

AR 226-1064

Guide

to the

**Safe
Handling**

of

**FLUOROPOLYMER
RESINS**

3rd Edition

Published by the Fluoropolymers Division
of The Society of the Plastics Industry, Inc.

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 should be directed to SPI.

EMERGENCY RESPONSE

- Hazardous fumes may be produced at temperatures above 625°F (330°C). (See pages 15 and 35)
- Toxic fumes may be formed at 840°F (450°C) and above. (See pages 15 and 35)
- Hazardous vapor and fumes will be liberated during a fire. (See page 36)

IN CASE OF FIRE

- Fluoropolymers do not burn without an external source of heat. (See page 35)
- The principle decomposition products in a fire are *hydrogen fluoride (HF)*, *carbonyl fluoride (HF)*, *carbon monoxide (CO)* and *low molecular weight fluoropolymers*. (See page 36)
- Wear *self-contained breathing apparatus (SCBA)* to protect from inhalation of HF. (See page 35)
- Wear *full turnout gear or Level A equipment*, to protect skin and eyes 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 35)
- See the National Fire Protection Association's publication, NFPA 49, "Hazardous Chemicals Data" (1994 edition), and 29 CFR 1910.120 (k), "Hazardous waste operations and emergency response," for guidance.

EMERGENCY RESPONSE NUMBERS

- Transportation Emergency (Chemtrec) — 800.424.9300

RECEIVED
OCT 1 1994
2002 FEB 21 PM 2:23

FLUOROPOLYMERS DIVISION

**GUIDE TO THE
SAFE HANDLING OF
FLUOROPOLYMER
RESINS**

**The Society of the Plastics Industry, Inc.
1801 K Street, N.W., Suite 600K
Washington, D.C. 20006**

Third Edition: June 1998

CONTAIN NO CB1

TABLE OF CONTENTS

NOTE TO USERS	Page v
FOREWORD	Page 1
INTRODUCTION	Page 3
FLUOROPOLYMER RESINS	Page 5
PRODUCT INFORMATION SOURCES	Page 9
POTENTIAL HEALTH EFFECTS	Page 11
REGULATIONS	Page 19
SAFETY MEASURES	Page 23
ENVIRONMENTAL INFORMATION AND WASTE DISPOSAL	Page 39
FOOD AND MEDICAL APPLICATIONS	Page 41
EMERGENCY MEASURES	Page 43
BIBLIOGRAPHY	Page 47
TFE IN FLUOROPOLYMERS	Page 50
THERMAL PROPERTIES	Page 65
TRADE NAME CROSS REFERENCES	Page 99
INHALATION TOXICITY	Page 101

DEPT 111111

Copyright 1992, 1995, 1998

**The Society of the Plastics Industry, Inc.
All Rights Reserved**

**First Edition: October 1992
Second Edition: October 1995
Third Edition: June 1998**

NOTE TO USERS

This Guide was developed by the Fluoropolymers Division of The Society of the Plastics Industry, Inc. 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 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. SPI, 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.

SPI 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.

Fluoropolymer resins are classified under the U.S. Department of Transportation (DOT) Hazardous Materials Regulations¹ as nonhazardous as shipped and can be safely handled by following the basic safety recommendations of this guide. It is the intent of this guide to provide an overview of processing and fabricating. Each user is responsible to comply with applicable Federal, state and local laws. As far as possible, this document includes the latest technical and research information currently available and may be updated in the future, but users are cautioned they are responsible for the interpretation and applicability of all information presented.

Dispersions containing solvents may be classified as hazardous. Consult your supplier of fluoropolymer-containing materials for classification information.

Another important document that may be of help in establishing a safe handling program for fluorocarbon resins is "Criteria for a Recommended Standard...Occupational Exposure to Decomposition Products of Fluorocarbon Polymers,"² published in 1977 by National Institute for Occupational Safety and Health (NIOSH).

¹ 49 CFR § 171 et seq.

² U. S. Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, *Criteria for a Recommended Standard ... Occupational Exposure to Decomposition Products of Fluorocarbon Polymers*, DHEW (NIOSH) Publication No. PB274727, (Washington, D.C.: NTIS, September 1977), viii + 112 pp.

Fluoropolymer resins are produced and sold worldwide by several manufacturers. They have found application in nearly every field of modern industrial, technological, and scientific endeavor.

Of the many properties that characterize fluoropolymer resins, one of the most important is their resistance to heat. While few plastic materials have continuous service temperatures much above the boiling point of water, fluoropolymer resins can withstand the temperatures inside baking ovens and in the engine compartments of jet aircraft. Combined with chemical resistance and excellent dielectric stability, the heat resistance of fluoropolymer resins yields an extremely versatile family of engineering materials. These unique properties may provide certain desirable performance characteristics needed in the event of fire, in fluid containment or exclusion, electrical overload and similar emergencies. As with any polymeric material, overheating or thermal degradation of these resins can produce toxic effluents.

This guide includes information on the safe handling and processing of the materials identified in Chapter III. It is not intended to address compounded fluoropolymers or resins in the form of micropowders due to the variety and number of formulations possible.

CHAPTER III

FLUOROPOLYMER RESINS

MONOMERS

Polymers are made from monomers. The monomers commonly used in fluoropolymer resin manufacturing are listed in Table I. These monomers have various chemical and physical characteristics, and potentially significant health hazards.

Table I

Monomers w/ CAS Registry Numbers	Physical characteristics
Tetrafluoroethylene ($\text{CF}_2=\text{CF}_2$) CAS #: 116-14-3	MW: 100.02 / gas / b.p.: -76.3°C / m.p.: -142.5°C / Den.: 1.519 ^{-76.3}
Vinylidene Fluoride ($\text{CH}_2=\text{CF}_2$) CAS #: 75-38-7	MW: 64.03 / gas / m.p.: $<-84^\circ\text{C}$
Ethylene ($\text{CH}_2=\text{CH}_2$) CAS #: 74-85-1	MW: 28.05 / gas, mcl pr / b.p.: -103.7°C / m.p.: -169°C
Chlorotrifluoroethylene ($\text{FCCl}=\text{CF}_2$) CAS #: 79-38-9	MW: 116.47/b.p.: -26.2°C / m.p.: -157.5°C / Den: 2.54 ^{-60/4}
Hexafluoropropylene ($\text{CF}_3-\text{CF}=\text{CF}_2$) CAS #: 116-15-4	MW: 150.02 / gas / b.p.: -29.4°C / m.p.: -156.2°C / Den: 1.583 ^{-40/4}
Perfluoropropylvinylether ($\text{C}_3\text{F}_7\text{O}-\text{CF}=\text{CF}_2$) CAS #: 1623-05-8	MW: 266.04 / liquid / b.p.: 35°C / m.p.: $<-35^\circ\text{C}$
Perfluoromethylvinylether ($\text{CF}_3\text{O}-\text{CF}=\text{CF}_2$) CAS #: 1187-93-5	MW: 166.02 / gas / b.p.: -23°C

FLUOROPOLYMERS

Fluoropolymers are manufactured by connecting individual monomers chemically to form new substances called polymers. The resulting polymers have vastly different chemical and physical properties than monomers. Consequently, the potential health effects of monomers should not be confused with those of polymers. This means the potential health effects caused by overexposure

to fluoropolymers are quite different and typically far less significant than the potential health effects caused by overexposure to monomers. Chapter V discusses the potential health effects of overexposure to fluoropolymer resins. The commercial fluoropolymer resins are described below.

Fluoropolymers retain useful strength, flexibility, and dielectric properties over broad ranges of environmental conditions. Many applications depend on fluoropolymers' ability to serve for limited periods at temperatures above the rated values, e.g., electrical arc-quenching equipment, fire alarm cable, flexible hose, nonlubricated bearings, and other components which may be subject to sudden changes in temperature.

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 $630^\circ\text{F} \pm 50^\circ$ ($332^\circ\text{C} \pm 10^\circ$). Once processed, the gel point (often referred to as the melting point) is 50°F (10°C) lower than that of the virgin resin. It is sold as a granular powder, a fine powder, or an aqueous dispersion.³ Each is processed in a different manner.⁴

FEP

FEP resin is a polymer of tetrafluoroethylene and hexafluoropropylene with the formula $[(\text{CF}(\text{CF}_3)\text{-CF}_2)_x(\text{CF}_2\text{-CF}_2)_y]_n$. It has a melting point range of $473^\circ\text{-}536^\circ\text{F}$ ($245^\circ\text{-}280^\circ\text{C}$) and is melt processible. It is supplied in the form of translucent pellets, powder, or as an aqueous dispersion.

ECTFE

ECTFE is a polymer of ethylene and chlorotrifluoroethylene having the formula $[(\text{CH}_2\text{-CH}_2)_x(\text{CFCl-CF}_2)_y]_n$. ECTFE has a melting point range of $428^\circ\text{-}473^\circ\text{F}$ ($220^\circ\text{-}245^\circ\text{C}$) and is melt processible. It is available in the form of translucent pellets and as a fine powder.

PCTFE

³ PTFE may be sold in the form of a micropowder. This Guide does not address the hazards of resins sold in this form. Contact your suppliers for technical information and processing information.

⁴ The melting point data were obtained from American Society for Testing Materials (ASTM), 100 Barr Harbor Drive, West Conshohocken, PA 19428-2959.

PCTFE is a polymer of chlorotrifluoroethylene with the formula $[\text{CF}_2\text{-CFCl}]_n$. It has a melting point range of 410° - 428°F (210° - 220°C) and is melt processible. It is available in the form of translucent pellets and powder.

PFA

PFA resin is a polymer of tetrafluoroethylene and a perfluorinated vinyl ether having the formula $[(\text{CF}(\text{OR}_f) - \text{CF}_2)_x(\text{CF}_2 - \text{CF}_2)_y]_n$ 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.

PVDF

PVDF homopolymers of vinylidene fluoride having the formula $[\text{CH}_2\text{-CF}_2]_n$ and copolymer of vinylidene fluoride and hexafluoropropene having the formula $[\text{CF}(\text{CF}_3)\text{-CF}_2]_x(\text{CH}_2\text{-CF}_2)_y]_n$. PVDF polymers melt at 273° - 352°F (134° - 178°C), are melt processible, and are supplied in the form of powder, pellets, and dispersions.

ETFE

ETFE is a polymer of ethylene and tetrafluoroethylene of the formula $[(\text{CF}_2\text{-CF}_2)_x(\text{CH}_2\text{-CH}_2)_y]_n$. ETFE melts at 482° F(250°C) minimum. It is melt processible and is supplied in pellet and powder form.

MFA

MFA is a random copolymer of tetrafluoroethylene and perfluoromethylvinylether. It belongs to the generic class of PFA polymers. MFA melts at 536° - 554°F (280° - 290°C). It is available in the form of translucent pellets and aqueous dispersions.

THV

THV is a terpolymer of tetrafluoroethylene, hexafluoropropylene, and vinylidene fluoride. THV is melt processible with melting points from 240° to 356°F (115° to 180°C) depending on grade. It is available in pellet, agglomerate or aqueous dispersions.

The suppliers of these materials include the following: Asahi Glass America, Inc.; Ausimont U.S.A. Inc.; Custom Compounding, a Subsidiary of Dyneon LLC; Daikin America, Inc.; DuPont Fluoroproducts; Elf Atochem North America, Inc.; ICI Fluoropolymers; and Solvay Polymers, Inc. Many different grades or classes of each type of fluoropolymer resins are available. Please contact individual suppliers for specific product information.

Fluoropolymer manufacturers produce a large variety of products and product forms. It is recommended that users contact their resin suppliers for information regarding the specific physical properties and other needed product data.

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

AGA Chemicals, Inc.
(Asahi Glass Group)
2201 Water Ridge Parkway, Suite 400
Charlotte, NC 28210

Product Information: (704) 357-3631

AUSIMONT U.S.A., INC.
10 Leonards Lane
Thorofare, NJ 08086

Product Information: (800) 221-0553

CUSTOM COMPOUNDING
A Division of Dyneon LLC
50 Milton Drive
Bridgewater Business Park
Aston, PA 19014

Product Information: (800) 55-HOSTA

DAIKIN AMERICA, INC.
20 Olympic Drive
Orangeburg, NY 10962

Product Information: (800) 365-9570

DUPONT FLUOROPRODUCTS

1007 Market Street
Wilmington, DE 19898

Product Information: (800) 441-7515

ELF ATOCHEM NORTH AMERICA, INC.

Speciality Chemicals Group
Technical Polymers Department
2000 Market Street
Philadelphia, PA 19103-3222

Product Information: (800) 225-7788
(215) 419-7520

ICI FLUOROPOLYMERS

Concord Plaza — McKean 1st
3411 Silverside Road
Wilmington, DE 19850-5391

Product Information: (800) ICI-PTFE
(800) 424-7833

SOLVAY ADVANCED POLYMERS, INC.

Performance Polymers Group
3333 Richmond Avenue
P.O. Box 27328
Houston, Texas 77227

Product Information: (800) 231-6313

FLUOROPOLYMER RESINS

Fluoropolymer resins are known for their chemical stability and low reactivity. The toxicologic properties of these compounds are also favorable. The resins themselves have demonstrated little if any toxicologic activity. Fluoropolymers are neither skin irritants nor sensitizers in humans. Polyvinyl fluoride, for example, produced no skin reactions when tested for irritation and sensitization in humans.⁵ No abnormalities attributable to polytetrafluoroethylene were observed in several short-term oral toxicity tests. Observed responses were attributed to additives present in the products tested.

According to Montgomery, grossly excessive exposure to fluoropolymer resin dust produced increases in urinary fluoride but were below levels considered toxic.

Fluoropolymer resins have been used to manufacture medical implants⁶ for over twenty years. The International Agency for Research on Cancer (IARC) concluded that information was insufficient to assess the carcinogenic risk in humans.

As noted above, the available information on the hazards associated with exposure to unheated fluoropolymer resin dust suggests that the toxicity is low. However, many resins are formulated with additives to provide favorable performance or processing characteristics which may create other hazards in the use of the resins. For example, fluoropolymer aqueous dispersions contain surfactants and dispersing agents that may produce adverse physiological effects as a result of overexposure. It is recommended the resin suppliers be contacted for specific health information on additives used in their products. For substances added by the processor, the supplier of the additive should be contacted.

⁵ Harris, L. R., and Sarvadi, D. G., "Synthetic Polymers," *Patty's Industrial Hygiene and Toxicology*, 4th ed., Vol. 2, Part E, George D. Clayton and Florence E. Clayton, Eds., (New York: John Wiley & Sons, 1994).

⁶ See page 41 for discussion of medical applications.

PROCESSING EMISSIONS

Although fluoropolymers are among the most thermally stable plastics, fluoropolymers will begin to generate effluents at low rates at, or slightly above, their normal processing temperatures. The rate of generation rises with increasing temperature and care must be taken not to heat fluoropolymers above the manufacturers' recommended processing limits. Operation of processing equipment above the manufacturers' recommended limits may produce sufficient degradation of the polymer to produce particulate fume as well as toxic gaseous by-products.

The most common adverse effect associated with human exposure to fluoropolymer decomposition products is widely recognized "polymer fume fever" or "PFF," characterized by a temporary (approximately 24 hours) flu-like condition similar to metal fume fever (foundry man's fever).¹⁰ Symptoms can include fever, chills and, sometimes, cough.

Inhalation of effluent products from overheated fluoropolymers or after smoking fluoropolymer-contaminated tobacco may also cause polymer fume fever. 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 (see Chapter VI).

There have been several anecdotal literature reports¹¹ of residual pulmonary effects in individuals who have had repeated episodes of polymer fume fever. In most cases, the affected individuals have a history of smoking. Because of complicating factors, the validity of these findings is uncertain. Complicating factors can include: (1) mixed exposures; (2) limited information on prior exposure history; (3) limited, if any, data on actual chemical exposures; and (4) limited information on nonoccupational medical data on subjects.

Rose¹² suggests that no known hazard to health from exposure exists unless the polymer is heated above 300°C (572° F), and that, when "PTFE is heated above 300°C, adequate ventilation is essential." (See Chapter VII.)

¹⁰ Harris, D. K., *Lancet* 261, 1008, December., 1951.

¹¹ Kales, SN, MD, MPH. "Progression of Chronic Obstructive Pulmonary Disease after Multiple Episodes of an Occupational Inhalation Fever." *Journal of Medicine*. 1994;36:75-78. Albrecht, WN., Ph.D., MSPH. "Polymer-Fume Fever Associated with Smoking and Use of a Mold-Release Spray Containing Polytetrafluoroethylene." *J Occup Med*. 1987;29:817-819.

¹² Rose, Cecile A., *Inhalation Fevers*, in Rom, W.N., ed. *Environmental and Occupational Medicine*, 2nd ed., Boston: Little, Brown and Company, 1992: pp. 373-380.

Johnson et al¹³, theorize that heating of PTFE releases fumes containing ultra-fine particles which they believe 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 PFF did not develop in the animals. Unfiltered air produced the expected PFF response.

Fluoropolymers may decompose at elevated processing temperatures and may release sufficient amounts of effluents — e.g., hydrogen fluoride (HF), carbonyl fluoride (COF₂), perfluoroisobutylene (PFIB), and tetrafluoroethylene (TFE), among others — to present a potential hazard. These gases are all toxic at low concentrations and should not be inhaled (see below). Brief discussions of the effects of individual chemicals appear below. See suppliers MSDS for more detailed information.

Legal occupational exposure limits, (OEL), called Permissible Exposure Limits (PEL), for some of these individual chemicals may be specified in the U.S. Code of Federal Regulations, Title 29, Part 1910 (29 CFR 1910). Recommended occupational exposure limits, called Threshold Limit Values (TLV) or Recommended Exposure Limits (REL), may be established by the American Conference of Governmental Industrial Hygienists or by the National Institute for Occupational Safety and Health (NIOSH), respectively. Suppliers' MSDS may provide information from all of these sources if available.

THERMAL PROPERTIES OF FLUOROPOLYMERS

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 usual continuous use and processing temperatures for fluoropolymers are given in Table 1.

¹³ Johnston, C J., Finkelstein, J. N., Gelein, R., Baggs, R., and Obrduster, G., "Characterization of Early Pulmonary Inflammatory Response Associated with PTFE Fume Exposure": *Toxicology and Applied Pharmacology*, Article No. 0208, Academic Press, May 1996.

Table 1. Continuous Use and Processing Temperatures of Fluoropolymers*		
Polymer	Typical Continuous Use Temperature, °F (°C)	Typical Processing Temperature, °F (°C)
PCTFE	250 (120)	510 (265)
PVDF/HFP	255 (125)	480 (250)
PVDF	300 (150)	450 (230)
THV	300 (150)	500 (260)
ECTFE	300 (150)	540 (280)
ETFE	300 (150)	590 (310)
FEP	400 (205)	680 (360)
MFA	480 (250)	680 (360)
PFA	500 (260)	715 (380)
PTFE	500 (260)	715 (380)

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

The type of decomposition products depends on the conditions under which heating occurs. Temperature, availability of oxygen, the physical form of the article, and the residence time of the reaction products at the high temperature are among the factors that determine the ultimate nature of the decomposition products. The presence of other substances may also affect the nature of the decomposition products. The three main types of products formed in the decomposition of fluoropolymers are fluorine compounds, oxidation products, and low-molecular-weight fluoropolymer particulates.

