCRA/US EPA WASTE INFORMATION:* The Resource Conservation and Recovery Act enacted by Congress in 1976. RCRA's primary goals are to protect human health and the environment from the potential hazards of waste disposal, to conserve energy and natural resources, to reduce the amount of waste generated, and to ensure that wastes are managed in an environmentally sound manner. Enabling legislation is U.S.C. title 42, chapter 82, subsections 6901 et seq. Additional information available from the US EPA Office of Solid Waste, or via the URL: <http://www.epa.gov/epaoswer/general/orientat/>.

*Skin notation:* Substances listed with designation "Skin" refer to the potential significant contribution to the overall exposure by the cutaneous route, including mucous membranes and the eyes, either by contact with vapors or, of probable greater significance, by direct skin contact with the substance. Vehicles present in solutions or

mixtures can also significantly enhance potential skin absorption. It should be noted that while some materials are capable of causing irritation, dermatitis, and sensitization in workers, these properties are not considered relevant when assigning a skin notation. It should be noted, however, that the development of a dermatological condition could significantly affect the potential for dermal absorption.

Use of the skin designation is intended to alert the reader that air sampling alone is insufficient to accurately quantitate exposure and that measures to prevent significant cutaneous absorption may be required.

[For additional information refer to the current ACGIH TLVs<sup>®</sup> and BEIs<sup>®</sup> book or see [www.acgih.org](http://www.acgih.org).]

**Systemic:** Systemic effect refers to an adverse health effect that takes place at a location distant from the body's initial point of contact and presupposes absorption has taken place.

**Threshold Limit Value (TLV<sup>®</sup>)** Threshold Limit Values (TLVs<sup>®</sup>) refer to airborne concentrations of substances and represent conditions under which it is believed that nearly all workers may be repeatedly exposed day after day without adverse health effects. Because of wide variation in individual susceptibility, however, a small percentage of workers may experience discomfort from some substances at concentrations at or below the threshold limit; a smaller percentage may be affected more seriously by aggravation of a pre-existing condition or by development of an occupational illness. Smoking of tobacco is harmful for several reasons. Smoking may act to enhance the biological effects of chemicals encountered in the workplace and may reduce the body's defense mechanisms against toxic substances. The amount and nature of the information available for establishing a TLV<sup>®</sup> varies from substance to substance; consequently, the precision of the estimated TLV<sup>®</sup> is also subject to variation and the latest TLV<sup>®</sup> Documentation should be consulted in order to assess the extent of the data available for a given substance.

**Threshold Limit Value / Time Weighted Average (TLV<sup>®</sup>-TWA):** The THA concentration for a conventional 8-hour workday and a 40-hour workweek, to which it is believed that nearly all workers may be repeatedly exposed, day after day, without adverse effect.

**THV:** THV is a copolymer of tetrafluoroethylene, hexafluoropropylene, and vinylidene fluoride. THV is melt processible with melting points ranging from 240° to 356°F (115° to 235°C) depending on grade. It is available in pellet, agglomerate or as an aqueous dispersion.

**Tumorigenic:** Tumors (benign and cancerous) are formed as swellings or abnormal growth of tissues. The probability that tumors will occur depends on the species, sex, strain, and age of the animal, as well as the dose, route and length of exposures to a substance.

## APPENDIX F: THERMAL PROPERTIES

*The data in this Appendix has been provided by individual material suppliers for their specific products, and, consequently, the appendix is not intended as a complete source. It should be used for informational purposes only and not for product comparisons. Data could vary significantly depending on the conditions under which testing is carried out and the specific product tested. Information provided here is not intended to be used in place of product-specific data provided in the respective Safety Data Sheets (SDS) available from the suppliers. Contact the specific material supplier for guidance on the use of these data and for additional information on the products contained in this Appendix, or for information on fluoropolymer resins not found in this Appendix.*

## *PART 1 — CHEMOURS*

### ***THERMAL PERFORMANCE OF CHEMOURS FLUOROPOLYMER RESINS AND TOXICITY OF DEGRADATION PRODUCTS***

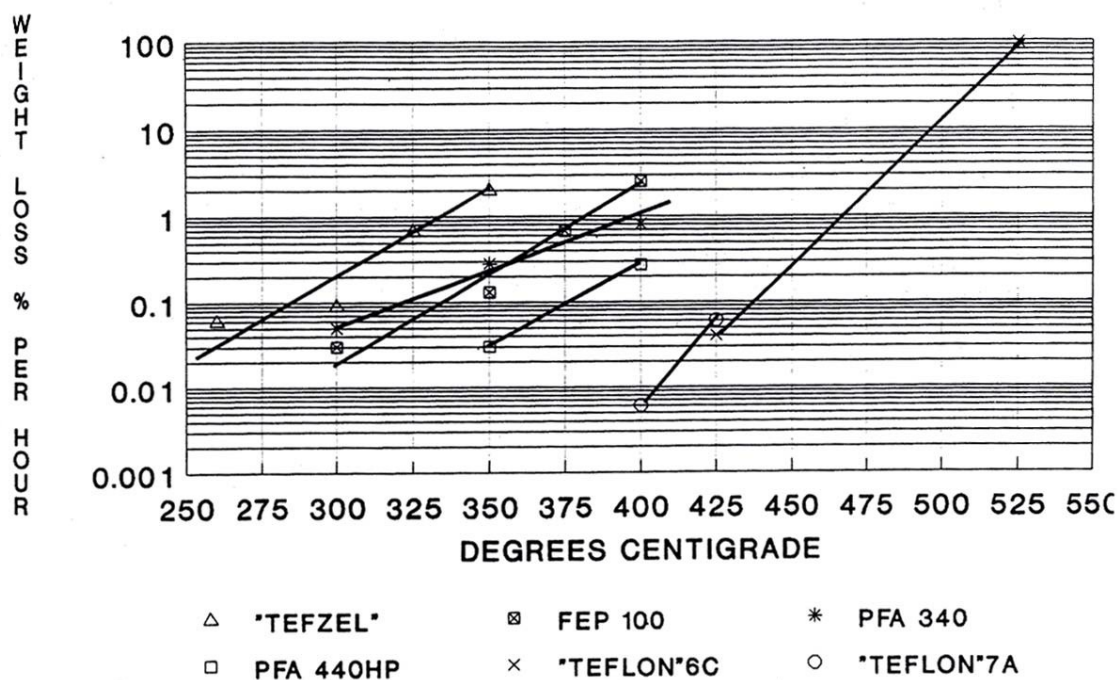
The Chemours Company (Chemours) fluoropolymer resins are very stable at their recommended continuous use temperatures; however, they do exhibit a small amount of degradation at higher processing temperatures. A study was completed on several Chemours fluoropolymer resins [Thermal Degradation of Commercial Fluoropolymers in Air, Vol. 42, 1994, 181-188] to determine the rate of degradation of several of their commercial fluoropolymers over the range of continuous use and processing temperatures and examined the nature and amount of the gases evolved. Six Chemours fluoropolymer resins were evaluated, including Teflon™ 7A Granular PTFE, Teflon™ 6C Fine Powder, Teflon™ PFA 340, Teflon™ PFA 440 HP, Teflon™ FEP 100, and Tefzel™ 200. All the resins were tested in the physical form in which they are commercially supplied.

The recommendations of different fluoropolymer producers as to the temperatures for commercial use of fluoropolymers may vary to a degree; **Table I** (Pg. 53) includes the values indicated by CHEMOURS for the resins used in this study.

**Figure II** (Pg. 5) shows the results of weight loss data from the rate of degradation experiments.

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**FIGURE II**  
**PERCENT WEIGHT LOSS ON HEATING IN AIR**



Weight loss data were obtained using a TA Instruments Thermal Analyst 2100, equipped with a 951 Thermogravimetric Analyzer (TGA). The duration of the run was usually 65 minutes. Because of the low rate of degradation of homopolymer (Teflon™ 7A and Teflon™ 6C) some runs were made for as long as 12 hours, using a Perkin- Elmer thermogravimetric balance, Model TGA-7.<sup>6</sup>

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Fluoropolymer resins when decomposed at high temperatures evolve toxic products. While several specific decomposition products have been identified, the spectrum of decomposition products and their toxicity depend on the method used to form the products, temperature, the rate of temperature rise and other conditions of pyrolysis. The most adverse effect associated with human exposure to fluoropolymer decomposition products is widely recognized as “polymer fume fever,” characterized by a temporary (approximately 24 hours) flu-like condition similar to metal fume fever (“foundry man's fever”). See Chapter 2 Section D.