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, generally, TFE monomer is the principle gaseous product at temperatures that just produce softening or melting of the polymer¹⁹. The TFE observed in the studies reported by NIOSH may be residual

¹⁹ U. S. Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, *Criteria for a Recommended Standard ... Occupational Exposure to Decomposition Products of Fluorocarbon Polymers*, DHEW (NIOSH) Publication No. PB274727, (Washington, D.C.: NTIS, September 1977), p. 16.

monomer that is trapped in the resin and is released as the temperature increases. However, while there is little or no direct evidence confirming this hypothesis, there are thermogravimetric data suggesting this is true.

As the 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 the hydrogen fluoride and carbon dioxide. Small amounts of hexafluoropropylene may also be found at these temperatures. The highly toxic 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. See also Appendix B, "Thermal Properties," for information provided by the individual manufacturers on their fluoropolymer products.

While there are no known fatalities directly attributed to exposure to fumes generated as a result of the heating of fluoropolymer resins in routine handling or processing²⁰, it continues to be important to require proper ventilation to prevent worker exposure (See Chapter VII).

Individuals with preexisting diseases of the lungs may have increased susceptibility to the toxicity of excessive exposures from thermal decomposition products. Consult the Material Safety Data Sheets (MSDS) supplied by the resin manufacturer for additional information.

Hazardous gases and vapors produced in fires involving fluoropolymers include hydrogen fluoride, carbonyl fluoride, carbon monoxide, and low molecular weight fluoropolymers.

²⁰ 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.

HEALTH EFFECTS OF DECOMPOSITION PRODUCTS

HYDROGEN FLUORIDE (HF)

The effects of overexposure due to inhalation of hydrogen fluoride may include: symptoms of choking, coughing, and severe eye, nose and throat irritation, possibly followed after by a symptomless period of 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, effective medical assistance is needed.

CARBONYL FLUORIDE (COF₂)

The effects of overexposure to carbonyl fluoride 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 overexposure to carbonyl fluoride may be delayed for several hours. If the effects observed include severe breathing difficulties, including congestion in the chest, immediate medical attention, including a period of observation, may be required.

TETRAFLUOROETHYLENE (TFE)

TFE is a flammable, gaseous monomer which may cause acute effects when inhaled, including irritation of the upper respiratory tract and eyes, mild central nervous system depression, nausea and vomiting, and dry cough. Intentional massive inhalation of the gas reportedly produced cardiac arrhythmia, cardiac arrest, and death.

A report has been issued by the U.S. National Toxicology Program (the NTP) on the results of a two year study on TFE. The NTP study reported kidney and liver tumors in rats and mice following lifetime (~2 years) inhalation of gaseous TFE. The relationship of these effects to potential human response has not been established. A working exposure limit of 5 ppm has been recommended by manufacturers who use TFE in making fluoropolymers. See Appendix A for more information on the NTP report and research being conducted on potential responses to TFE from fluoropolymer processing.

PERFLUOROISOBUTYLENE (PFIB)

The effects of inhalation exposure to PFIB have been studied in animals. Severe adverse effects occurred, including pulmonary edema in animals exposed to high concentrations, which can lead to death. Symptoms in exposed animals include wheezing, sneezing, difficulty breathing, and abnormally deep or rapid breathing. Animals that survive for 24 hours after the exposure apparently recover with no after-effects. Little human exposure data exists, but the ACGIH TLV-C is 0.01 ppm.²¹

EMISSIONS FROM FINISHED PRODUCTS

Depending upon the material and finished product manufacturing conditions, it is theoretically possible that small quantities of residual gases, including PFIB, hexafluoropropylene (HFP), TFE, and 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 underscores the importance of following manufacturer instructions in sintering and other finishing operations.

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.

Sealed packages 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 performed.

²¹ Documentation of TLVs, American Conference of Governmental Industrial Hygienists, "Perfluoroisobutylene" 1997.

Regulations exist that apply to the manufacture and use of fluoropolymers and new regulations are announced on a regular basis. Current information about regulations can be obtained directly from your Federal, state or local regulatory agency or your fluoropolymer manufacturer or supplier. Manufacturers' addresses are listed in Chapter IV.

To cite Federal regulations listed below, use title, part and section number. Thus 21 CFR 177.1550 Perfluorocarbon resins (1b, below) refers to title 21 of the Code of Federal Regulations, part 177, section 1550.

GENERAL REGULATIONS

VIII. Title 21 Code of Federal Regulations: Food and Drugs

1. Part 110 — Current Good Manufacturing Practice in Manufacturing, Packing, or Holding Human Food.
 - a. 177.1550 Perfluorocarbon resins.
 - b. 177.2510 Polyvinylidene fluoride.
 - c. 177.1380 Fluorocarbon resins.

IX. 29 CFR — Occupational Safety and Health

The following OSHA standards apply in nearly every fluoropolymer processor facility. It is NOT a complete list of all standards that a processor might have to follow. Rather, it includes the ones that OSHA is most likely to consider when inspecting a fluoropolymer processor facility. Fluoropolymer processors should make sure that their operations are in compliance with these standards, but also should be aware of the other standards that affect them. In addition, fluoropolymer processors who have more than ten employees on any day in a given year are required to keep and maintain for five years a log of occupational injuries and illnesses (OSHA Form 200) and the supporting documentation for all serious or disabling injuries and illnesses occurring in their workplace in that year. Copies of the OSHA standards may be obtained from a local OSHA office, or the Government Printing Office outlet nearest you. A computerized version of the standards and official interpretations is included in a subscription service on CD-ROM available from the Government Printing Office for less than \$80 per year.

A. Recordkeeping

1. Part 1904 — Recording and Reporting Occupational Injuries and Illnesses
2. Part 1910 — Occupational Safety and Health Standards
 - a. 1910.147 The control of hazardous energy (lockout/tagout).
 - b. 1910.1200 Hazard Communication
3. Subpart O — Machinery and Machine Guarding
 - a. 1910.216 Mills and calenders in the rubber and plastics industries.

- b. 1910.241-244 Hand and portable powered tools; Guarding; Other portable tools and equipment.
- 4. Subpart S — Electrical
 - a. 1910.176 Materials Handling — general.
 - b. 1910.178 Powered industrial trucks.
 - c. 1910.151 Medical services and first aid.
- 5. Subpart I — Personal Protective Equipment
 - a. 1910.145 Specifications for accident prevention signs and tags.
 - b. 1910.146 Permit-required confined spaces.
- 6. Subpart Q — Welding, Cutting and Brazing
 - a. 1910.1000 Air-contaminants (Permissible Exposure Limits).
 - b. 1910.134 Respiratory protection.
- B. Emergency Preparedness
 - a. 1910.37 Means of egress, general.
 - b. 1910.38 Employee emergency plans and fire prevention plans.
 - c. 1910.120 Hazardous waste operations and emergency response (HAZWOPER).
 - d. 1910.157 Portable fire extinguishers.

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

- C. Bulk Storage
 - a. 1910.106 Flammable and combustible liquids.
- D. Ventilation
 - a. 1910.94 Ventilation.
 - b. 1910.107 Spray finishing using flammable and combustible materials.
 - c. 1910.119 Process safety management of highly hazardous chemicals.
 - d. 1910.1450 Occupational exposure to hazardous chemicals in laboratories.

The following EPA standards generally apply to fluoropolymer processors:

- X. 40 CFR Protection of Environment
 - A. Part 261 — Identification and Listing of Hazardous Waste
 - 1. Subpart A — General
 - a. 261.3 Definition of hazardous waste.
 - b. 261.7 Residues of hazardous waste in empty containers.
 - 2. Subpart C — Characteristics of Hazardous Waste
 - a. 261.21 through 261.24 Characteristics of ignitability, corrosivity, reactivity, toxicity.
 - 3. Subpart D — Lists of Hazardous Wastes
 - B. Part 264 — Standards for Owners and Operators of Hazardous Waste Treatment,

Storage and disposal Facilities

1. Subpart B — General Facility Standards
 - a. 264.15 General inspection requirements.
2. Subpart I — Use and Management of Containers
 - a. 264.174 Inspections.
3. Subpart J — Tank Systems
 - a. 264.196 Response to leaks or spills and disposition of leaking or unfit-for-use tank systems.
4. Appendix V to Part 264 — Examples of Potential Incompatible Wastes
- C. Part 280 — Technical Standards and Corrective Action Requirements for Owners and Operators of Underground Storage Tanks (UST)
- D. Part 302 — Designation, Reportable Quantities, and Notification
 1. 302.6 Notification requirements.
- E. Part 355 — Emergency Planning and Notification
 1. 355.30 Emergency planning.
 2. 355.40 Emergency release notification.
 3. Appendices A and B to Part 355 — The List of Extremely Hazardous Substances and Their Threshold Planning Quantities
- F. Part 370 — Hazardous Chemical Reporting: Community Right-To-Know
 1. Subpart D — Inventory Forms
- G. Part 372 — Toxic Chemical Release Reporting: Community Right-to-know
 1. Subpart D — Specific Toxic Chemical Listings
 2. Subpart E — Forms and Instructions

The following DOT standards generally apply to fluoropolymer processors:

XI. 49 CFR — Transportation

A. Hazardous Materials Regulations

1. Part 171 — General Information, Regulations, and Definitions
 - a. 171.15 Immediate notice of certain hazardous materials incidents.
 - b. 171.16 Detailed hazardous materials incidents reports.
2. Part 172 — Hazardous Materials Table, Special Provisions, Hazardous Materials Communications, Emergency Response Information, and Training Requirements
 - a. 172.101 Purpose and use of hazardous materials table.
3. Part 173 — Shippers — General Requirements For Shipments and Packagings
4. Part 177 — Carriage By Public Highway
 - a. 177.816 Driver training.
 - b. 177.817 Shipping papers
 - c. 177.834 General requirements.
 - d. 177.837 Class 3 (flammable liquid) materials.
5. Part 397 — Transportation of Hazardous Materials; Driving and Parking Rules.

CALIFORNIA PROPOSITION 65

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). This list must be updated at least once a year. Over 604 chemicals have been listed as of September 1, 1996.

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.cahwnet.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.

INTRODUCTION

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 (OSH Act) 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 knowledgeable individuals are not employed by the processor, 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.

VENTILATION

As with most polymers, minute quantities of residual gases may diffuse from the resins even at room temperature. Therefore, as a matter of good 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 MSDS 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 page 14.

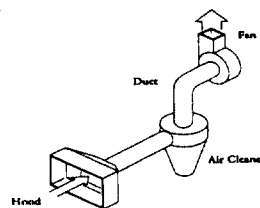


Figure 1 Exhaust Systems

LOCAL EXHAUST VENTILATION SYSTEMS

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).

The reasons LEV is so effective are as follows:

- 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]).
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 duct work of this type is commercially available.

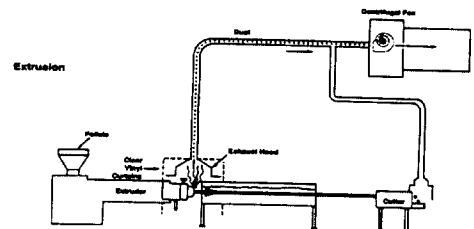


Figure 2 Typical Setup for Exhaust

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.

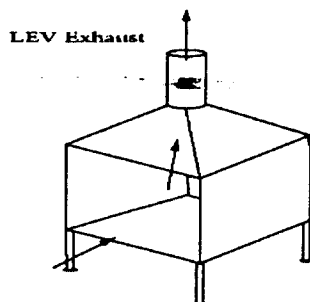


Figure 3 Hood

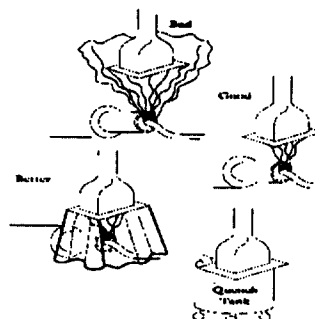


Figure 4 Extruder Die Hood

The airflow around the area where the contaminants are generated is sensitive to cross-currents, 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 off-gases released from hot polymers 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**.²² These designs present several alternatives to allow adequate exhaust volumes for effective capture and removal of off-gases. Situations normally 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 1**.²³

²² American Conference of Governmental Industrial Hygienists, *Industrial Ventilation: A Manual of Recommended Practice*, 17th ed., (Cincinnati, OH: 1982), 4-1 to 4-5. (Consult the most current edition).

²³ Ibid.

The work situation is selected from **Table 1** and the center-line velocity required to capture all gases is then used to calculate the volumetric rate of air flow 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 ft². The volume of air required is given by the equation:

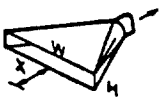
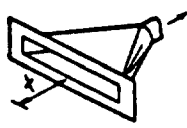
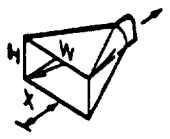
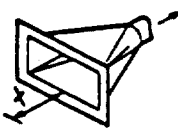
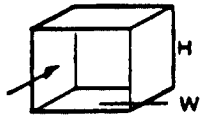
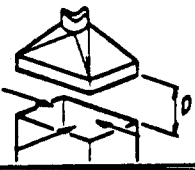
$$Q = V (10X^2 + A)$$

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 (m³/s)
 A = Area at face of hood, sq ft (m²)
 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 1: Capture Velocities Recommended in Various Work Situations

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

Dispersions of Contaminants into Air	Examples	Capture Velocity, fpm (m/s)
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:

Lower End of Range	Upper End of Range
1. Room air currents minimal or favorable to capture.	1. Disturbing room air currents.
2. Contaminants of low toxicity.	2. Contaminants of high toxicity.
3. Intermittent, low production.	3. High production, heavy use.
4. Large hood—large air mass in motion.	4. Small hood—local control only.

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 $200 (10 \times 1^2 + 0.5) = 2100$ cfm, a rise of 350%.

DESIGNS FOR RESIN PACKAGE OPENING AND MANUAL TRANSFER OF MATERIALS

Fluoropolymer resins may contain residues of gases used to manufacture the resins which 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.

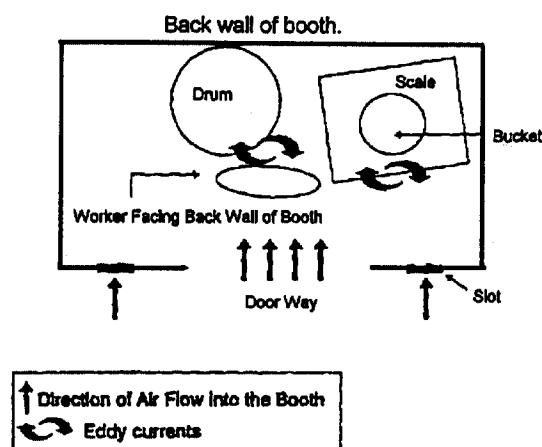


FIGURE 6: Bag opening/weighing station

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 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' MSDS 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.

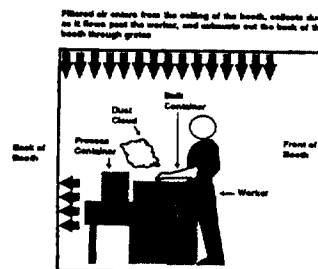


FIGURE 7 Weighing Station

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.

EQUIPMENT AND TEST DEVICES

1. Ventilation Smoke Tubes: to visually check the air currents around an exhaust hood (see figure 8).
2. Air Velocity Meters: to measure airflow and "capture" velocity.
3. Static Pressure Gauges.
4. Portable LEV units.
5. Adjustable Duct Systems.

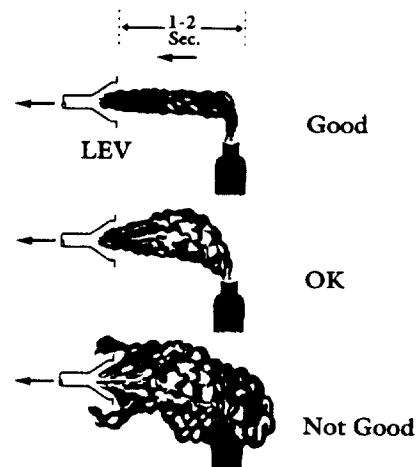


FIGURE 8: Use of Smoke Tubes

PROCESSING

SINTERING OPERATIONS require the use of high-temperature ovens in which various amounts of decomposition products are formed. Ovens must have forced ventilation with sufficient air flow to prevent formed gases from entering the work space during oven operation and when the doors are opened. Ovens must be properly maintained to keep gases from the oven from leaking into the work area.

Temperatures in excess of normal sintering temperatures must be avoided. To assist in this, ovens should be equipped with an independent, high-temperature cut-off switch triggered by an increase of temperatures 50° — 60°F (28° — 33°C) higher than the sintering temperature. Both systems need to be calibrated at regular intervals. If the oven temperature exceeds the high temperature cut-off setting, the heaters must be switched off and the oven must be cooled to ambient temperature and properly vented before the door is opened.

When opening sintering ovens after overheating, appropriate personal protective equipment is recommended, e.g., protective clothing, a self-contained breathing apparatus or supplied-air respirator, gloves, safety glasses, etc.

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 supplier and the information on the MSDS from the PTFE supplier.

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.

Processing fluoropolymer *AQUEOUS DISPERSIONS* normally requires a heating process to remove water and surfactant prior to sintering the fluoropolymer. Some surfactants and their degradation products are flammable and/or irritants. The oven used to remove these products must be provided with forced ventilation to prevent a hazardous build-up of vapor. Contact your dispersion supplier for specific product information.

Processing *NON-AQUEOUS DISPERSIONS* utilizing fluoropolymer materials may incorporate the use of combustible and flammable liquids similar to paste extrusion resins described above. Similar precautions must be taken for the safe use, storage, and handling of fluoropolymer resins containing a solvent-based dispersion medium or additives. Follow the recommendations of the dispersion supplier.

MELT PROCESSING of fluoropolymer resins at excessively high temperatures or exposing them at processing temperatures for extended times can cause rapid decomposition of the resins. Decomposition will produce gases and generate pressures in processing equipment sufficient to "blow back" through the feed port. If no exit 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 which is processing any thermoplastic, especially during start up.

To prevent accelerated decomposition of fluoropolymers, corrosion-resistant materials must be used 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).

PIGMENTS AND FILLERS

Filled and pigmented fluoropolymers are in widespread use. The normal precautions for handling fluoropolymers need to be observed. In addition, users need to note any additional hazards arising from the fillers or pigments themselves. Although many of the commonly used fillers and pigments have low toxicity, some are abrasive and may cause irritation in contact with the skin. 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 is required. Contact your supplier prior to using filled and/or pigmented fluoropolymers for specific safety recommendations. When a user mixes pigments, fillers, or other materials with 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 added materials, 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 MSDS and appropriate label must be provided.

GRINDING AND MACHINING

Grinding, sawing, and machining fluoropolymers and fluoropolymer-coated articles are performed routinely in fabricators' shops. All normal high-speed machining techniques can be used provided the tools have sharp cutting edges. Coolants are recommended to improve production rates and quality and they will serve to control any tendency toward overheating, eliminating the need for special ventilation. Dust generated by machining products manufactured from fluoropolymer resins are classified as Particulates Not Otherwise Classified (PNOC) for which the American Conference of Governmental Industrial Hygienists (1997) recommends a Threshold Limit Value (TLV) of 10 mg/m³ TWA (inhalable) and 3 mg/m³ TWA (respirable). The OSHA PEL (Permissible Exposure Limit) is 15 mg/m³ total dust or 5 mg/m³ respirable dust. However, machining products manufactured from resins which contain fillers, pigments, or other additives may produce hazardous dusts due to the presence of the fillers and other additives. If the local exhaust cannot reduce air contaminants below occupational exposure limits, wear respiratory protection. Use a NIOSH/MSHA approved respirator equipped with high-efficiency particulate air (HEPA) filters and develop and implement a respiratory protection program under OSHA's standard, 29 CFR 1910.134. Consult the additive supplier or MSDS for further information for the additives.

SOLDERING AND MELT STRIPPING

Major uses for fluoropolymers are in electrical insulation for electronics, computers, and in industrial equipment. In many cases, soldering or use of a heated element to remove insulation from wire and cable are routine operations.

As in most uses of fluoropolymers, the combined effects of temperature, quantity of resin, exposure time, and ventilation conditions during soldering and melt stripping are important factors for worker comfort and safety. The use of local fume hoods as described in the

ventilation section is strongly recommended.

WELDING AND FLAME CUTTING

Direct application of welding arcs and torches can quickly destroy the usefulness of parts made with most plastics, including those from fluoropolymers. For practical reasons, therefore, it is necessary to remove all such parts from equipment to be welded. Where removal is not possible, such as in welding or cutting coated parts, mechanical ventilation should be provided to prevent exposure to fluoropolymer fumes. The guidelines given earlier can effectively be applied to the design of ventilation hoods for this purpose. Specific designs for welding operations can be found in the publication, *Industrial Ventilation, A Manual of Recommended Practice*.²⁴ Safety precautions such as appropriate respiratory protection and fire prevention precautions must be taken when welding operations are performed.

Fluoropolymers and the components of fluoropolymer coatings are "self-extinguishing," i.e., they will not support combustion unless there is an external source of oxygen, however, if exposed to flames or other sources of extreme heat, fluoropolymers and fluoropolymer coatings will thermally degrade and, like other organic materials, produce toxic fumes.

CLEANING AND MAINTENANCE OF PROCESS EQUIPMENT

Cleaning and maintaining process equipment components (dies, screen packs, screws, etc.) may involve pyrolysis of residual polymer. 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 beginning of this chapter for additional information on ventilation.

PROTECTIVE CLOTHING

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, NIOSH approved respiratory protection for use against dusts and mists having a TLV of not less than 0.05 mg/m³

²⁴ American Conference of Governmental Industrial Hygienists, *Industrial Ventilation: A Manual of Recommended Practice*, 17th ed., (Cincinnati, OH: 1982), 4-1 to 4-5. (Consult the most current edition).
Guide to the Safe Handling of Fluoropolymer Resins, Third Edition
Copyright 1992, 1995, 1998 The Society of the Plastics Industry, Inc., All Rights Reserved

should be worn. While processing and handling filled compounds, in addition to the dust masks, goggles and protective gloves should be specified. Resins containing solvent may require the use of NIOSH approved organic vapor cartridges fitted with dust/mist prefilters or HEPA filters. Consult your resin supplier for guidance.

Fluoropolymer dispersions contain residues of fluorinated wetting agents which should not come in contact with the skin. It is necessary to wear protective gloves and other protective clothing and equipment to prevent skin contact when handling these products.

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. See Chapter VIII (Pg 39) for disposal guidance.

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 V) 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.

FIRE HAZARD CONSIDERATIONS

Fluoropolymers, in the absence of an independent external source of flame, will not continue to burn when tested in accordance with UL 94.²⁵ However, if the resins are present in a fire, they can decompose and add to the fumes being generated. Since the possibility of a fire can never be

²⁵ Underwriters' Laboratories, *Tests for the Flammability of Plastic Materials for Parts On Devices and Appliances*, (Northbrook, IL: UL 94)

ruled out in a factory, the local fire service should be advised of the probable nature of fumes generated from the combustion or thermal decomposition of fluoropolymer resins. Self-contained breathing apparatus (SCBA) and full turn out gear (fire fighters) or Level A equipment (HAZMAT teams) must be worn when involved in extinguishing a chemical fire, rescuing people, or cleaning up in the presence of potentially toxic fumes. Following exposure to toxic fumes or substances, decontamination of emergency response personnel's protective clothing and equipment according to accepted procedures is essential. See the National Fire Protection Association's publication, NFPA 49, "Hazardous Chemicals Data" (1994 edition), and 29 CFR 1910.120 (k), "Hazardous waste operations and emergency response," for guidance. See Appendix D for a technical discussion of the fire hazard properties of fluoropolymers.

Incomplete combustion of fluoropolymers in fires can produce hydrogen fluoride, perfluoroisobutylene, carbonyl fluoride, and other gases in potentially hazardous quantities. Therefore, if individuals are exposed to products of combustion from a fire containing fluoropolymers, they may need treatment for inhalation of hydrogen fluoride or the other decomposition products or for skin contact with hydrogen fluoride. Refer to Chapter X for emergency measures information.

The Emergency Planning and Community Right-To-Know Act requires companies to provide material safety data sheets on the products in their facilities and to identify hazardous materials that can be released in emergencies. Emergency plans should be developed, based on the information in the materials safety data sheets, in conjunction with fire authorities. The emergency plan should specifically identify the gases that may be present and the appropriate precautions to be taken in the event of a fire to protect the public from toxic smoke.

Appropriate fire prevention measures must be taken when storing, handling, and processing of lubricated fluoropolymers if there is a possibility of ignitable vapor/air mixtures forming. See 29 CFR 1910.106 Flammable and combustible liquids (Chapter VI).

Filled fluoropolymer compounds, in the form of powders and especially those containing metals, should be handled in a manner to prevent static charge accumulation and exposure to other ignition sources where dust air mixtures occur (e.g., mixing operations).

Small particles of fluoropolymer resins can become extremely combustible in the presence of various metal fines materials. For example, metal fines (e.g., aluminum and magnesium) mixed with powdered PTFE when exposed to temperatures above 790°F (420°C) may react violently producing fire and/or explosion.²⁶

²⁶ Internal DuPont Company correspondence.

INCOMPATIBILITY WITH POWDERED MATERIALS

Other fluoropolymer resins may react at lower or higher temperatures. In addition, other materials known to catalyze these reactions include silica, TiO_2 , bromides, metallic salts and glass fibers/beads. There may be other materials that can cause such reactions. Contact your materials suppliers for specific information.

Two examples of situations where heat generated may be sufficient to cause such a reaction are:

- ▶ Pumps utilizing fluoropolymer-based packings to pump dispersions of aluminum flake.
- ▶ Reclamation of parts coated with fluoropolymers by grinding or buffing operations, or by belt sanding or grit blasting with abrasives.

SPILLAGE

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.

CHAPTER VIII *ENVIRONMENTAL INFORMATION AND WASTE DISPOSAL*

ENVIRONMENTAL INFORMATION

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.

DISPOSAL

Treatment, storage, handling, transportation, and disposal of all fluoropolymer waste must follow applicable Federal, state/provincial, 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, powder, and granular products 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. Discharge liquid filtrate to a waste water treatment system in accordance with applicable permits and/or agreements with publicly owned treatment works. 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.

CHAPTER VIII ENVIRONMENTAL INFORMATION AND WASTE DISPOSAL

RESIN PACKAGING

The *Guide for the Proper Disposition of PTFE Resin Packaging* (SPI catalog number BP-102) provides information for the fluoropolymer industry on how to dispose of packaging used to transport PTFE resin.

CHAPTER IX

FOOD AND MEDICAL APPLICATIONS

FOOD CONTACT

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 issued 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. Many fluoropolymers have been cleared by the U.S. Food and Drug Administration 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 Chapter VI. However, stabilizers, antioxidants, colorants, and other adjuncts that are not an essential part of the polymerization process must also be cleared under an appropriate food additive regulation, be the subject of a prior sanction or approval, be considered GRAS, or not be reasonably expected to become a component of food. Most FDA regulations for antioxidants, stabilizers, and adjuncts appear in 21 CFR Part 178.

Manufacturers 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. Persons 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.

MEDICAL APPLICATIONS

Some fluoropolymers have been used to manufacture medical devices which are regulated by the U. S. Food and Drug Administration (FDA). The manufacturer and seller of the medical device are responsible for obtaining authorization or approval for their device(s) as a whole, and FDA does not approve individual components, such as fluoropolymer resins used in the manufacture of medical devices. SPI has not sought or received approval from any regulatory authority concerning the use of fluoropolymers in medical devices. Manufacturers wishing to use fluoropolymers in medical applications must make their own decision regarding the suitability of individual fluoropolymers for use in their particular application. Persons 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.

CHAPTER X

EMERGENCY MEASURES

EMERGENCY TELEPHONE NUMBERS

AGA CHEMICALS, INC.

Medical Emergency: (704) 357-3631 (Daytime)
Product Information: (704) 357-3631

AUSIMONT USA, INC.

Medical Emergency: (609) 853-8119
Product Information: (800) 221-0553

CUSTOM COMPOUNDING, A Division of DYNEON LLC

Medical Emergency: (610) 497-8899
Transport Emergency: (800) 424-9300
CHEMTREC: (800) 424-9300
Product Information: (800) 55-HOSTA

DAIKIN AMERICA, INC.

Medical Emergency: (914) 365-9500
Transport Emergency: (800) 424-9300
Product Information: (800) 365-9570

DUPONT

Medical Emergency: (800) 441-3637
Transport Emergency: (800) 424-9300
Product Information: (800) 441-7515

CHAPTER X

EMERGENCY MEASURES

ELF ATOCHEM NORTH AMERICA, INC.

Medical Emergency:	(303) 623-5716
Transport Emergency:	(800) 424-9300
Product Information	(800) 225-7788
	(215) 419-7520

ICI FLUOROPOLYMERS

Medical Emergency:	(800) 228-5635 Ext. 181
Transport Emergency:	(800) 424-9300
Product Information:	(800) ICI-PTFE (800 424-7833)

SOLVAY ADVANCED POLYMERS, INC.

Medical Emergency:	(713) 479-2381
CHEMTREC:	(800) 424-9300
Product Information	(800) 231-6313

FIRST AID*INHALATION*

Inhalation of fluoropolymer dust is not likely to be hazardous under normal handling conditions. If affected by inhalation of dust, consult a physician.

If affected by fumes from handling, heating, or combustion, move to fresh air. Keep the patient warm and at rest. In the event it is necessary to rescue a victim overcome by fumes or otherwise unconscious in a contaminated area, a self-contained breathing apparatus (SCBA) must be used. Consult a physician. The physician should be advised of the "HEALTH HAZARD INFORMATION" for fluoropolymers included in Chapter V. Because overexposure to hydrogen fluoride requires specific medical treatment, the treating physician should be informed of the possibility that hydrogen fluoride might be present in such situations. Following the rescue operation, **THOROUGHLY** ventilate the room.

If overcome or affected by inhalation of solvent vapors (toluene, xylene, etc.), remove the victim to fresh air. Keep the air passage clear and administer artificial resuscitation if necessary. Call a physician.

If a person is overcome or adversely affected by inhalation of fluoropolymer processing fumes or gases, medical treatment is required. Medical personnel should be advised that hydrogen fluoride, perfluoroisobutylene and other fluorinated gases may be present and that treatment should consider the possible effects of these substances. See Chapter V for brief descriptions of overexposure, or the fluoropolymer resins manufacturer's MSDS for more details.

*EYE CONTACT***FLUOROPOLYMER POWDERS AND PELLETS**

Flush eyes with plenty of clean water. Call a physician if irritation develops and persists. Provide the physician with a copy of the MSDS for the product.

FLUOROPOLYMER AQUEOUS DISPERSIONS

In case of eye contact, immediately flush the eyes with plenty of clean water for at least

15 minutes. Call a physician if irritation develops and persists. Provide the physician with a copy of the MSDS for the product(s) in use.

SKIN CONTACT

FLUOROPOLYMER POWDERS AND PELLETS

Fluoropolymers are not likely to be hazardous by skin contact, but cleansing the skin after use is advisable. If molten polymer gets on the skin, cool the affected area rapidly with cold water. Do not attempt to peel a polymer from skin. Obtain medical treatment for a thermal burn.

FLUOROPOLYMER AQUEOUS DISPERSIONS

Flush skin with water after contact. Wash contaminated clothing before reuse. The solids from aqueous solutions should be treated as resin powders and pellets as described above.

INGESTION

FLUOROPOLYMER POWDERS AND PELLETS

No specific intervention is indicated as fluoropolymers are not likely to be hazardous by ingestion. Call a physician if irritation develops and persists.

FLUOROPOLYMER AQUEOUS DISPERSIONS

If swallowed, immediately take two (2) glasses of water and induce vomiting. Never give anything by mouth to an unconscious person. Call a physician.

American Conference of Governmental Industrial Hygienists, *Industrial Ventilation: A Manual of Recommended Practice*, 17th ed., Cincinnati, OH, 1982, (Consult the most current edition).

American Society for Testing and Materials (ASTM), 100 Barr Harbor Drive, West Conshohocken, PA 19428-2959.

- ASTM D1430 "Standard Specification for Polychlorotrifluoroethylene (PCTFE) Plastics."
- ASTM D1457 "Standard Specification for Polytetrafluoroethylene (PTFE) Molding and Extrusion Materials."
- ASTM D2116 "Standard Specification for FEP-Fluorocarbon Molding and Extrusion Materials."
- ASTM D3159 "Standard Specification for Modified ETFE-Fluoropolymer Molding and Extrusion Materials."
- ASTM D3222 "Specification for Poly (Vinylidene Fluoride) (PVDF) Molding, Extrusion and Coating Materials."
- ASTM D3275 "Standard Specification for ECTFE-Fluoroplastic Molding, Extrusion and Coating Materials."
- ASTM D3307 "Standard Specification for 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."
- ASTM D4895 "Standard Specification for Polytetrafluoroethylene (PTFE) Resin Produced from Dispersion."
- ASTM D5575 "Standard Specification for Copolymers of Vinylidene Fluoride (VDF) with Other Fluorinated Monomers."

Baker, B. B. and Kaiser, M. A., "Analytical Approach — Understanding what happens in a fire." *Analytical Chemistry*, pp. 63, 79A, 1991.

Baker, B.B., and Kasprzak, D. J., "Thermal Degradation of Commercial Fluoropolymers in Air," *Polymer Degradation and Stability*, Vol. 42, p. 181, 1993.

Clarke, F. B., van Kuijk, H. M., Valentine, R., Baker, B. B., Bonesteel, J. K., Kasprzak, D. J., Makovec, G. T., Seidel, W. C., Herpol, C. H., and Janssens, M., "The toxicity of smoke from fires involving perfluoropolymers: Full-Scale fire studies." *Journal of Fire Science*, pp. 10, 488, 1992.

Clayton, J. W., "Fluorocarbon toxicity and biological action." *Fluorine Chemical Review* 1, 1967.

Harris, D. K., *Lancet* 261 1008, Dec. 1951.

Internal DuPont company correspondence.

Johnston, C J., Finkelstein, J. N., Gelein, R., Baggs, R., and Obrduster, G., "Characterization of Early Pulmonary Inflammatory Response Associated with PTFE Fume Exposure." *Toxicology and Applied Pharmacology*, Article No. 0208, Academic Press, 1996

Kales, SN, MD, MPH. "Progression of Chronic Obstructive Pulmonary Disease after Multiple Episodes of an Occupational Inhalation Fever." *Journal of Medicine*. 1994.
Albrecht, WN., Ph.D., MSPH. "Polymer-Fume Fever Associated with Smoking and Use of a Mold-Release Spray Containing Polytetrafluoroethylene." *J Occup Med*. 1987.

Kaplan, H. L., Grand, A. F., and Hartzell, G. E., "Review of Principle Laboratory Methods, National Bureau of Standards Method" *Combustion Toxicology -- Principles and Test Methods*, Lancaster, PA: Technomic Publishing Company, 1983.

Kaplan, H. L., Grand, A. F., Switzer, W. C., and Gad, S. C., "Acute inhalation toxicity of the smoke produced by five halogenated polymers" *J. Fire Sci.* 2, 1984.

Levin, B. C., Fowell, A. J., Birky, M. M., Paabo, M., Stolte, A., and Malek, D., "Further development of a test method for the assessment of acute inhalation toxicity of combustion products" *National Bureau of Standards Technical Report (U.S.) NBSIR 82-2532*, 1982.

Montgomery, Ruth R., "Polymers" *Patty's Industrial Hygiene and Toxicology*, 4th ed., vol. 2, George D. Clayton and Florence E. Clayton, Eds., New York: John Wiley & Sons, 1994.

Rose, Cecile A., "Inhalation Fevers," in Rom, W.N., ed. *Environmental and Occupational Medicine*, 2nd ed., Boston: Little, Brown and Company, 1992.

Scheel, L. D., Lane, W. C., and Coleman, W. E., "The toxicity of polytetrafluoroethylene pyrolysis products - including carbonyl fluoride and a reaction product, silicon tetrafluoride" *American Industrial Hygienists Association Journal* 29, 1968.

Seidel, W.C., Scherer, K. V., Cline, D. Jr., Olson, A. H., and Bonesteel, J. K., "Chemical, physical, and toxicological characterization of fumes produced by heating tetrafluoroethylene homopolymer and its copolymers with hexafluoropropylene and perfluoropropylvinylether)" *Chem. Res. in Toxicol* 4, 1991.

U. S. Department of Health, and Human Services, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, "Criteria for a Recommended Standard ... Occupational Exposure to decomposition products of Fluorocarbon Polymers." *DHEW (NIOSH) Publication No. 77-193*, Washington, D.C.: GPO, September 1977.

U.S. Department of Health and Human Services, Public Health Service, National Institutes of Health, "Toxicology and Carcinogenesis Studies of Tetrafluoroethylene (CASA No. 116-14-3) in F344/N Rats and B6C3F1 Mice (Inhalation Studies)," NTIS Publication No. PB 97-208508.

Underwriters' Laboratories (UL) 94, *Tests for the Flammability of Plastic Materials for Parts on Devices and Appliances*.

Warheit, D. B., Seidel, W. C., Caracostas, M. C., and Hartsky, M. A., "Attenuation of fluoropolymer fume toxicity: effect of filters, combustion method and aerosol age" *Exp. Mol. Pathol.* 52, 1990.

Williams, S. J., Baker, B. B., and Lee, K. P., "Formation of acute pulmonary toxicants following thermal degradation of perfluorinated polymers: evidence for a critical atmospheric reaction" *Food Chemical Toxicol.* 25, p. 177, 1987.

Williams, S. J., and Clarke, F. B., "Combustion product toxicity: Dependence on the mode of product generation" *Fire Material* 6, 1982.

APPENDIX A

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 written summary is based on the attached individual presentations prepared by Gerry Kennedy, DuPont, Colin Kinnear, ICI, and David Sarvadi, Keller and Heckman. These materials should be shared with the individuals in your organization responsible for regulatory compliance.