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## DEGRADATION OF FEP FLUOROPOLYMER DURING MELT EXTRUSION

### *Introduction*

This Appendix provides additional information that supplements information in the main body of the 2018 Plastics Industry Association booklet entitled “Guide to the Safe Handling of Fluoropolymer Resins, 5th Edition.” Specifically, the additional information is on extrusion coating of wire with FEP resin, both solid and foamed coatings.

Processors and equipment vendors must take the information contained herein as that developed from FEP resin melt extrusions. The circumstances used represent attempts to examine harsh conditions; however, it may be possible to encounter more severe conditions. This technical information is not meant to represent specific commercial processes.

Processors and equipment vendors must take this technical information and determine for themselves what hazards do, or could, exist in their facilities. The technical information is intended for reference purposes only and should not be used alone as the basis for designing processes or process ventilation or storage systems.

FEP resin melt extrusion always leads to some degradation of the polymer. The degradation addressed in this Appendix H has two results:

- Lower molecular weight polymer (higher melt flow rate).
- Evolution of the toxic compound perfluoroisobutylene (PFIB).

PFIB becomes trapped in coatings and its later slow evolution can present a hazard to persons if substantial quantities of foamed constructions are stored in areas with poor ventilation. **It is essential that ventilation in process areas and storage facilities be reviewed.**

It is further recommended that professional assistance be obtained for review and design of ventilation systems to ensure their adequacy, performance, and compliance with all regulations. Monitoring instrumentation is recommended to ensure proper operation of the ventilation system and to indicate when there is a need for maintenance of associated ducts and fans. Alarms to indicate ventilation failure are important in providing for the safety of operating personnel.

This bulletin explains the effect of extrusion conditions on the extent of the degradation of FEP, discusses its health and safety significance, and offers suggestions for evaluating hazards.

### Effect of Extrusion Conditions on Resin Properties

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### *Solid or Foamed Coatings*

Moderate extrusion temperatures are used in producing solid FEP wire coatings. In low-speed extrusions, melt flow rate changes of less than 10% are normal. Extrusion foaming processes formerly recommended involve injected gases like Freon™ 22 blowing agent or, more recently, nitrogen (N<sub>2</sub>). Some nitrogen injection gas foamed high-speed extrusions produce resin melt flow rate changes greater than 10%. In addition to temperature, the shear rate seen by the resin also affects melt flow rate changes. Shear rate is dependent on screw speed and screw design factors, such as metering, flight depths, screw compression ratio, and design of mixing elements of the screw.

In addition to the processes recommended, another not-recommended foaming procedure was also examined. Both high local temperatures and high melt shear are characteristic of a procedure used in laboratories to produce foam cores of FEP without the use of an injection gas. In this foaming procedure it is presumed that the gas from resin degradation produces the foam. This procedure also leads to an increase in FEP melt flow rate (as much as 115%).

### *Effect of Extrusion Conditions on Perfluoroisobutylene Evolution*

In earlier work, the formation of PFIB as a degradation product of FEP in air was thought not to occur below 400°C (752°F). However, recent studies have shown that its formation occurs at temperatures as low as 360°C (680°F). This finding may simply be the result of the use of a more sensitive analytical technique, electron-capture gas chromatography, but because of the high toxicity of PFIB, the finding is significant.

After reviewing the PFIB toxicity data available, the American Industrial Hygiene Association established 0.1 ppm PFIB as their Emergency Response Planning Guideline-2, defined as “the maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to one hour without experiencing or developing irreversible or other serious health effects or symptoms which could impair an individual’s ability to take protective action.” The American Conference of Governmental Industrial Hygienists established for a ceiling (C) threshold limit value (TLV) for PFIB of C 0.01 ppm. This ceiling is a concentration that is not to be exceeded during any part of the working exposure.

The structure of FEP, with its -CF<sub>3</sub> branch from the incorporation of

hexafluoropropylene (HFP) in the  $-CF_2-$  backbone chain, makes it less thermally stable than TFE homopolymer or PFA resin. FEP degrades thermally with evolution of HFP as a principal degradation product, together with a smaller amount of PFIB. Both gases have been observed in laboratory experiments in nitrogen at temperatures of 360 to 400°C (680 to 752°F). In similar tests conducted in air, carbonyl fluoride ( $COF_2$ ) is also formed.