Briefly, TFE is the 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.

Testing is underway to determine whether there is any TFE evolved during use of fluoropolymer resins. The quantities of TFE observed in preliminary analyses of some resins and products were described in the second of the presentations, after a brief description of the NTP study and its conclusions. Following that, a description of the potential regulatory obligations of processors and resin producers was presented. The three papers discuss these subjects in greater detail, and summarize each person's presentation. They do not represent official positions of the Fluoropolymers Division.

The major points made during the presentations were:

- Tetrafluoroethylene 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 being investigated, but are expected to be very low; potential levels produced in processing are also being evaluated, and sampling techniques and laboratory methods of analysis are being developed to allow measurement of occupational exposure;
- The potential exposures in processing and use of resins and fluoropolymer products are being investigated by the resin manufacturers in greater detail in a program conducted through the Association of Plastic Manufacturers in Europe (APME), including development of new analytical methods to detect low levels of TFE monomer in resins

APPENDIX A

TFE IN FLUOROPOLYMERS

and fluoropolymer products;

- The resin manufacturers have recommended an occupational exposure limit (OEL) of 5 parts per million (ppm) of TFE based on an eight-hour time weighted average in their facilities that produce and use TFE monomer;
- Until the resin manufacturers notify processors that there may be some TFE monomer in, or evolved from, the resins, no specific obligations are imposed on processors;
- As information develops, processors may have to evaluate their operations to determine if their employees have the potential for exposure and, if so, to provide training under the Occupational Safety and Health Administration (OSHA) Hazard Communication Standard (HCS);
- If information becomes available suggesting that TFE monomer may be released in measurable quantities during use of products fabricated from fluoropolymer resins, processors may have to assess their products under the OSHA HCS and prepare appropriate material safety data sheets and labels.

Since the meeting, it has come to our attention that some employees of processors may confuse exposure to TFE with the occurrence of polymer fume fever (PFF). As you know, 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 V and ventilation in Chapter VII their employees and make sure they use appropriate controls, such as enclosures and ventilation, to limit potential employee exposure.

In addition, on May 1, 1994, the State of California listed TFE monomer under the "The Safe Drinking Water and Toxic Enforcement Act of 1986 (Proposition 65)." This law requires the California Environmental Protection Agency Office of Environmental Health Hazard Assessment (OEHHA) to publish a list of chemicals which are known to the State to cause cancer or reproductive toxicity.



The Society of the Plastics Industry, Inc.

Summary of TFE Presentations
FPD Fall '97 Conference
Atlanta, GA — October 7, 1996

Presented by the :
Fluoropolymers Division
The Society of the Plastics Industry, Inc.
Presentation to SPI Fluoropolymers Section

Toxicology of Tetrafluoroethylene Monomer-Workplace Control Guides

The purpose of this talk was to give the participants an overview of the toxicologic properties of tetrafluoroethylene monomer and to discuss how this information could be used to set workplace airborne control levels. Particular attention was given to the results of the recently reported long-term inhalation studies in rats and mice and the implications of these findings to the above.

A brief introduction/grounding in the definition of toxicology and some of the main principles which need to be understood to appreciate the experimental data was given. Included was a discussion of the difference between toxicologic properties (inherent in the chemical) and hazard (which combines the former with exposure potential). A discussion of dose-response relationships and the types of toxicity studies (acute, intermediate, chronic) and routes used to conduct these tests (oral, dermal, inhalation) was presented for grounding purposes. The two main questions then become what can the chemical do? and how much and by what route of exposure does it take to produce the effects'?

Earlier inhalation studies (TFE monomer is a gas) showed that the rodent kidney is the first target of TFE monomer toxicity. Based on dose-response characteristics following intermediate duration exposure studies in rats the workplace control level was suggested to be 50 ppm (should be associated with no adverse health effects for a normal working lifetime in man).

Work conducted by the National Toxicology Program (NTP) and reported late 1995 confirmed that TFE monomer was not very toxic following acute inhalation exposures and that the kidney was the target tissue following intermediate length exposures. The quantitative and qualitative aspects of the intermediate length NTP studies were presented in detail. No observed adverse effect levels (NOAEL) were determined to be 312 ppm in the rat, 625 ppm in the mouse.

In two year (chronic) inhalation studies, exposure of rats to 312 ppm or greater produced an increase in both liver and kidney cancers along with the expected kidney non-cancer toxicity. A NOAEL was not determine but the effects at the lowest level testing (156 ppm) were slight. In the mouse, survival was reduced and kidney damage was seen at the lowest level tested-312 ppm. In addition, increases in liver cancers, particularly hemangiosarcomas, was seen in both male and female mice. Genetic toxicity testing conducted by NTP (micronucleus test) and those found in the literature suggest that TFE monomer is not genetically-active.

A follow-up-up program looking at metabolic comparisons of rodent and human tissues along with toxicity comparisons following exposure to TFE monomer metabolites will help to place these findings in a more appropriate human perspective. The aim of these studies, which will begin in early 1998, is to validate the acceptability (or no) of the current workplace airborne control limit of 5 ppm.

PRESENTATION TO SPI FLUOROPOLYMERS SECTION
COLIN KINEAR — ICI FLUOROPOLYMERS
ATLANTA, GA, OCTOBER 7, 1996

TFE in Fluoropolymers

There are four areas of potential concern for the processor or user of Fluoropolymers arising from the possible presence of tetrafluoroethylene monomer (TFE) in fluoropolymer.

How much TFE is there in polymer from the polymer manufacturer?

Is TFE formed from processing Fluoropolymers? (e.g., sintering)

Is there any TFE in sintered or melt processed articles?

Can TFE form when the product is used at its maximum continuous service temperature?

Information on these topics has been assembled by the PTFE group of APME (Association of Plastic Manufacturers in Europe). This presentation summarizes some of the available information.

Sources of information

Studies of the TFE content of fluoropolymers have been conducted since about 1979. Most of the historic data comes from work commissioned in the TNO laboratories in the Netherlands or PIRA in the UK, both internationally recognized authorities in the field of polymer testing. Most of the recent data comes from analyses carried out by the polymer producers as they have expanded the data base of information.

TFE in polymer from the polymer producer

The results, summarized in TABLE 1, show the concentrations of TFE found in solid polymer (powder or granule) or aqueous dispersions as supplied by the polymer manufacturers. As can be seen from the Table TFE is not normally detected in powder or granules with a limit of detection which varies from 0.01 to 1 ppm on a weight/weight basis. TFE is always found in aqueous dispersion as TFE is soluble in water. Measured values to date are below 1 ppm on a weight/weight basis on the dispersion and are typically around 0.5 ppm. These results are at present based on a limited number of measurements and the manufacturers are committed to developing more data.

Significance of the TFE Monomer in Polymer data for the converter

It is possible to calculate roughly the concentration of tetrafluoroethylene which may arise in the workplace knowing the quantity of polymer used, assuming a reasonably conservatively high value of TFE contained in polymer and the size and ventilation in the workshop. A later presentation will provide much more information on the methodology. Calculations need to be done for each individual case but the indications are that values are likely to be well below the 5 ppm 8 hour TWA standard which the polymer manufacturers have generally adopted for their own workplaces.

TFE formation in processing Fluoropolymers? (e.g., during sintering)

Not much data is available because even at processing temperatures, Fluoropolymers degrade very slowly and it requires sophisticated analysis to determine the nature and quantities of the substances formed. It is known, however, that TFE is one of the degradation products when PTFE and other Fluoropolymers are heated.

It is recognized that any analytical work on the decomposition of Fluoropolymers needs to be treated with great caution. The products are very dependent on the conditions, especially temperature, amount of air, time gas is at temperature, etc. A study of the literature shows that even at very high temperatures, where analysis is simpler, there is a great deal of variation in the substances formed.

Nonetheless some indication can be obtained from the results of some very recent work on the formation of TFE during the decomposition of PTFE at temperatures from about 260-400°C are shown in FIGURE 1. In this experimental work 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/hour wt/wt on polymer dependent on temperature and whether decomposition takes place in air or inert gas.

The formation of TFE during melt processing or sintering should not be a cause of special concern. It is already well recognized that other components, such as hydrogen fluoride and the agent causing polymer fume fever, which have acute toxic effects, are formed at normal processing temperatures. Ventilation to protect against exposure to these acute toxicants will also offer protection against exposure to TFE.

TFE in articles

The level of TFE in the product or articles sold by the converter is one of the key pieces of information for the industry. Results of measurements made to date are shown in TABLE 1. This indicates that, using techniques with detection limits generally down to about 0.01 ppm weight/weight, TFE has not been found in articles, manufactured using standard recommended processing conditions.

While this is basically very good news it must be emphasized that the data on which it is based is very limited and further work is planned to develop a more extensive data base of information.

TFE formation at maximum continuous service temperatures

The experimental work described in the section on TFE formation in processing PTFE included an analysis for TFE at temperatures around and above the maximum continuous service temperature normally recommended of 260°C. Using analytical techniques which gave detection limits of around 0.05 ppm to 0.01 ppm per hour (weight/weight basis on polymer), the following observations were made:

1. TFE first became detectable at temperatures of 320°C when PTFE was heated in air, being found in one of two runs at that temperature.
2. When PTFE was heated in an inert gas TFE first became detectable at 280°, being found in one of two runs at that temperature.

This data is consistent with the higher temperature data shown in Figure 1.

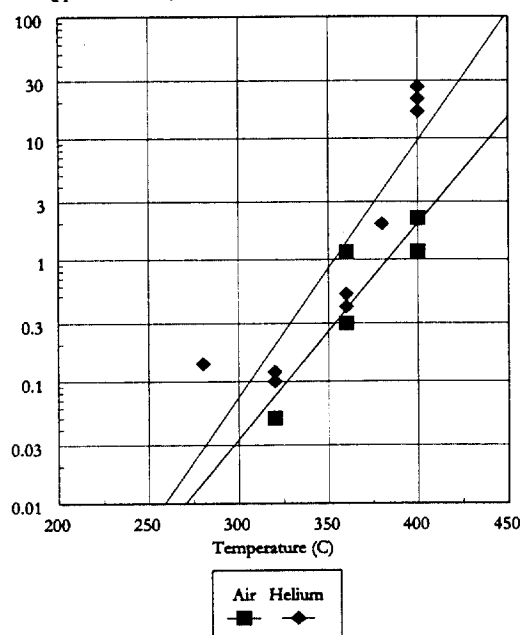
With the very low concentrations of TFE it is difficult to envisage circumstances in which there might be significant exposure to TFE. Any particular conditions can be checked by the calculation methods described in the paper by David Savardi.

TABLE 1 - TFE CONCENTRATION IN POLYMER
(Data collected by APME)

Data Source		Powder	Aqueous	Sintered
		ppm (w/w)	ppm (w/w)	ppm (w/w)
TNO 1979	val lod	nd 0.01		nd 0.01
PIRA 1987	val lod	nd 0.01		nd 0.01
TNO 1994	val lod	nd 0.3	0.24	
Producers 1996	val lod	nd 0.01-1.00	0.2-0.7	nd 0.01

va l= Value
lod = Limit of Detection
nd = Not Detected

Figure 1 - TFE FORMATION FROM PTFE
TFE (ppm/hour w/w)



Regulatory and Product Safety Obligations and Guidelines
Fall Meeting
SPI Fluoropolymers Division
October 1996

Presented by

David G. Sarvadi
Keller and Heckman, LLP

The report of the National Toxicology Program (NTP) study on the cancer-causing potential of tetrafluoroethylene (TFE) indicates that the fluoropolymer industry faces a potential hazard not previously identified. TFE is a chemical used to make fluoropolymers and is also produced by thermal degradation of fluoropolymers when they are heated above temperatures at which the polymers are normally processed and used. This paper describes the regulatory obligations of polymer producers and users to their own employees and customers under the regulations of the Occupational Safety and Health Administration (OSHA) and good practices under product stewardship principles.

Regulatory Obligations to Employees and Customers

The OSHA Hazard Communication Standard (HCS) is the most important regulation governing a company's responsibilities with respect to TFE and its employees. The HCS incorporates requirements for training about the hazards to which employees are exposed, and for communicating the hazards of chemical substances to downstream employers via material safety data sheets (MSDS) and labels. Obligations to a company's own employees require a company to: (1) identify the chemicals in use in its facilities, (2) identify those to which its employees are exposed, (3) quantify those exposures qualitatively compared to the levels of exposure to the chemicals which are hazardous; (4) obtain MSDS for purchased chemicals from suppliers; (5) develop MSDS for chemicals made or produced during processing or use of purchased products and make them available to employees and customers; and (6) train employees in the hazards of chemicals, how to read and use MSDS and labels, and the location of MSDS and related regulatory information.

In training employees and preparing MSDS, employers are required to describe the jobs in which the chemicals are used, the health and physical hazards of the chemicals, methods of recognizing chemicals (such as odor or color), and methods employees can follow to avoid the effects of over exposure. The MSDS and labels must accurately and fairly reflect the hazards associated with the use of the employer's products.

An employer's obligations under the HCS continue as new information develops. Generally, manufacturers are required under product liability law to keep up with technology and knowledge in their specialized field. This includes following the literature and scientific developments related to the hazards of their products. When new information about chemicals becomes known, the manufacturer must revise its MSDS and labels within 90 days as appropriate for the new information, and train its employees to the extent required to inform them of the new data. MSDS must then be sent to customers with the first shipment after the MSDS is revised.

Employee Exposure Assessment and Control

Employees must evaluate the new information about chemicals in light of the exposures to their employees under normal circumstances of use and in foreseeable emergencies. They must consider:

- Magnitude or level of exposure
- Duration of exposure
- Frequency (per day, week, month, year) of exposure
- Presence and efficacy of engineering controls.

For fluoropolymer processing, the SPI Fluoropolymer Division's (FPD) Safe Handling Guide Chapter VII provides guidance on suitable engineering controls, principally enclosures and ventilation. These are the kinds of controls that should be considered, and discussed with employees, in complying with the OSHA HCS.

As is well-known within the industry and is described in Chapter V of the Safe Handling Guide, highly irritating and toxic gases may be emitted by fluoropolymers at temperatures above normal operating temperature for equipment such as extruders and molding equipment, and in sintering ovens. The phenomenon known as "polymer fume fever" is a condition which is believed to be caused by inhalation of some of these gases and fine particulates generated in thermal decomposition of fluoropolymers.

The general principle to be followed in regard to employee exposure is to keep exposures as low as reasonably possible. Once that has been accomplished, exposures are compared to existing governmental or voluntary standards of safety. These standards are then used as guides of workplace quality to assure that equipment operates properly. If the comparison shows that the employee exposures exceed the regulatory limits, then additional controls, including personal protective equipment such as respirators, protective clothing or other appropriate gear, must be used to reduce exposures to the existing limits.

Engineering Controls: Enclosures and Ventilation

Engineering controls described in the Safe Handling Guide in Chapter VII include isolation, local exhaust ventilation, and general mechanical ventilation. Isolation involves the creation of a physical barrier in the path between the potentially exposed employee and the source of the contaminant. Enclosures can surround the source, as with a cabinet used to house grit blasting or other metal cleaning apparatus for small parts, or to surround the employee, as with the operator's booth on a crane.

Normally, enclosures incorporate some kind of ventilation, either to capture and remove contaminants or to control heat. When exhaust ventilation is connected to a partial or full enclosure, it is called "local exhaust ventilation" or "LEV." Examples of LEV used in the fluoropolymer industry are found in the Safe Handling Guide, 3rd edition.

General mechanical ventilation (GMV) refers to the use of exhaust and supply systems to control contaminants in the workplace by slowly removing contaminated air and diluting the contaminant with clean air. Floor exhausts commonly seen in flammable liquids storage rooms or wall fans in warehouses to control carbon monoxide and other combustion gases from industrial trucks are examples. GMV is very inefficient at controlling exposures to highly toxic materials, or those which produce acute effects such as severe irritation. Accordingly, the Safe Handling Guide does not recommend GMV for control of chemicals emissions in fluoropolymer processing.

Guidelines for the design of LEV that may be used in fluoropolymer processing are found in OSHA standards and publications of private organizations. OSHA standards in 29 CFR Part 1910 which may apply to fluoropolymer operations, include:

1910.94(c) Ventilation for spray finishing operations;

1910.107 Spray finishing using flammable and combustible materials (various paragraphs);

1910.108(b) Dip tanks containing flammable or combustible liquids — ventilation.

These standards set minimum design criteria for various kinds of operations and are legally enforceable.

Private organizations establish design guidelines for ventilation systems also. The American Conference of Governmental Industrial Hygienists (ACGIH), located at 1330 Kemper Meadow Drive, Cincinnati, OH 45240 (513.742.2020/Fax: 513.742.3355/<http://www.acgih.org>), publishes a book, *Industrial Ventilation, A Manual of Recommended Practice*, which is the principle source for industrial hygienists and engineers regarding exhaust ventilation systems. It contains design information and principles for industrial exhaust systems.

The American National Standards Institute (ANSI), located at 11 West 42nd St, New York, NY, issues

various standards for the design and operation of industrial ventilation systems as well. The National Fire Protection Association (NFPA) in Boston similarly has standards for ventilation, principally directed at fire hazard control, but also at life safety.

Assessing Employee Exposures

In examining potential exposures, an employer's conclusions must be based on "objective" data. Calculations can be used, but measurements are preferred. Industrial hygiene sampling can be obtained to provide the data required. Typically, such services cost \$800—\$2000 per day, and \$25—\$150 per sample analyzed. A list of consultants in the field can be obtained from the American Industrial Hygiene Association in Fairfax, Virginia (703.849.8888). Look for an industrial hygienist who is certified in general practice and who has had experience in evaluating low level exposures to organic contaminants.

In the absence of specific data on a company's operations, calculations can be based on data from other sources, provided there is a reasonable showing that the data supporting the calculations were taken from substantially similar kinds of operations. The most important piece of information is the amount of tetrafluoroethylene (TFE) released from the process, which can normally be based on the number of pounds of resin processed, or the rate of processing. The following example illustrates the calculation, assuming:

- ✓ 50 foot x 40 foot processing room with 15 foot ceilings;
- ✓ 3 extruders, consuming 2000 kg/day per extruder;
- ✓ 1 part per million (weight basis) TFE in resin (*e.g.*, 1 mg of residual TFE released for each kg of resin processed);
- ✓ 0.1 mg regenerated TFE per kg resin processed (*e.g.*, 1 mg TFE produced for each kg of resin processed);
- ✓ Complete mixing in room air; and
- ✓ No fresh air replacement;

The last assumption is important because it ignores the very important effect that infiltration and supply of fresh, uncontaminated air has on the magnitude and duration of exposures. The assumption that there is no fresh air coming into the work area is highly conservative and provides a wide margin of safety to account for variations in the other parameters, such as emission rate and proximity of exposed employees to the source of the contaminant, that could result in exposures higher than those calculated. Given these conservative assumptions, processors can be reasonably sure that actual exposures will be less than those predicted by the following mathematical model.

Based on the above assumptions, the total TFE released into the workroom from the residual TFE in the resin is:

APPENDIX A

TFE IN FLUOROPOLYMERS

3 extruders x 2000 kg resin processed/day/extruder x 1 mg/kg resin = 6000 mg TFE.

Similarly, the total regenerated TFE from processing is: $3 \times 2000 \times 0.1 = 600$ mg, giving a total TFE released each day in the workroom of 6600 mg. If the total volume of the room is 850 cubic meters (see box nearby), the average TFE concentration would be approximately 1.0 ppm. The calculation and conversion from weight per unit volume of room air to parts per million is as follows:

$$\begin{aligned}\frac{6600 \text{ mg}}{850 \text{ m}^3} &= 7.8 \text{ mg/m}^3; \\ 1 \text{ ppm} &= 4.17 \text{ mg/m}^3 \text{ TFE}; \\ 7.8 / 4.17 &= 1.87 \text{ ppm TFE.}\end{aligned}$$

Compared to the level which the resin manufacturers are using as a guideline for employee exposure in their facilities, which is 5 ppm, the processor employees are likely to be exposed to levels well below that criterion. This would be the average exposure over a working period in which the employee spends a significant amount of time in the workroom, but is not constantly exposed near the die of the extruder, the location where most of the TFE is likely to be released. Note also that the calculation assumes that there is no LEV over the die head, as is recommended in the Safe Handling Guide. Similar calculations can be made of other types of processing equipment and general exposures.

Product Stewardship

Product stewardship principles and OSHA standards require manufacturers to examine their products and to produce MSDS for the products they make which are hazardous.

Mixtures or products which contain more than 0.1% (w/w) of substances listed or regulated by NTP, OSHA, or the International Agency for Research on Cancer (IARC) as carcinogens should be presumed to present a cancer hazard, unless the product is tested as a whole and found not to produce cancer in a comparable test. The product MSDS and labels must reflect these hazards, and may require a specific cancer warning on the label. Whether such warnings are required depends on the hazard determination made by the manufacturer. The specific procedure to follow for plastic materials and products is described in detail in SPI's "Guidance Document for Preparing MSDS for Plastics." Contact SPI's publications department at (202) 974-5200 for pricing and availability.

Calculation of Room Volume $(15 \times 40 \times 50) \times \frac{1 \text{ m}^3}{35.3 \text{ f}^3} = \frac{30000}{35.3} = 850 \text{ m}^3$
--

When performing a product assessment, manufacturers must answer the following questions:

- ✓ Is there residual TFE in my product?
- ✓ If so, is it more than 0.1%?

- ✓ If not, can enough TFE be released under normal conditions of use or foreseeable emergency to cause exposures to exceed an established limit or to otherwise present a health hazard?

Processors may wish to use the manufacturers' 5 ppm criteria as a guideline in health hazard evaluation.

Conclusion

Processors should be prepared to receive MSDS from their resin suppliers that may contain references to the cancer study performed by NTP. It is not clear from the data presented today that all manufacturers' MSDS will, in fact, contain this reference or that all types of resins will contain or release TFE in measurable quantities. Some resin materials may not. Thus, their use by a processor may not result in exposure of the processor's employees to TFE, unless unusual circumstances exist, such as reaching excessive operating temperatures, resulting in regeneration of significant amounts of TFE by degradation of the polymer. Processors should consult with their suppliers for more details about their specific case and for assistance in analyzing their particular operation. Extruders and other heated processing equipment should be reviewed to assure that maximum service temperatures for the resins being processed, as recommended by the manufacturer of the resin, are not exceeded.

Coaters and processors that use filled, lubricated resins may be more likely to have resins with residual TFE in their operations. They should carefully examine their operations to assure that unusual exposures are avoided, and work with their suppliers to assure that their spray finishing operations are adequately ventilated. Generally, if the solvent concentrations resulting in the spray operation are controlled, chances are that the residual TFE levels will also be controlled adequately.

Ovens will require more careful analysis, particularly if they are operated at or near the maximum temperature recommended by the supplier of the resin. Otherwise, significant amounts of TFE may be regenerated. Again, data are limited, so it is important to consult with suppliers for more specific guidance. In any event, processors should review their oven operating procedures and not exceed temperatures recommended by the resin supplier.

The data in this Appendix have 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 Material Safety Data Sheets (MSDS) 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 — DUPONT

THERMAL PERFORMANCE OF DUPONT FLUOROPOLYMER RESINS
AND TOXICITY OF DEGRADATION PRODUCTS

DuPont fluoropolymer resins are very stable at their recommended continuous use temperatures, however, they do exhibit a small amount of degradation at higher processing temperatures. DuPont has completed a study²⁷ to determine the rate of degradation of several of their commercial fluoropolymer resins over the range of continuous use and processing temperatures and examined the nature and amount of the gases evolved. Six DuPont 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 63) includes the values indicated by DuPont for the resins used in this study.

Figure II (Pg 66) shows the results of weight loss data from the rate of degradation experiments.

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.

²⁷ Baker, B. B., Jr., and Kasprzak, D. J., "Thermal Degradation of Commercial Fluoropolymers in Air," *Polymer Degradation and Stability*, Vol. 42, 1994, 181-188.

This information is offered without charge as part of DuPont's service to their customers, but they cannot guarantee favorable results will be obtained from the use of such data. It is intended for use by persons having technical skills at their own discretion and risk. The DuPont Company assumes no obligation or liability in connection with its use. The disclosure of the information is not a license to operate under, or a recommendation to infringe, any patent of DuPont or others.

TABLE I
CONTINUOUS USE AND TYPICAL POLYMER PROCESSING TEMPERATURES

RESIN	CONTINUOUS USE DEGREES C	TYPICAL PROCESSING DEGREES C
Tefzel®	150	310
Teflon® FEP	205	360
Teflon® PFA	260	390
Teflon® PTFE	260	400

A 60 ml/min stream of air from a cylinder was split so that one-half passed through a water bubbler and then recombined to yield 50% relative humidity air. This stream was directed through the TGA and into an 8 liter "Tedlar®" polyvinyl fluoride gas sampling bag. A sample of polymer weighing 25-80 mg was placed on the platinum pan of the TGA, whose furnace had been heated to the desired temperature and the run was begun by moving the furnace over the sample on the balance pan. Weight loss data was then obtained for the duration of the run, usually 65 minutes.

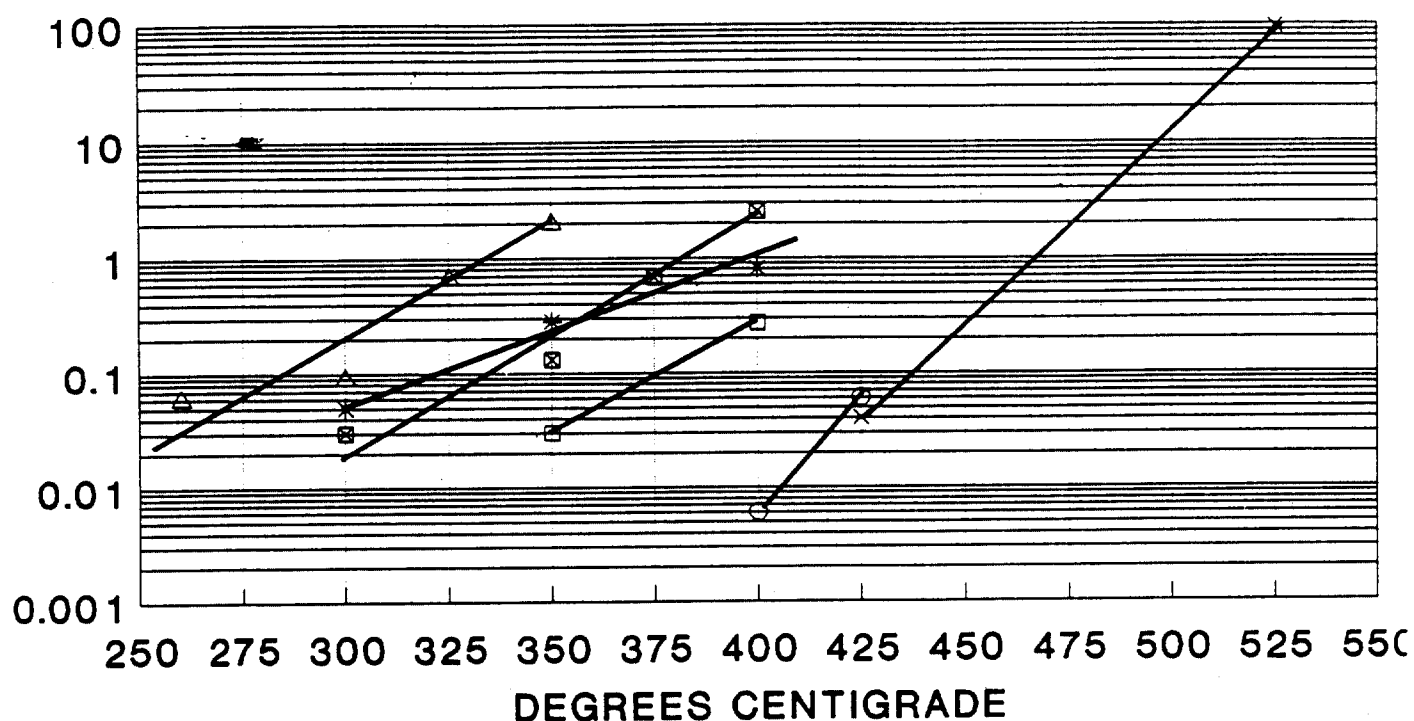
A 2 ml portion was removed from the sample bag and examined by GC (Gas Chromatography) for PFIB (perfluoroisobutylene). The column was 10 feet by 1/8 inch, n-octane/dinonyl phthalate/Krytox® on Poracil C Durapak, run isothermally at 35°C. The PFIB retention time with 18 psi head pressure was 9 minutes. The identification was confirmed by running one sample on a second column: 20 feet by 1/8 inch, 25% di(2-ethylhexyl) sebacate on 100/120 mesh Chromasorb P-AW, using the same GC conditions; the PFIB retention time was 10.4 minutes. Measurement was by an electron capture detector with a detection limit of about 0.001 ppm.

The contents of the gas sampling bag were then transferred to an evacuated 10 meter path length infrared cell of 2.2 liters volume and the spectrum of the gases run on a Nicolet 20SX infrared spectrometer. From previously established calibration data, the various components were identified and their amounts calculated.

This information is offered without charge as part of DuPont's service to their customers, but they cannot guarantee favorable results will be obtained from the use of such data. It is intended for use by persons having technical skills at their own discretion and risk. The DuPont Company assumes no obligation or liability in connection with its use. The disclosure of the information is not a license to operate under, or a recommendation to infringe, any patent of DuPont or others.

FIGURE II

PERCENT WEIGHT LOSS ON HEATING IN AIR



△ "TEFZEL"

⊠ FEP 100

* PFA 340

□ PFA 440HP

× "TEFLON" 6C

○ "TEFLON" 7A

This information is offered without charge as part of DuPont's service to their customers, but they cannot guarantee favorable results will be obtained from the use of such data. It is intended for use by persons having technical skills at their own discretion and risk. The DuPont Company assumes no obligation or liability in connection with its use. The disclosure of the information is not a license to operate under, or a recommendation to infringe, any patent of DuPont or others.

The principal evolved gas when fluoropolymers are heated in air at 400 deg C is carbonyl fluoride, COF_2 . This compound then hydrolyzes to a significant extent in the 50% RH air to HF and CO_2 . HF is a weak infrared absorber and is difficult to measure by other means as well, because of reaction with the quartz TGA tube and its propensity to absorb strongly on solid surfaces. Therefore we measured the amount of un-hydrolyzed COF_2 by IR and calculated the amount of hydrolyzed COF_2 from CO_2 measurement.

For a typical 65 minute run the volume of gas in the sample bag should have been 3.9 liters. This was verified by filling the 2.2 liter IR cell, running the spectrum, evacuating the cell and transferring all the remaining gas to the IR cell. The pressure in the cell was then read with a gauge on the cell, allowing calculation of the total amount of gas in the bag. These measurements gave values ranging between 3.3 and 4.2 liters, versus the expected 3.9. The difference is probably due to the difficulty on transferring all the sample from the bag and some inaccuracy in the pressure measurement. We have elected to use the expected 3.9 liters in our calculations of the amount of the various gases evolved.

Table II (Pg 71) gives the weight loss data for the six samples and, where it exists, shows the difference between the early and late weight loss rate. The values for the TE (thermal equilibrium) to 15 minute and 15 to 65 minute loss rates were taken from the slope of the TGA curve over the time interval. TE was usually reached in 3 or 4 minutes. The final column (TE plus 60) is the actual weight loss over this period (or, where indicated, a longer period). Some of the TE+60 minute values are from a single run; others are averages of two or three measurements. Weight loss representation of "<0.05" indicates the limit of detection in that particular experiment.

This information is offered without charge as part of DuPont's service to their customers, but they cannot guarantee favorable results will be obtained from the use of such data. It is intended for use by persons having technical skills at their own discretion and risk. The DuPont Company assumes no obligation or liability in connection with its use. The disclosure of the information is not a license to operate under, or a recommendation to infringe, any patent of DuPont or others.

TABLE II
WEIGHT LOSS DATA

Resins	Temp °C	% Weight Loss/Hr		
		TE to 15 min.	15 to 65 min.	TE + 60 min.
Tefzel® 200	150			<0.05
	260	0.31	0.06	0.11
	300	0.42	0.09	0.14
	325			0.67
	350	~2		6.8
Teflon® 100	205			<0.05
	300		~0.03	<0.05
	350	0.45	0.13	0.18
	375			0.67
	400			3.2
Teflon® PFA 340 260				<0.05
	300	0.18	0.05	0.07
	350			0.22
	400			0.58
Teflon® PFA 440 260				<0.05
	300			<0.05
	350	0.12	~0.03	0.05
	400			0.26
Teflon® 6C	400			~0.06
	425			0.15
	425			0.04*
	525	255**		95.0
Teflon® 7A	350			0.02
	350			0.005*
	400			0.03
	400			0.006*
	425			0.06
	425			0.06*

* Hourly rate from 8 to 11.8 hours after beginning run.

Hourly rate from 3.3 to 6.6 hours after beginning run.

** Gross decomposition in one hour. Initial rate 255% per hour.

This information is offered without charge as part of DuPont's service to their customers, but they cannot guarantee favorable results will be obtained from the use of such data. It is intended for use by persons having technical skills at their own discretion and risk. The DuPont Company assumes no obligation or liability in connection with its use. The disclosure of the information is not a license to operate under, or a recommendation to infringe, any patent of DuPont or others.

The data on the evolved gases from the four resins that have significant amounts of effluents are presented in **Table III** (Pg 68). The numbers are all weight percent so that the sum of the gases can be compared with TGA weight loss shown in **Table III**. Table values have the weight of oxygen subtracted assuming the oxygen came from air and should not be considered when comparing weight of off gases with TGA weight loss. Where no value is given for the seven gases measured by IR, none was detected. The detection limit is variable, typically about 0.05 ppm in the 10 meter cell (about 0.02%). Formation of PFIB (perfluoroisobutylene), even in small amounts, is noted because of its high toxicity (2 hour LC₅₀ for rats is 1 ppm). FEP polymer's branched chain would be expected to produce PFIB more readily than PTFE. It was found that FEP produces PFIB at 400°C, but PTFE does not. PFIB is produced by heating PTFE to 525°C, where gross decomposition occurs, well above normal processing temperature. No PFIB was formed from FEP at 350°C. The electron capture gas chromatograph used had a detection limit of <1 ppb in the evolved gas sample, which corresponds to a yield of about 0.5 ppm (0.00005%) on a polymer basis.

Fluoropolymer resins when decomposed at high temperatures evolve toxic products.²⁸ 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.²⁹ 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").³⁰

²⁸ Clayton, J. W., "Fluorocarbon toxicity and biological action," *Fluorine Chemical Review* 1, 1967, 233-252.

²⁹ Williams, S. J., and Clarke, F. B., "Combustion product toxicity: Dependence on the mode of product generation," *Fire Material* 6, 1982, 161-162.

³⁰ Harris, D. K. *Lancet* 261 1008, Dec. 1951.

This information is offered without charge as part of DuPont's service to their customers, but they cannot guarantee favorable results will be obtained from the use of such data. It is intended for use by persons having technical skills at their own discretion and risk. The DuPont Company assumes no obligation or liability in connection with its use. The disclosure of the information is not a license to operate under, or a recommendation to infringe, any patent of DuPont or others.

TABLE III
(Revised September 18, 1995)

COMPARISON OF ONE HOUR TGA WEIGHT LOSS WITH WEIGHT OF EVOLVED GASES

RESIN	°C TEMP.	WEIGHT OF EVOLVED GASES AS % OF SAMPLE						COF ₂ Meas / Calc.	CO	SUM	% REC
		TGA % LOSS	WTPFIB	TFE	HFP	HCF ₃	PFBE ⁽¹⁾				
TEFZEL® 200	350	5.3		0.06			0.3	0.11 2.5	0.06	4.7 ⁽³⁾	89
FEP 100	400	2.5	0.003	~0.06	0.38	0.19		0.64 1.2		2.7 ⁽⁴⁾	110 ⁽²⁾
PFA 340	400	0.43							0.53	0.53	123 ⁽²⁾
PFA 440	400	0.26						0.01 1.2		1.2	460 ⁽²⁾

¹Perfluorobutylethylene.

²Artifact of the analytical technique for values 100%.

³This sum includes 1.7% CO₂ from oxidation of the ethylene units.

⁴Includes 0.19% of CF₃COF.

This information is offered without charge as part of DuPont's service to their customers, but they cannot guarantee favorable results will be obtained from the use of such data. It is intended for use by persons having technical skills at their own discretion and risk. The DuPont Company assumes no obligation or liability in connection with its use. The disclosure of the information is not a license to operate under, or a recommendation to infringe, any patent of DuPont or others.

In 1982, a small scale combustion toxicity test developed at the U.S. National Bureau of Standards (NBS, renamed National Institute of Standards and Technology [NIST] in 1987, showed PTFE resin to have an unexpectedly high animal (laboratory rats) toxicity.³¹ When PTFE was tested using the NBS protocol, laboratory rats died from a 30 minute exposure to pyrolysis products from 0.04 mg of polymer per L of chamber volume. Investigation at a number of laboratories using the NBS protocol^{32,33} confirmed the NBS results. However, chemical analysis of the expected content of the fumes from the NBS test apparatus could not explain why the rats died.³⁴ The principle products detected were TFE (tetrafluoroethylene) and COF₂ (carbonyl fluoride). TFE is relatively nontoxic, and COF₂ was found, but at concentrations far below what is lethal. A search was then initiated to try and detect the presence of PFIB (perfluoroisobutylene) which is known to be very toxic. None was detected.