In the effluent gases from an extruder die operated at a melt temperature of 390 to 410°C (734 to 770°F), HFP and PFIB are observed but  $COF_2$  is not. This leads to the conclusion that conditions inside the extruder are essentially anaerobic. **The formation of PFIB emphasizes the necessity for local exhaust ventilation above the extruder die, along the coating line, in storage areas where spools of coated wire may be stored or anywhere the gases can escape into the air of the facility. This would include the exhaust from the vacuum pump used to control the length of the melt cone in solid or in foam extrusion. It is recommended that a minimum of 6 air changes per hour be maintained for general ventilation in all areas. Consult the reference guide issued by the SPI and mentioned earlier.**

In laboratory foaming experiments without injection of Freon<sup>®</sup> or nitrogen blowing gas, the polymer was heated to more than 400°C (752°F) while being subjected to high shear. It is this combination of shear and its associated thermal stress (local heating) in the presence of a nucleating agent that leads to foaming without the addition of a gas. The foaming agents are presumed to be the degradation gases from the resin, principally hexafluoropropylene. High shear resulting in higher polymer temperatures is responsible for more PFIB formation than would be predicted from equipment temperature alone.

#### Analytical Data on PFIB from FEP Wire Coating

In considering the analytical data, three types of operations are discussed below: solid coatings, foams made with injected nitrogen gas, and foams made with polymer degradation gases.

##### **Solid FEP Coatings**

In experiments with coating a 30-mil wire with 5 mil of solid FEP, it has been found that PFIB formed equivalent to 40 µg/g of FEP. The melt temperature was 403°C (757°F), the screw rpm was 6, and the residence time in the hot zone of the extruder was about 15 minutes.

The extrusion rate was 9 kg (20 lb)/hr and, therefore, the production rate of PFIB was approximately 5 mg/min. As mentioned earlier, the TLV for PFIB is C 0.01 ppm. This is equivalent to 0.082 mg/m<sup>3</sup> or 0.0023 mg/ft<sup>3</sup>. To ensure this TLV is not exceeded in such a process area without local exhaust ventilation, one would have to supply diluting room ventilation equal to:  $5 \text{ mg/min} \div 0.0023 \text{ mg/ft}^3 = 2,200 \text{ ft}^3/\text{min}$ .

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This assumes perfect mixing. As a conservative safety measure, a mixing factor of ten would necessitate 22,000 ft<sup>3</sup>/min of air flow. Even this might not provide a safe atmosphere for a worker in the immediate vicinity of the extrusion die. This amount of air flow is obviously impractical even at this modest extrusion rate of 20 lb/hr. Therefore, local exhaust hoods are necessary.

With solid coatings, about 50% of the PFIB escapes into the surrounding air and 50% remains dissolved in the FEP coating. The PFIB within the coating slowly diffuses into the air over a period of many days.

#### ***Nitrogen Injection Gas Foaming***

In an experiment with a 34-mil nitrogen injection gas foamed coating on a #22 AWG solid conductor, PFIB was formed in an amount equivalent to 11 µg/g of FEP. The melt temperature was 391°C (736°F), the screw rpm was 15, and the residence time in the extruder was 8 minutes.

With nitrogen injection gas foamed coatings, about 50% of the PFIB escapes immediately into the air and 50% remains in the foam. The PFIB within the coating slowly diffuses into the air over a period of many days.

#### ***Degradation Gas Foaming***

In an experiment making a similar 34-mil foamed coating with degradation gas, we found 62 µg of PFIB formed per gram of FEP. The melt temperature was 412°C (774°F), the screw rpm was 35, and the extruder residence time was 3 minutes.

**Table 1** summarizes the PFIB measured from extrusions in the laboratory. PFIB formed during foaming without injection gas cannot be explained by equipment temperature alone. Higher polymer melt temperatures generated by high shear are likely to be the explanation.

**Table 1**  
**Plot Conditions**

<b>Operation</b>	<b>Temperature, °C (°F)</b>	<b>Residence, min</b>	<b>µg PFIB/g Resin Measured</b>
Solid	403 (757)	15	40
N <sub>2</sub> Foamed	391 (736)	8	11
Degradation Gas Foamed	412 (774)	3	62
Degradation Gas Foamed	405 (761)	3	56

**Note:** Foaming experiments were carried out on a 60-mm extruder with a 30:1 L/D. The screw has a 450-mil feed depth and a 150-mil deep metering section leading to a 21-in long Saxton mixing head.