In earlier studies², particulate material was implicated as contributing to toxicity, therefore, rats were exposed to the NBS test atmosphere through filters to remove particulate. Rats exposed to these filtered gases did not exhibit an unusual toxic response while those exposed to unfiltered gases did,³⁵ leading to the conclusion that particulate was the probable cause of unexpected high toxicity displayed in the NBS toxicity test. Study of the minute fraction removed by filters revealed that a condensation aerosol of ultra fine particles (20-30 nm) produced by the combustion of PTFE resins is lethal to rats in

-
- ³¹ Levin, B.C., Fowell, A. J., Birky, M. M., Paabo, M., Stottle, A., and Malek, D., "Further development of a test method for the assessment of acute inhalation toxicity of combustion products," *National Bureau of Standards [Technical Report] NBSIR 82-2532*, 1982.
- ³² Kaplan, H. L., Grand, A. F., Switzer, W. C. and Gad, S. C., "Acute inhalation toxicity of the smoke produced by five halogenated polymers," *J. Fire Science* 2, 1984, 153-172.
- ³³ Kaplan, H. L., Grand, A. F., and Hartzell, G. E., "Review of Principle Laboratory Methods, National Bureau of Standards Method," *Combustion Toxicology — Principles and Test Methods*, Lancaster, PA: Technomic Publishing Company, 1983.
- ³⁴ Williams, S. J., Baker, B. B., and Lee, K. P., "Formation of acute pulmonary toxicants following thermal degradation of perfluorinated polymers: Evidence for a critical atmospheric reaction," *Food Chem. Toxicol* 25, 1987, 177-185.
- ³⁵ Warheit, D. B., Seidel, W. C., Caracostas, M. C., and Hartsky, M. A., "Attenuation of fluoropolymer fume toxicity: Effect of filters, combustion method and aerosol age," *Exp. Mol. Pathol.* 52, 1990, 309-329.

This information is offered without charge as part of DuPont's service to their customers, but they cannot guarantee favorable results will be obtained from the use of such data. It is intended for use by persons having technical skills at their own discretion and risk. The DuPont Company assumes no obligation or liability in connection with its use. The disclosure of the information is not a license to operate under, or a recommendation to infringe, any patent of DuPont or others.

concentrations of the order of 10^7 - 10^8 particles per milliliter.³⁶ The unique conditions of the NBS toxicity protocol result in formation of this aerosol from combusting fluorocarbon resin PTFE.

Aerosol particles agglomerate readily in the presence of smoke from other materials that burn, a fact born out by studies of full scale fires at the State University of Ghent in Belgium.^{37,38} Cables insulated with fluoropolymers were installed in a burn room overhead in a tray simulating a plenum. The design connected the burn room to a corridor through which the combustion smoke traveled. In a typical test 120 kilograms (264 pounds) of wood was burned as a heat source to burn 25 kilograms (55 pounds) cable insulation. As the smoke passed down the corridor, samples were drawn to chambers containing rats. Over the course of twenty tests, the rats showed no evidence of exposure to the toxic aerosol generated by the NBS toxicity protocol. These results are consistent with the absence of field reports of unusual toxicity associated with the presence of fluoropolymers in real fires.

-
- ³⁶ Seidel, W., Scherer, K., Cline, D. Jr., Olson, A. & Bonesteel, J., "Chemical, physical and toxicological characterization of fumes produced by heating tetrafluoroethylene homopolymer and its copolymers with hexafluoropropylene and perfluoro(propyl vinyl ether)," *Chem. Res. in Toxicol.* 4, 1991, 229-236.
- ³⁷ Baker, B. B. and Kaiser, M. A., "Analytical Approach — Understanding what happens in a fire," *Analytical Chemistry*, 63, 79A 1991.
- ³⁸ Clarke, F. B., vanKuijk, H. M., Valentine, R., Baker, B. B., Bonsteel, J. K., Krasprzak, D. J., Makovec, G. T., Seidel, W. C., Herpol, C. H., and Janssens, M., "The toxicity of smoke from fires involving perfluoropolymers: Full-scale fire studies," *Journal of Fire Science*, 10, 488, 1992.

This information is offered without charge as part of DuPont's service to their customers, but they cannot guarantee favorable results will be obtained from the use of such data. It is intended for use by persons having technical skills at their own discretion and risk. The DuPont Company assumes no obligation or liability in connection with its use. The disclosure of the information is not a license to operate under, or a recommendation to infringe, any patent of DuPont or others.

This information is offered without charge as part of DuPont's service to their customers, but they cannot guarantee favorable results will be obtained from the use of such data. It is intended for use by persons having technical skills at their own discretion and risk. The DuPont Company assumes no obligation or liability in connection with its use. The disclosure of the information is not a license to operate under, or a recommendation to infringe, any patent of DuPont or others.

PART 2 — ELF ATOCHEM

THERMAL PERFORMANCE OF
ELF ATOCHEM KYNAR® PVDF FLUOROPOLYMER RESINS

Sample	K2750 Lot 88C8056	K2800 Lot 87C8163	K2850 Lot 87C8080
TGA Run #	1334B	1335B	1336B
Atm.	Air	Air	Air
5% wt. loss temp., °C	431.6	427.4	448.7
10% wt. loss temp., °C	440.6	442.0	457.6
Deriv. Peak Temp., °C	479.0	469.7	472.5
1 st wt. loss region, °C	400 to 478	400 to 478	400 to 481
% wt. loss	58.2	90.1	79.4
2 nd wt. loss region, °C	478 to 625	476 to 625	481 to 625
% wt. loss	41.8	9.9	20.6

Samples were heated 10°C/min. in air to 1000°C

This information is offered without charge as part of ELF Atochem's service to their customers, but they cannot guarantee favorable results will be obtained from the use of such data. It is intended for use by persons having technical skills at their own discretion and risk. ELF Atochem North America assumes no obligation or liability in connection with its use. The disclosure of the information is not a license to operate under, or a recommendation to infringe, any patent of ELF Atochem North America or others.

APPENDIX B

THERMAL PROPERTIES

Sample	K2750 Lot 88C8056	K2800 Lot 87C8163	K2850 Lot 87C8080
TGA Run #	2652B	2653B	2654B
Atm.	N ₂	N ₂	N ₂
5% wt. loss temp., °C	457.3	459.4	461.5
10% wt. loss temp., °C	465.6	469.7	470.6
Deriv. Peak temp., °C	491.2	493.2	485.5
Residual mass% at 1000°C	11.9	11.3	24.4
1 st mass loss region, °C	399 to 508	382 to 510	421 to 506
% mass loss	81.9	82.3	66.7
2 nd mass loss region, °C	508 to 1000	510 to 1000	506 to 1000
% mass loss	6.2	6.4	8.9

Samples were heated 10°C/min. in N₂ to 1000°C

This information is offered without charge as part of ELF Atochem's service to their customers, but they cannot guarantee favorable results will be obtained from the use of such data. It is intended for use by persons having technical skills at their own discretion and risk. ELF Atochem North America assumes no obligation or liability in connection with its use. The disclosure of the information is not a license to operate under, or a recommendation to infringe, any patent of ELF Atochem North America or others.

APPENDIX B

THERMAL PROPERTIES

Sample	K730 Lot 89C6025	K740 Lot 89C6021	K760 Lot 86C6049	K2750 Lot 88C8056
TGA Run #	2649B	2650B	2651B	2652B
Atm.	N ₂	N ₂	N ₂	N ₂
5% wt. loss temp., °C	466.0	459.4	468.0	457.3
10% wt. loss temp., °C	474.6	469.7	478.7	465.6
Deriv. Peak Temp., °C	489.5	484.6	491.5	491.2
Residual mass% at 1000°C	22.4	29.8	22.4	11.9
1 st mass loss region, °C	391 to 513	400 to 505	369 to 510	399 to 508
% mass loss	69.2	61.6	68.9	81.9
2 nd mass loss region, °C	513 to 1000	505 to 1000	510 to 1000	508 to 1000
% mass loss	8.4	8.6	8.7	6.2

Samples were heated 10°C/min. in N₂ to 1000°C

This information is offered without charge as part of ELF Atochem's service to their customers, but they cannot guarantee favorable results will be obtained from the use of such data. It is intended for use by persons having technical skills at their own discretion and risk. ELF Atochem North America assumes no obligation or liability in connection with its use. The disclosure of the information is not a license to operate under, or a recommendation to infringe, any patent of ELF Atochem North America or others.

APPENDIX B

THERMAL PROPERTIES

Sample	K2800 Lot 87C8163	K2850 Lot 87C8080	Kynar SL Lot 86J8003	Kynar ADS Lot 8422
TGA Run #	2653B	2654B	2655B	2656B
Atm.	N ₂	N ₂	N ₂	N ₂
5% wt. loss temp., °C	459.4	461.5	474.4	457.3
10% wt. loss temp., °C	469.7	470.6	482.6	472.0
Deriv. Peak Temp., °C	493.2	485.5	501.8	497.6
Residual mass% at 1000°C	11.3	24.4	2.8	0.0
1 st mass loss region, °C	382 to 510	421 to 506	434 to 516	379 to 542
% mass loss	82.3	66.7	89.8	97.7
2 nd mass loss region, °C	510 to 1000	506 to 1000	516 to 1000	
% mass loss	6.4	8.9	6.8	6.2

Samples were heated 10°C/min. in N₂ to 1000°C

This information is offered without charge as part of ELF Atochem's service to their customers, but they cannot guarantee favorable results will be obtained from the use of such data. It is intended for use by persons having technical skills at their own discretion and risk. ELF Atochem North America assumes no obligation or liability in connection with its use. The disclosure of the information is not a license to operate under, or a recommendation to infringe, any patent of ELF Atochem North America or others.

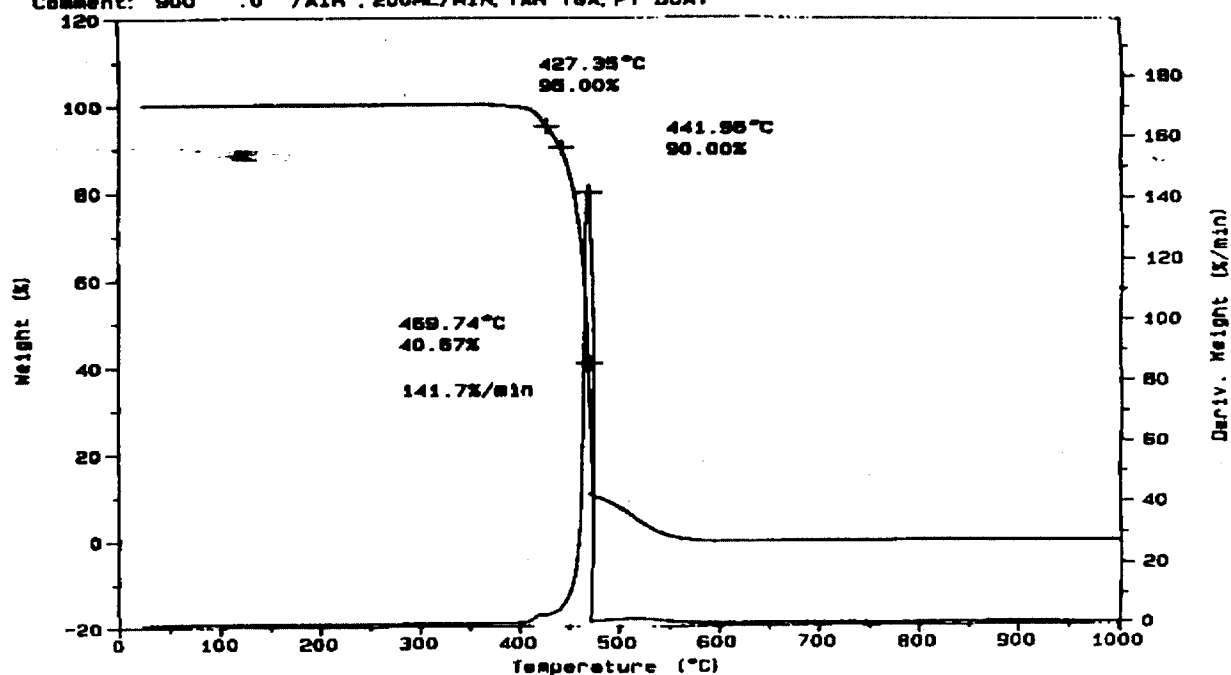
APPENDIX B

THERMAL PROPERTIES

Sample: K2800 LOT 87C-B163 5843-34K
Size: 19.3330 mg
Method: TGA 10°C/MIN TO 1000°C
Comment: 900 .0 /AIR .200ML/MIN, TAN TGA, PT BOAT

TGA

File: A: 13358.01
Operator: M84
Run Date: 02/07/90 08:59



This information is offered without charge as part of ELF Atochem's service to their customers, but they cannot guarantee favorable results will be obtained from the use of such data. It is intended for use by persons having technical skills at their own discretion and risk. ELF Atochem North America assumes no obligation or liability in connection with its use. The disclosure of the information is not a license to operate under, or a recommendation to infringe, any patent of ELF Atochem North America or others.

This information is offered without charge as part of ELF Atochem's service to their customers, but they cannot guarantee favorable results will be obtained from the use of such data. It is intended for use by persons having technical skills at their own discretion and risk. ELF Atochem North America assumes no obligation or liability in connection with its use. The disclosure of the information is not a license to operate under, or a recommendation to infringe, any patent of ELF Atochem North America or others.

PART 3 — SOLVAY

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 cm²

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 ₁		T ₂		Weight Loss
	°F	°C	°F	°C	°F	°C	%
SOLEF® 1010/0001 Melting temperature = 174°C (345°F) Average processing temperature = 230°C (446°F) Sample load: 10 mg Appendix n°: 1	768	409	455	235	354	179	1
	808	431	495	257	384	201	2
	828	442	514	268	414	212	3
SOLEF® 6010/0000 Melting temperature = 173°C (343°F) Average processing temperature = 230°C (446°F) Sample load: 10 mg Appendix n°: 2	774	412	462	239	360	182	1
	813	434	502	261	399	204	2
	833	445	522	272	419	215	3

T1 = Difference between TGA temperature and melting temperature.

T2 = Difference between TGA temperature — Average processing temperature.

All information is given in good faith but without guarantee.

To the best of knowledge the information contained herein is accurate. However, neither Solvay Advanced Polymers, Inc. nor any of its affiliates assumes any liability whatsoever for the accuracy or completeness of the information contained herein. Final determination of the suitability of any information or material for the use contemplated, the manner of use, and whether there is any infringement of patents is the sole responsibility of the user. The above information gives typical properties only and is not to be used for specification purposes

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 cm²

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 ₁		T ₂		Weight Loss
	°F	°C	°F	°C	°F	°C	%
SOLEF® 11008/0003	680	360	392	200	266	130	1
Melting temperature = 160°C (320°F)	685	363	397	203	271	133	2
Average processing temperature = 230°C (446°F)	693	367	405	207	279	137	3
Sample load: 10 mg							
Appendix n° 3							

T₁ = Difference between TGA temperature and melting temperature.

T₂ = Difference between TGA temperature — Average processing temperature.

All information is given in good faith but without guarantee.

To the best of knowledge the information contained herein is accurate. However, neither Solvay Advanced Polymers, Inc. nor any of its affiliates assumes any liability whatsoever for the accuracy or completeness of the information contained herein. Final determination of the suitability of any information or material for the use contemplated, the manner of use, and whether there is any infringement of patents is the sole responsibility of the user. The above information gives typical properties only and is not to be used for specification purposes.

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 cm²

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 ₁		T ₂		Weight Loss
	°F	°C	°F	°C	°F	°C	%
SOLEF® 31008/0003	684	362	379	193	270	132	1
Melting temperature = 169°C (336°F)	693	367	388	198	279	137	2
Average processing temperature = 230°C (446°F)	698	370	394	201	284	140	3
Sample load: 10 mg							
Appendix n°: 4							
SOLEF® 31008/0009	696	369	392	200	282	139	1
Melting temperature = 169°C (336°F)	700	371	396	202	286	141	2
Average processing temperature = 230°C (446°F)	700	371	396	202	286	141	3
Sample load: 10 mg							
Appendix n°: 5							

T1 = Difference between TGA temperature and melting temperature.

T2 = Difference between TGA temperature — Average processing temperature.

All information is given in good faith but without guarantee.

To the best of knowledge the information contained herein is accurate. However, neither Solvay Advanced Polymers, Inc. nor any of its affiliates assumes any liability whatsoever for the accuracy or completeness of the information contained herein. Final determination of the suitability of any information or material for the use contemplated, the manner of use, and whether there is any infringement of patents is the sole responsibility of the user. The above information gives typical properties only and is not to be used for specification purposes

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 cm²

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 ₁		T ₂		Weight Loss
	°F	°C	°F	°C	°F	°C	%
SOLEF® 31508/0003	680	360	376	191	266	130	1
Melting temperature = 169°C (336°F)	689	365	385	196	275	135	2
Average processing temperature = 230°C (446°F)	696	369	392	200	282	139	3
Sample load: 10 mg							
Appendix n°:6							
SOLEF® 31508/0009	698	370	394	201	284	140	1
Melting temperature = 169°C (336°F)	702	372	397	203	288	142	2
Average processing temperature = 230°C (446°F)	703	373	399	204	289	143	3
Sample load: 10 mg							
Appendix n°: 7							

T1 = Difference between TGA temperature and melting temperature.

T2 = Difference between TGA temperature — Average processing temperature.

All information is given in good faith but without guarantee.

To the best of knowledge the information contained herein is accurate. However, neither Solvay Advanced Polymers, Inc. nor any of its affiliates assumes any liability whatsoever for the accuracy or completeness of the information contained herein. Final determination of the suitability of any information or material for the use contemplated, the manner of use, and whether there is any infringement of patents is the sole responsibility of the user. The above information gives typical properties only and is not to be used for specification purposes

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 cm²

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 ₁		T ₂		Weight Loss %
	°F	°C	°F	°C	°F	°C	
SOLEF® 32008/0003	684	362	379	193	270	132	1
Melting temperature = 169°C (336°F)	691	366	387	197	277	136	2
Average processing temperature = 230°C (446°F)	696	369	392	200	282	139	3
Sample load: 10 mg							
Appendix n°: 8							
SOLEF® 32008/0009	694	368	390	199	280	138	1
Melting temperature = 169°C (336°F)	698	370	394	201	284	140	2
Average processing temperature = 230°C (446°F)	700	371	396	202	186	141	3
Sample load: 10 mg							
Appendix n°: 9							

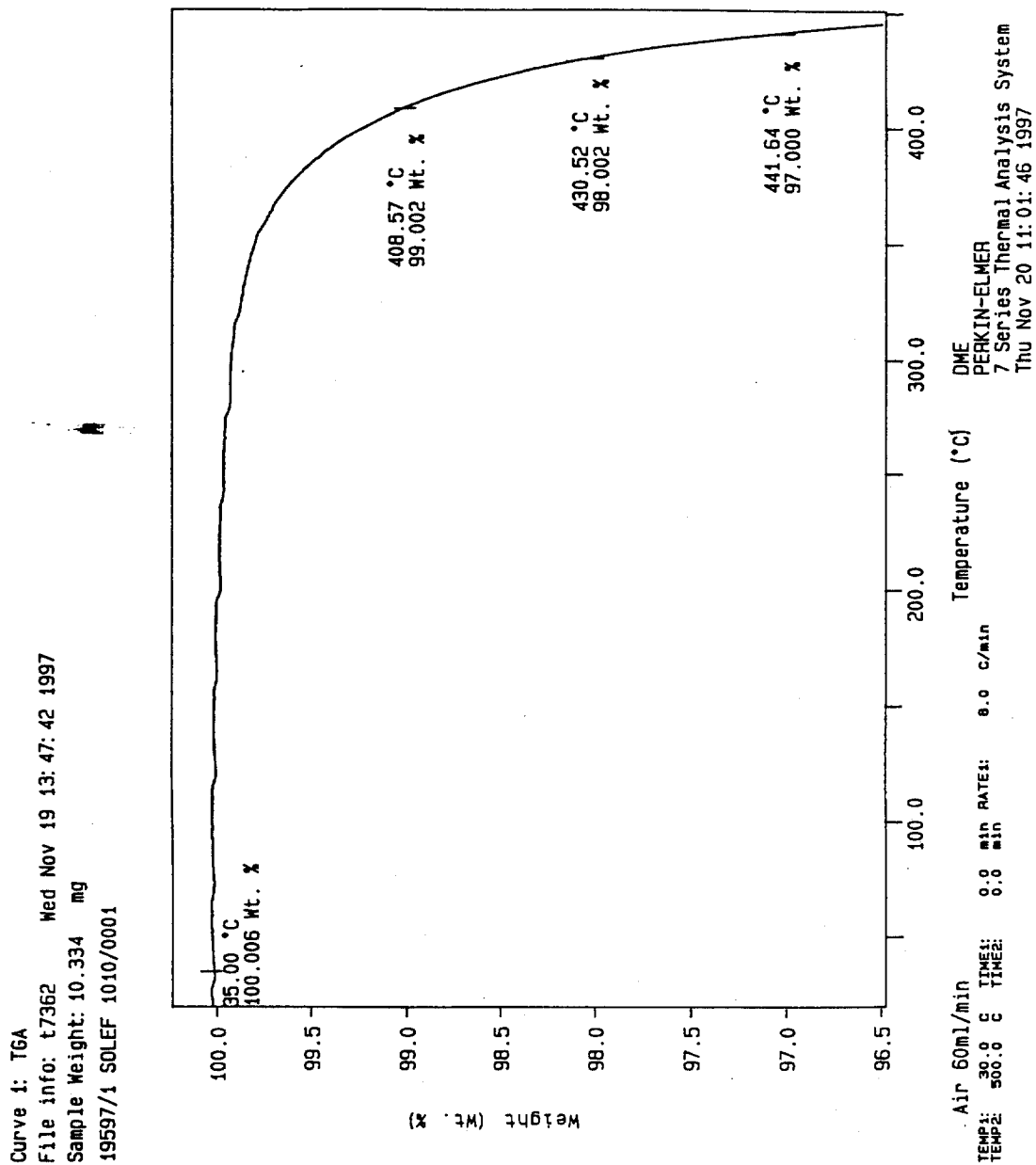
T₁ = Difference between TGA temperature and melting temperature.

T₂ = Difference between TGA temperature – Average processing temperature.

All information is given in good faith but without guarantee.

To the best of knowledge the information contained herein is accurate. However, neither Solvay Advanced Polymers, Inc. nor any of its affiliates assumes any liability whatsoever for the accuracy or completeness of the information contained herein. Final determination of the suitability of any information or material for the use contemplated, the manner of use, and whether there is any infringement of patents is the sole responsibility of the user. The above information gives typical properties only and is not to be used for specification purposes

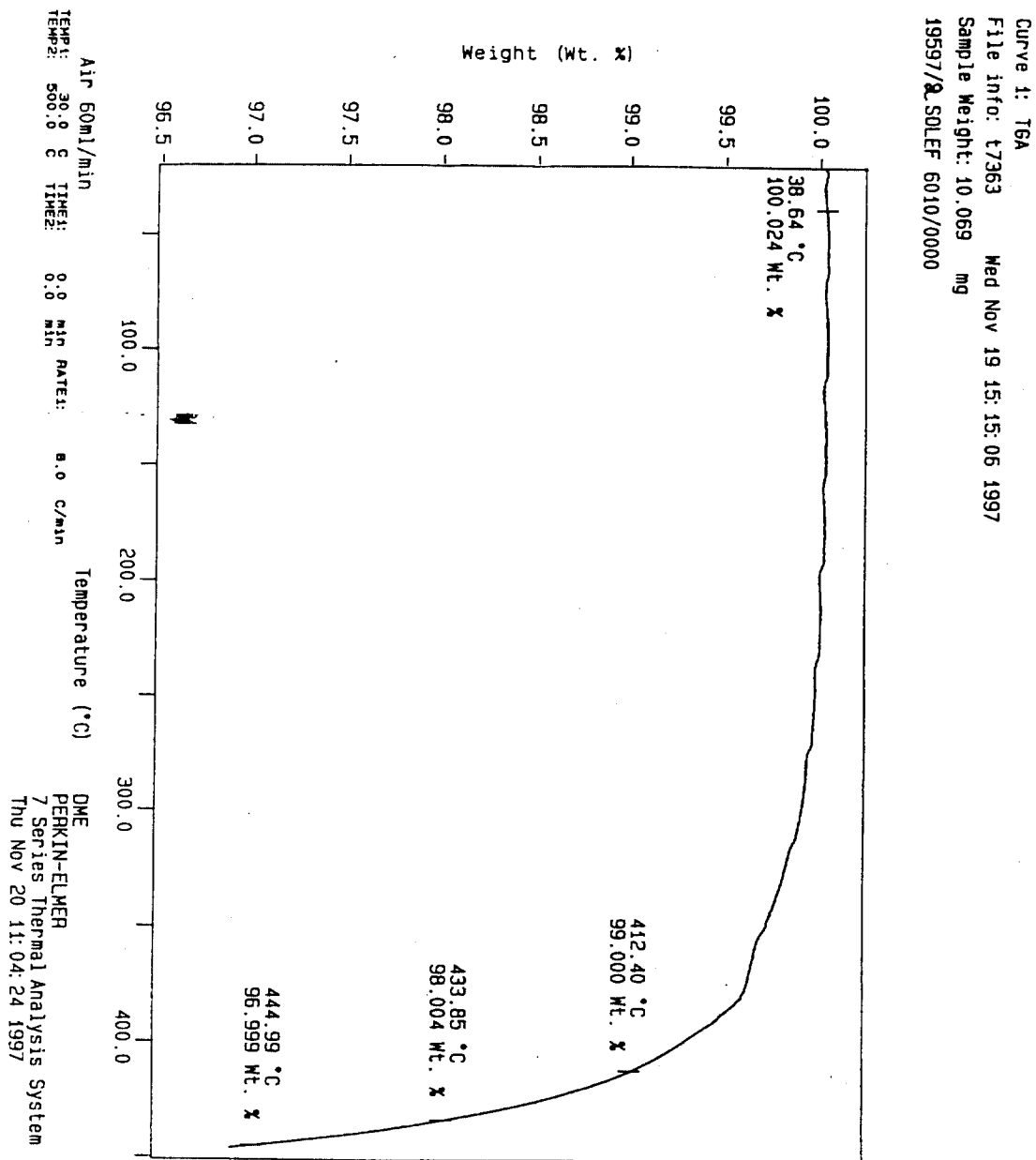
To the best of knowledge the information contained herein is accurate. However, neither Solvay Advanced Polymers, Inc. nor any of its affiliates assumes any liability whatsoever for the accuracy or completeness of the information contained herein. Final determination of the suitability of any information or material for the use contemplated, the manner of use, and whether there is any infringement of patents is the sole responsibility of the user. The above information gives typical properties only and is not to be used for specification purposes



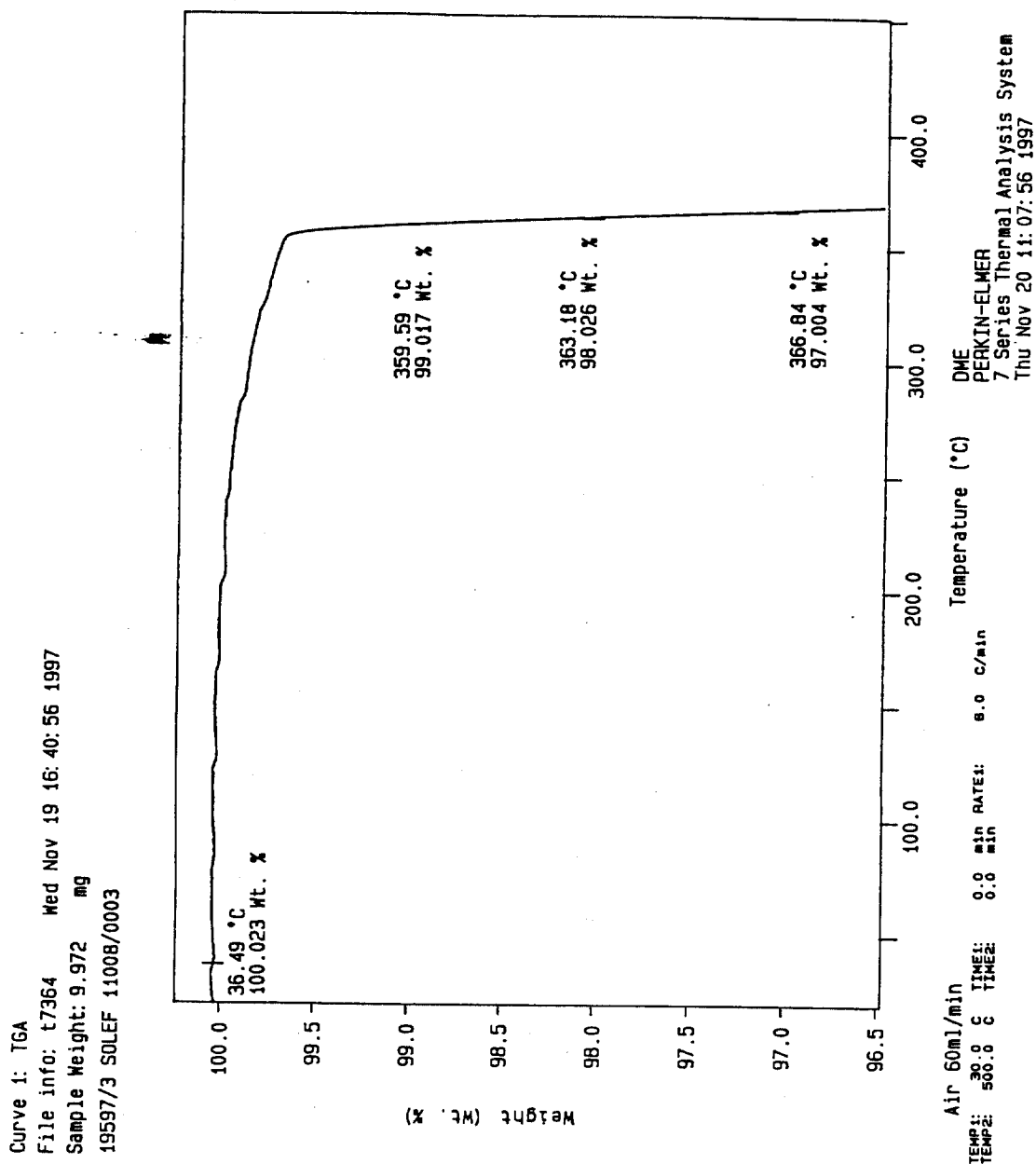
To the best of knowledge the information contained herein is accurate. However, neither Solvay Advanced Polymers, Inc. nor any of its affiliates assumes any liability whatsoever for the accuracy or completeness of the information contained herein. Final determination of the suitability of any information or material for the use contemplated, the manner of use, and whether there is any infringement of patents is the sole responsibility of the user. The above information gives typical properties only and is not to be used for specification purposes.

APPENDIX B

THERMAL PROPERTIES



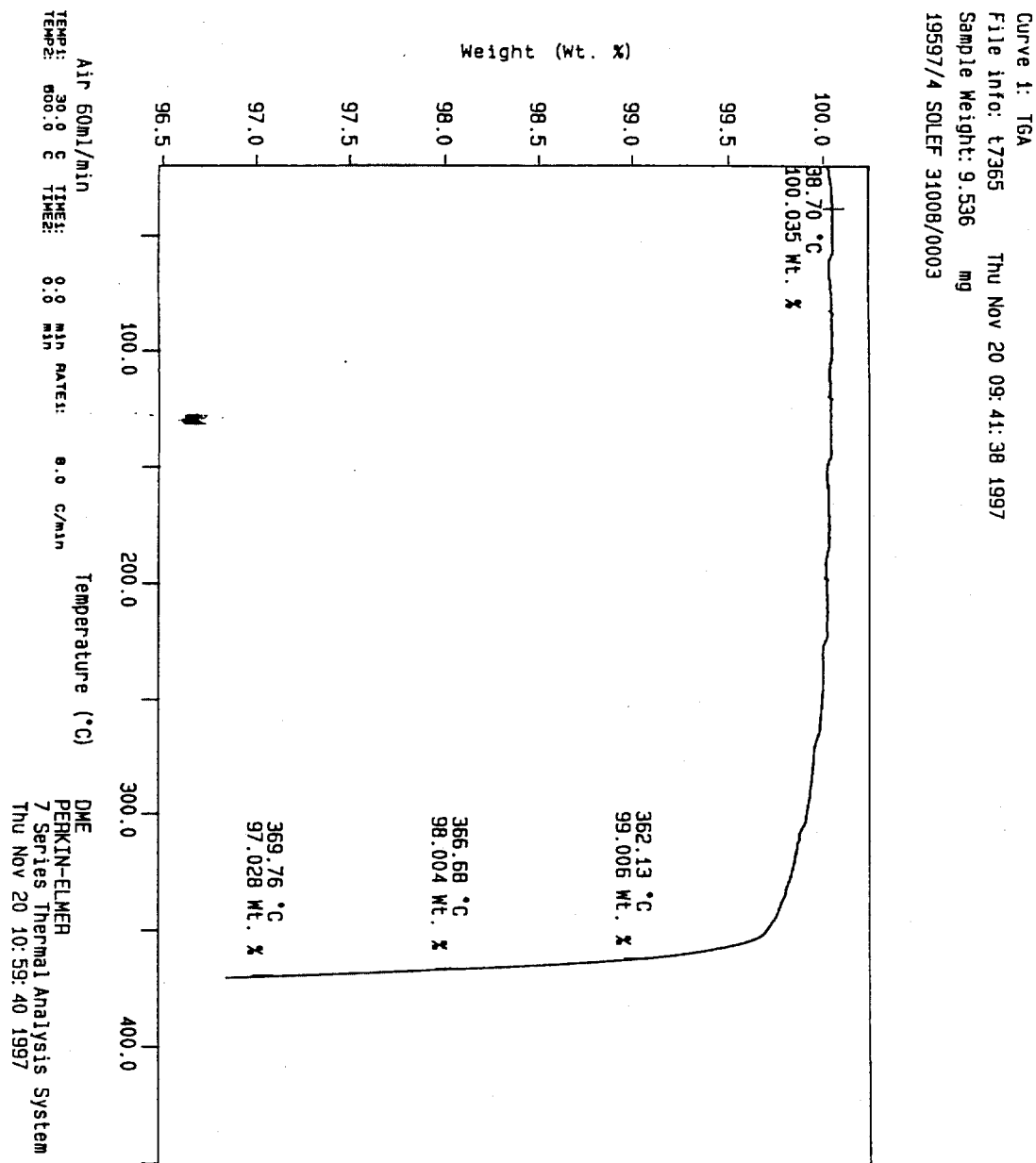
To the best of knowledge the information contained herein is accurate. However, neither Solvay Advanced Polymers, Inc. nor any of its affiliates assumes any liability whatsoever for the accuracy or completeness of the information contained herein. Final determination of the suitability of any information or material for the use contemplated, the manner of use, and whether there is any infringement of patents is the sole responsibility of the user. The above information gives typical properties only and is not to be used for specification purposes



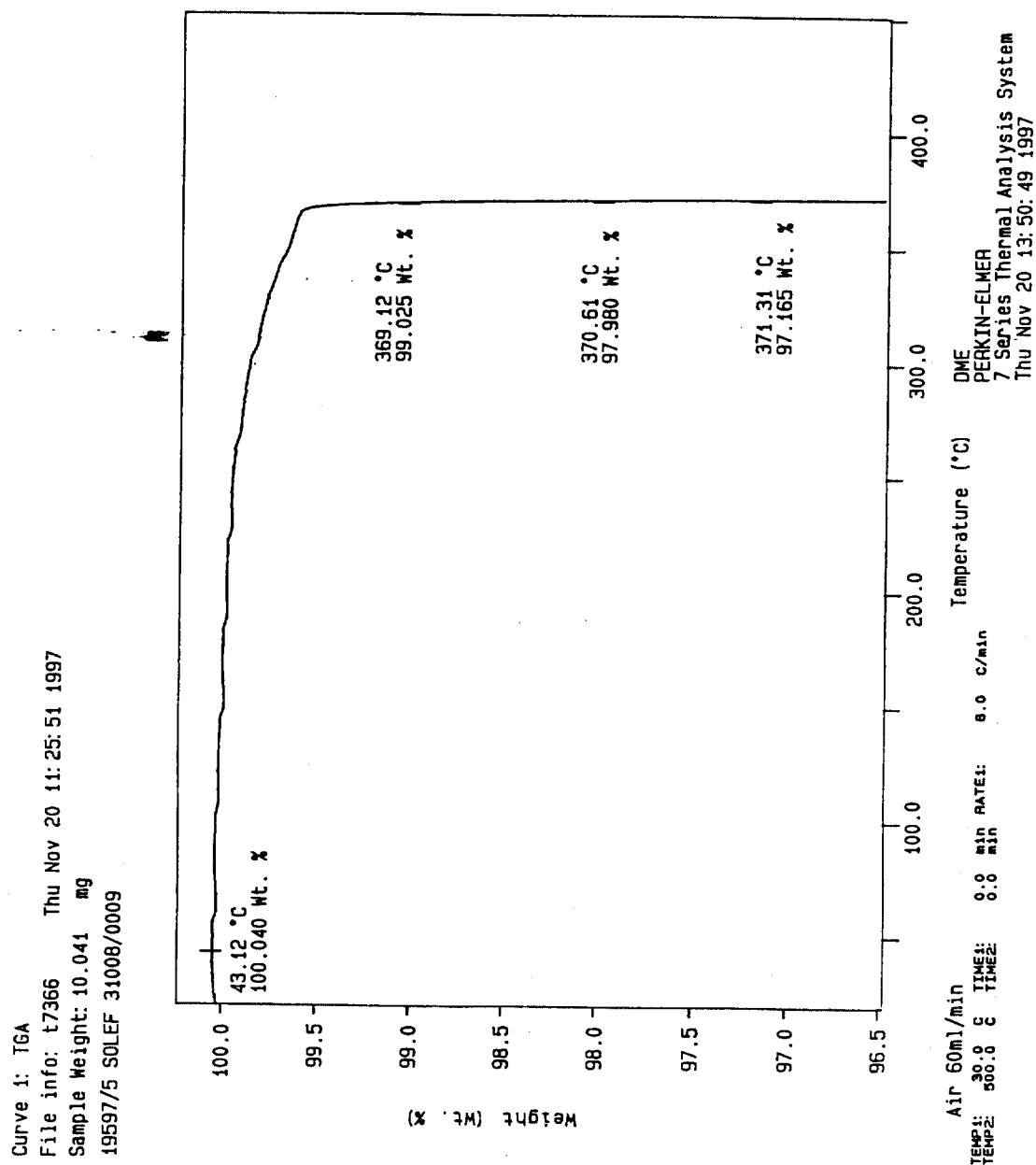
To the best of knowledge the information contained herein is accurate. However, neither Solvay Advanced Polymers, Inc. nor any of its affiliates assumes any liability whatsoever for the accuracy or completeness of the information contained herein. Final determination of the suitability of any information or material for the use contemplated, the manner of use, and whether there is any infringement of patents is the sole responsibility of the user. The above information gives typical properties only and is not to be used for specification purposes