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### Significance of the PFIB That Remains Dissolved in the Coating

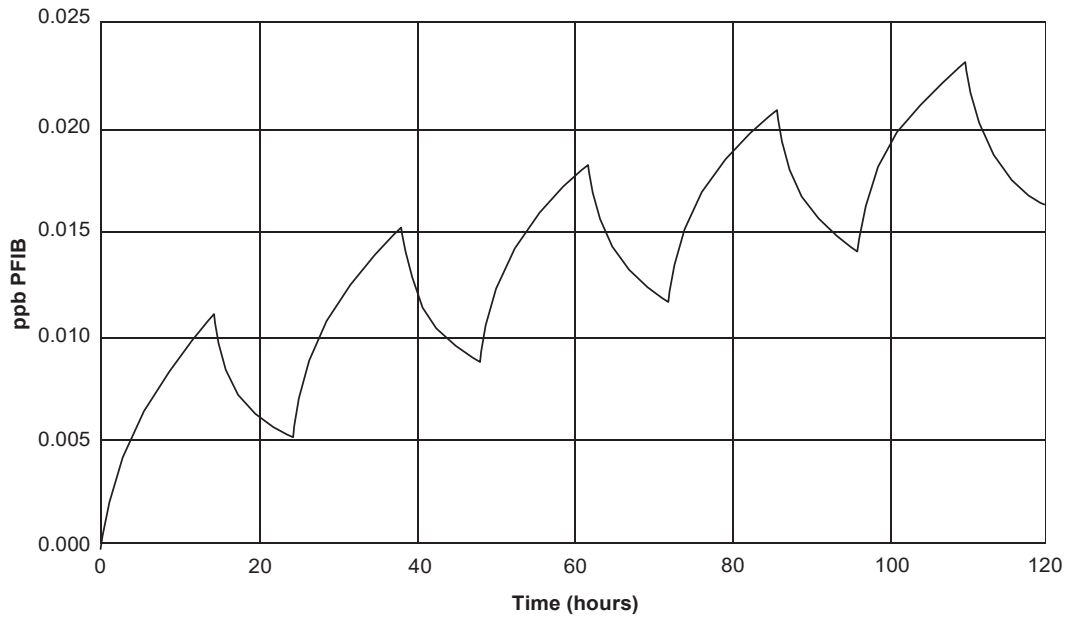
There is safety significance to this finding regarding the dissolved or entrapped PFIB. Calculations show a hazard may exist if large quantities of cores are stored in poorly ventilated areas. **Figure 1**, prepared with the aid of a computer program, graphically shows the degree of hazard for the procedures examined. The curves show the buildup of PFIB in an enclosed space with typical industrial building ventilation. **Figure 1** illustrates that the typical evolution of the PFIB concentration (starting with a concentration of 10µg of PFIB per g of FEP) from this simulation may be near 0.020 ppb (0.00002 ppm) which may be compared to the ceiling TLV of C 10.0 ppb (0.01 ppm).

The conditions assumed for the plot were:

- Type of Wire—#24 AWG solid conductor, 7-mil coating thickness
- Production Rate of Wire— 600 ft./min.
- Storage Compartment Volume—35,100 ft<sup>3</sup>
- Number of Air Changes per Hour—6
- Mixing Efficiency—0.5
- Hours per Day of Production—14
- Consecutive Days of Production—5
- Initial PFIB Concentration—0 ppb in the atmosphere, and 10µg of PFIB per g of FEP
- Diffusion Constant for PFIB in a Solid Coating— $3.0 \times 10^{-11}$  cm<sup>2</sup>/s

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**Figure 1. Model of the Evolution of PFIB from Coaxial Cable Core**  
**Ceiling (C) TLV for PFIB = C 10 ppb**



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### *Experimental Method for Determination of PFIB Content of Melt Processible Fluoropolymer Resins and Resin from Coated Wires*

Freshly extruded resin or freshly extruded fluoropolymer coated wires were collected and stored in an open environment to allow for diffusion of the dissolved gas from the resin or the wire coating for a specified period of time. At a selected time interval (Day 1, 2, 3, where Day 0 is the day the wire was extruded), either the feed resin or the resin coatings that was stripped from approximately 10 feet of extruded wire were analyzed for dissolved gas as described below.

The heat source used was a Lindberg/Blue M Model 55035 "Mini-mite" 800-watt tube furnace with a 30 cm heating zone. A thermocouple was positioned within 2 cm of the sample boat to record the actual temperature. The furnace was equipped with a stainless steel flow-through tube to house the sample holder and was preheated to a designated temperature with nitrogen flowing at a fixed flow rate.

In a typical run, the tube furnace was preheated to a temperature of 280°C to facilitate the rapid diffusion of the gas from the polymer melt. The resin sample weighing approximately 2.0 grams was placed in a quartz boat and the boat was inserted into the stainless steel tube. Gas flow was established at 80 mL/minute with a calibrated rotameter. The evolved gases were directly collected into a polyvinyl fluoride gasbag. The gasbag was analyzed for volatiles by gas chromatography with a mass selective detector (Hewlett Packard 6890 Gas Chromatograph equipped with an HP5873 Mass Selective Detector). The GC/MSD separation was performed with a Rtx-1 105m GC column (Restek). A nominal test run time duration is 20 minutes.

The concentration versus time data were analyzed with a Fick's law diffusion model to determine the diffusion constant.

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## THERMAL PERFORMANCE OF SOLVAY SOLEF® PVDF FLUOROPOLYMER RESINS

### *Weight Loss of Fluoropolymer Resin: Dynamic Thermal Gravimetry Analysis*

Conditions:

Material: Solvay Solef® PVDF Fluoropolymer Resins

Atmosphere: air

Output: 60 ml/min

Melting Pot in Pt - area: 0.4 cm<sup>2</sup>

Form: tray

Load Sample: 10 mg

Form: pellets

Temperature Profile: initial temperature: 30°C (86°F)

linear heating rate: 8°C/min (46°F/min)

	TGA T°	T <sub>1</sub>	T <sub>2</sub>	Weight Loss
	°F	°F	°F	%
SOLEF® 1010/0001	768	455	354	1
Melting temperature = 174°C (345°F)	808	495	384	2
Average processing temperature = 230°C (446°F)	828	514	414	3
Sample load: 10 mg				
Appendix n°: 1				
SOLEF® 6010/0000	774	462	360	1
Melting temperature = 173°C (343°F)	813	502	399	2
Average processing temperature = 230°C (446°F)	833	522	419	3
Sample load: 10 mg				
Appendix n°: 2				

T1 = Difference between TGA temperature and melting temperature.

T2 = Difference between TGA temperature — Average processing temperature.

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## THERMAL PERFORMANCE OF SOLVAY SOLEF® PVDF FLUOROPOLYMER RESINS

### *Weight Loss of Fluoropolymer Resin: Dynamic Thermal Gravimetry Analysis*

#### Conditions:

Material: Solvay Solef® PVDF Fluoropolymer Resins

Atmosphere: air

Output: 60 ml/min

Melting Pot in Pt - area: 0.4 cm<sup>2</sup>

Form: tray

Load Sample: 10 mg

Form: pellets

Temperature Profile: initial temperature: 30°C (86°F)

linear heating rate: 8°C/min (46°F/min)

	TGA T°	T <sub>1</sub>	T <sub>2</sub>	Weight Loss
	°F	°F	°F	%
SOLEF® 11008/0003	680	392	266	1
Melting temperature = 160°C (320°F)	685	397	271	2
Average processing temperature = 230°C (446°F)	693	405	279	3
Sample load: 10 mg				
Appendix n°: 3				

T1 = Difference between TGA temperature and melting temperature.

T2 = Difference between TGA temperature — Average processing temperature.

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## THERMAL PERFORMANCE OF SOLVAY SOLEF® PVDF FLUOROPOLYMER RESINS

### *Weight Loss of Fluoropolymer Resin: Dynamic Thermal Gravimetry Analysis*

#### Conditions:

Material: Solvay Solef® PVDF Fluoropolymer Resins

Atmosphere: air

Output: 60 ml/min

Melting pot in Pt - area: 0.4 cm<sup>2</sup>

Form: tray

Load Sample: 10 mg

Form: pellets

Temperature Profile: initial temperature: 30°C (86°F)

linear heating rate: 8°C/min (46°F/min)

	TGA T°	T <sub>1</sub>	T <sub>2</sub>	Weight Loss
	°F	°F	°F	%
SOLEF® 31008/0003	684	379	270	1
Melting temperature = 169°C (336°F)	693	388	279	2
Average processing temperature = 230°C (446°F)	698	394	284	3
Sample load: 10 mg				
Appendix n°: 4				
SOLEF® 31008/0009	696	392	282	1
Melting temperature = 169°C (336°F)	700	396	286	2
Average processing temperature = 230°C (446°F)	700	396	286	3
Sample load: 10 mg				
Appendix n°: 5				

T<sub>1</sub> = Difference between TGA temperature and melting temperature.

T<sub>2</sub> = Difference between TGA temperature — Average processing temperature.

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## THERMAL PERFORMANCE OF SOLVAY SOLEF® PVDF FLUOROPOLYMER RESINS

### *Weight Loss of Fluoropolymer Resin: Dynamic Thermal Gravimetry Analysis*

#### Conditions:

Material: Solvay Solef® PVDF Fluoropolymer Resins

Atmosphere: air

Melting pot in Pt - area: 0.4 cm<sup>2</sup>

Load Sample: 10 mg

Output: 60 ml/min

Form: tray

Form: pellets

Temperature Profile: initial temperature: 30°C (86°F)

linear heating rate: 8°C/min (46°F/min)

	TGA T°	T <sub>1</sub>	T <sub>2</sub>	Weight Loss
	°F	°F	°F	%
SOLEF® 31508/0003	680	376	266	1
Melting temperature = 169°C (336°F)	689	385	275	2
Average processing temperature = 230°C (446°F)	696	392	282	3
Sample load: 10 mg				
Appendix n°:6				
SOLEF® 31508/0009	698	394	284	1
Melting temperature = 169°C (336°F)	702	397	288	2
Average processing temperature = 230°C (446°F)	703	399	289	3
Sample load: 10 mg				
Appendix n°: 7				

T1 = Difference between TGA temperature and melting temperature.

T2 = Difference between TGA temperature — Average processing temperature.

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## THERMAL PERFORMANCE OF SOLVAY SOLEF® PVDF FLUOROPOLYMER RESINS

### *Weight Loss of Fluoropolymer Resin: Dynamic Thermal Gravimetry Analysis*

#### Conditions:

Material: Solvay Solef® PVDF Fluoropolymer Resins

Atmosphere: air

Melting pot in Pt - area: 0.4 cm<sup>2</sup>

Load Sample: 10 mg

Output: 60 ml/min

Form: tray

Form: pellets

Temperature Profile: initial temperature: 30°C (86°F)

linear heating rate: 8°C/min (46°F/min)

	TGA T°	T <sub>1</sub>	T <sub>2</sub>	Weight Loss
	°F	°F	°F	%
SOLEF® 32008/0003	684	379	270	1
Melting temperature = 169°C (336°F)	691	387	277	2
Average processing temperature = 230°C (446°F)	696	392	282	3
Sample load: 10 mg				
Appendix n°: 8				
SOLEF® 32008/0009	694	390	280	1
Melting temperature = 169°C (336°F)	698	394	284	2
Average processing temperature = 230°C (446°F)	700	396	186	3
Sample load: 10 mg				
Appendix n°: 9				

T1 = Difference between TGA temperature and melting temperature.

T2 = Difference between TGA temperature — Average processing temperature.

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### PART 3 — Arkema

## THERMAL PERFORMANCE OF ARKEMA KYNAR® PVDF FLUOROPOLYMER RESINS

### Weight Loss of Fluoropolymer Resin: Dynamic Thermal Gravimetry Analysis

Material:	Kynar PVDF
Fluoropolymer Type:	Copolymer
Form:	Pellets
Load Sample:	20 mg
Method:	TGA 10°C/min
Environment:	Air
Temperature Profile	23°C to 1000°C

Grade	Decomposition Temperature °C	
	5% Weight Loss	10% Weight Loss
Kynar® 2500	367	374
Kynar® 2800	379	387
Kynar® 2850	384	399

Material:	Kynar PVDF
Fluoropolymer Type:	Copolymer
Form:	Pellets
Load Sample:	20 mg
Method:	TGA 10°C/min
Environment:	Nitrogen
Temperature Profile	23°C to 1000°C

Grade	Decomposition Temperature °C	
	5% Weight :Loss	10% Weight Loss
Kynar® 2500	439	451
Kynar® 2800	433	447
Kynar® 2850	450	458

THERMAL PERFORMANCE OF  
ARKEMA KYNAR® PVDF FLUOROPOLYMER RESINS

Weight Loss of Fluoropolymer Resin: Dynamic Thermal Gravimetry Analysis

Material:	Kynar PVDF
Fluoropolymer Type:	Homopolymers
Form:	Pellets
Load Sample:	20 mg
Method:	TGA 10°C/min
Environment:	Nitrogen
Temperature Profile	23°C to 1000°C

Grade	Decomposition Temperature °C	
	5% Weight Loss	10% Weight Loss
Kynar® 740	459.4	469.7
Kynar® 760	468.0	478.7

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THERMAL PERFORMANCE OF  
ARKEMA KYNAR® PVDF FLUOROPOLYMER RESINS

Weight Loss of Fluoropolymer Resin: Dynamic Thermal Gravimetry Analysis

Material: Kynar PVDF Fluoropolymer  
Type: Flame Retardant Grades  
Form: Pellets  
Load Sample: 20 mg  
Method: TGA 10°C/min  
Environment: Air  
Temperature Profile: 23°C to 1000°C

Grade	Decomposition Temperature °C	
	5% Weight Loss	10% Weight Loss
Kynar® 2900-04	341	346
Kynar® 2950-05	333	339

Material: Kynar PVDF Fluoropolymer  
Type: Flame Retardant Grades  
Form: Pellets  
Load Sample: 20 mg  
Method: TGA 10° C/min  
Environment: Nitrogen  
Temperature Profile: 23°C to 1000°C

Grade	Decomposition Temperature °C	
	5% Weight Loss	10% Weight Loss
Kynar® 2900-04	341	346
Kynar® 2950-05	333	339

## **APPENDIX G: INHALATION TOXICITY OF FIRE EFFLUENT AND COMBUSTION BY-PRODUCTS**

A number of studies have been conducted over the past two decades to investigate the toxicity of the combustion/thermal degradation products of PTFE. Prior to 1982, it was believed that the major products (including hydrogen fluoride and carbonyl fluoride) were responsible for the toxic effects on rats exposed to the evolved combustion products of PTFE (a toxicity approximately 10 times greater than the combustion products of wood). However, in 1982, Levin, et al., using a newly developed National Bureau of Standards (NBS) small-scale test method for assessing the toxicology of combustion products, reported an unexpectedly high toxicity when testing PTFE. They found an LC<sub>50</sub> of 0.045 mg/l for PTFE products, compared to 20-40 mg/l for a standard sample of wood (Douglas fir). This unexpected result, which could not be explained in terms of the expected combustion products, led to extensive investigation by a number of laboratories.

Several reviews of these studies were presented at the Interflam '90 conference (Purser 1990; Fardell 1990; Clarke, van Kuijk, et al. 1990; Clarke, Seidel, et al. 1990). Together with recent publications (Warheit et al. 1990, Lee and Seidel 1991), an interesting explanation for the extreme toxicity associated exclusively with thermal degradation products of PTFE or similar perfluoropolymers emerges.

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 the 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 450° to 800°C (840° to 1,470°F), the particles generated are extremely fine, typically less than 0.05 microns. In an apparatus such as the NBS chamber, the particles will be confined to a relatively small volume. They will rapidly undergo thermal coagulation, producing fume particles of greater size and lower number concentration that will spread throughout the 200-liter exposure chamber. As they recirculate through the furnace, they may undergo deaggregation and dispersal, stabilizing 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 be related to free radical production during pyrolysis. 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 even more important, 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 than larger particles (Oberdorster, et al. 1990) 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 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. Although such conditions could possibly be reproduced in a real fire, other factors must also be considered.

First, experimental studies have shown effects only when using PTFE or fluoropolymers alone. A number of studies on mixed materials — for example, PTFE combusted with wood (Purser 1990) — did not produce extreme toxicity. This is more appropriate to real fires, which generally involve mixtures of materials and larger smoke particles that may tend to scavenge and detoxify fine PTFE particles.

Second, in full-scale fire tests using a number of potential ignition sources for perfluoropolymer-insulated cables (Clarke, van Kuijk, et al. 1990), the toxicity reported in rats exposed to the combustion products was consistent with that expected of the principle toxic agents (carbon monoxide, hydrogen fluoride, and carbonyl fluoride). There was no indication of extreme toxicity.

Therefore, it is more likely in a real fire situation that any of the 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.





For more information regarding the  
Fluoropolymers Products Division,  
contact Terry Peters at  
(202) 974-5280 or [tpeters@plasticsindustry.org](mailto:tpeters@plasticsindustry.org).



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