APPENDIX B

THERMAL PROPERTIES



To the best of knowledge the information contained herein is accurate. However, neither Solvay Advanced Polymers, Inc. nor any of its affiliates assumes any liability whatsoever for the accuracy or completeness of the information contained herein. Final determination of the suitability of any information or material for the use contemplated, the manner of use, and whether there is any infringement of patents is the sole responsibility of the user. The above information gives typical properties only and is not to be used for specification purposes

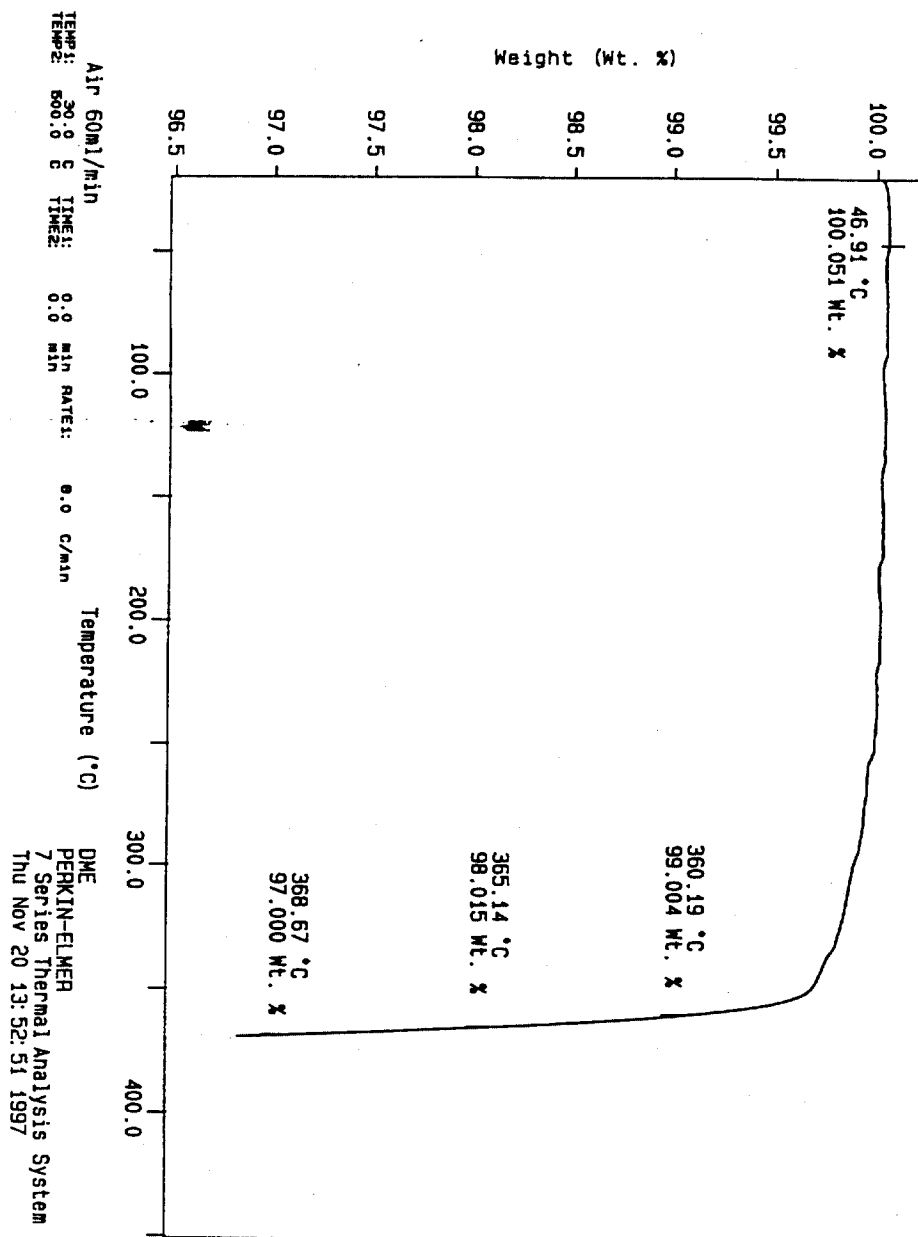


To the best of knowledge the information contained herein is accurate. However, neither Solvay Advanced Polymers, Inc. nor any of its affiliates assumes any liability whatsoever for the accuracy or completeness of the information contained herein. Final determination of the suitability of any information or material for the use contemplated, the manner of use, and whether there is any infringement of patents is the sole responsibility of the user. The above information gives typical properties only and is not to be used for specification purposes

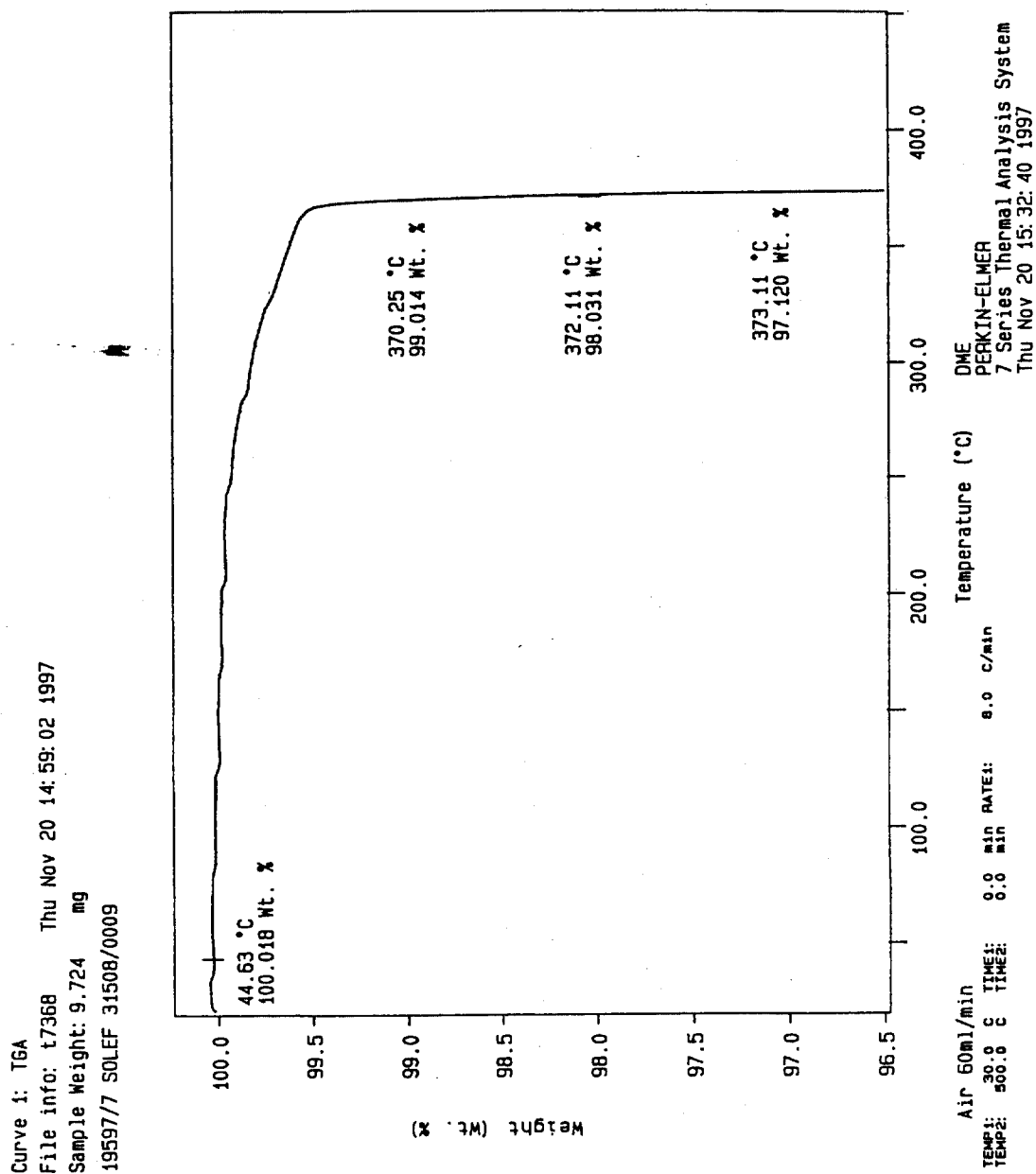
APPENDIX B

THERMAL PROPERTIES

Curve 1: TGA
File Info: t7367 Thu Nov 20 13:47:58 1997
Sample Weight: 9.500 mg
19597/6 SOLEF 31508/0003



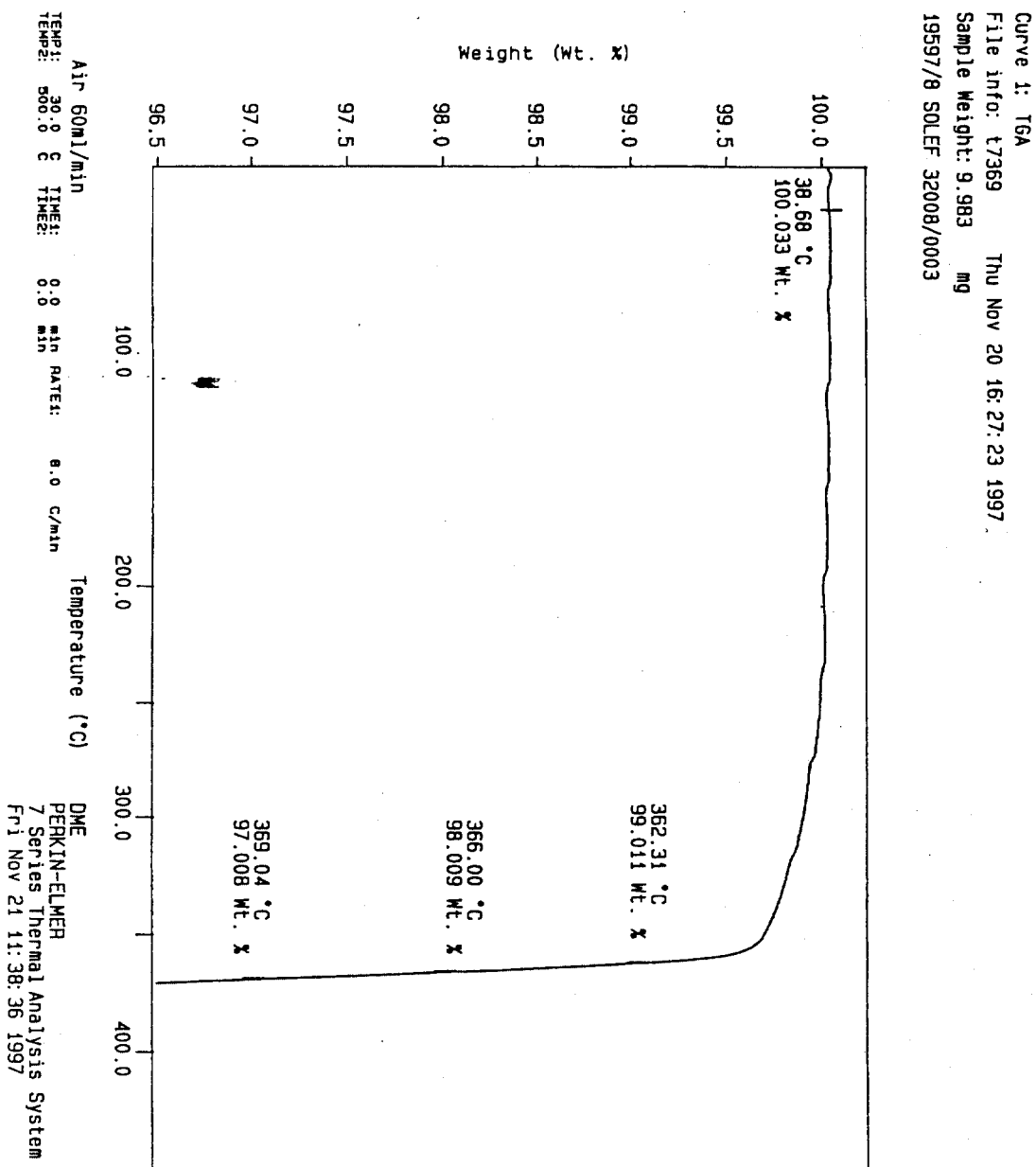
To the best of knowledge the information contained herein is accurate. However, neither Solvay Advanced Polymers, Inc. nor any of its affiliates assumes any liability whatsoever for the accuracy or completeness of the information contained herein. Final determination of the suitability of any information or material for the use contemplated, the manner of use, and whether there is any infringement of patents is the sole responsibility of the user. The above information gives typical properties only and is not to be used for specification purposes



To the best of knowledge the information contained herein is accurate. However, neither Solvay Advanced Polymers, Inc. nor any of its affiliates assumes any liability whatsoever for the accuracy or completeness of the information contained herein. Final determination of the suitability of any information or material for the use contemplated, the manner of use, and whether there is any infringement of patents is the sole responsibility of the user. The above information gives typical properties only and is not to be used for specification purposes

APPENDIX B

THERMAL PROPERTIES

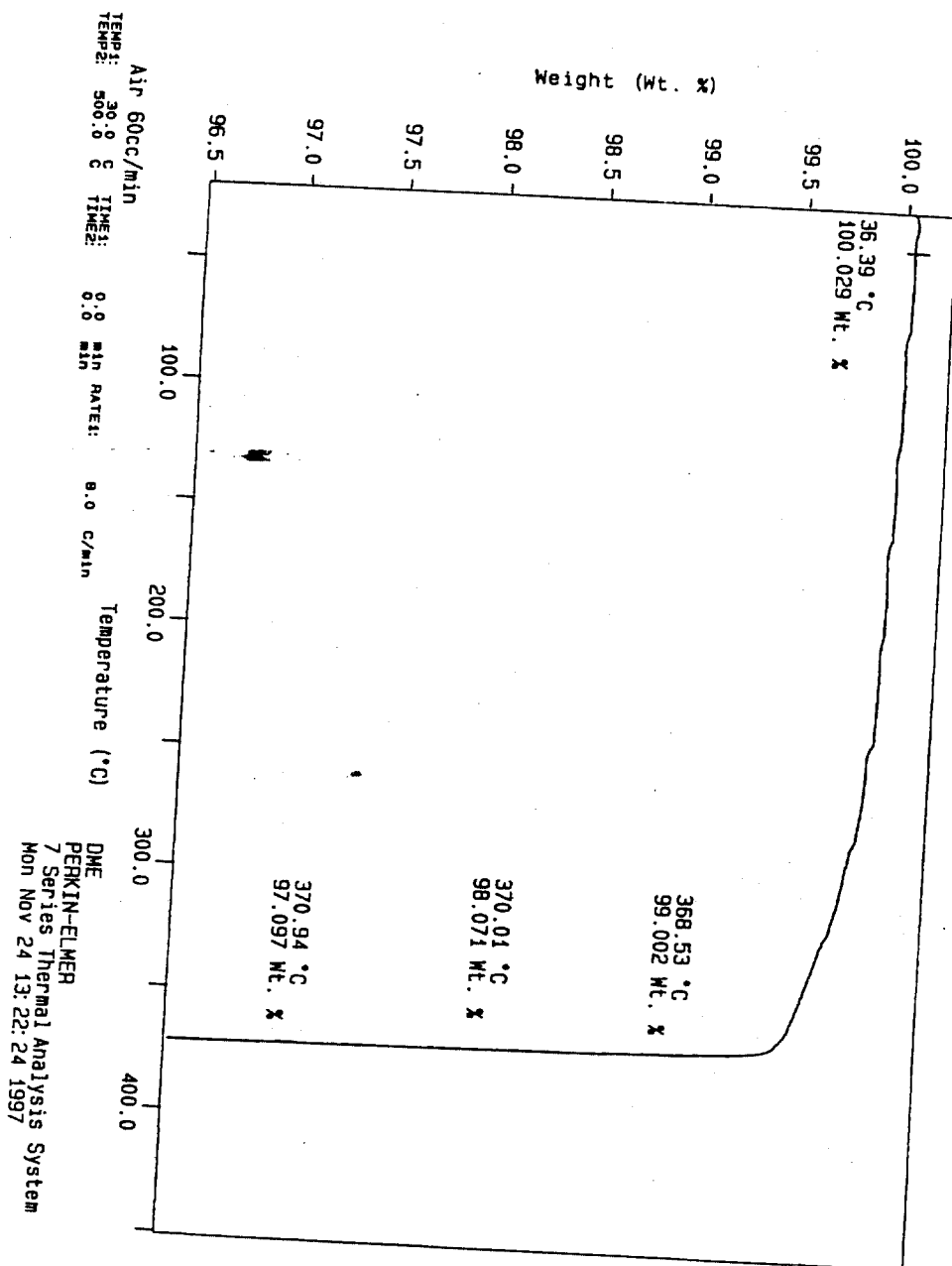


To the best of knowledge the information contained herein is accurate. However, neither Solvay Advanced Polymers, Inc. nor any of its affiliates assumes any liability whatsoever for the accuracy or completeness of the information contained herein. Final determination of the suitability of any information or material for the use contemplated, the manner of use, and whether there is any infringement of patents is the sole responsibility of the user. The above information gives typical properties only and is not to be used for specification purposes

APPENDIX B

THERMAL PROPERTIES

Curve 1: TGA
File info: t7370 FRI Nov 21 11:39:13 1997
Sample Weight: 9.607 mg
19597/9 SOLEF 32008/0009



To the best of knowledge the information contained herein is accurate. However, neither Solvay Advanced Polymers, Inc. nor any of its affiliates assumes any liability whatsoever for the accuracy or completeness of the information contained herein. Final determination of the suitability of any information or material for the use contemplated, the manner of use, and whether there is any infringement of patents is the sole responsibility of the user. The above information gives typical properties only and is not to be used for specification purposes

APPENDIX B

THERMAL PROPERTIES

APPENDIX C

TRADE NAME CROSS REFERENCES

<u>FLUOROPOLYMER</u>	<u>MATERIAL SUPPLIER</u>	<u>TRADE NAME</u>
ECTFE	AUSIMONT USA, INC.	"HALAR"
ETFE	AGA CHEMICALS, INC. AUSIMONT USA, INC. DAIKIN AMERICA, INC. DUPONT FLUOROPRODUCTS	"AFLON" COP "HALON ET" "HYFLON" "NEOFLON" "TEFZEL"
FEP	DAIKIN AMERICA, INC. DUPONT FLUOROPRODUCTS	"NEOFLON" "TEFLON"
MFA	AUSIMONT USA, INC.	"HYFLON"
PCTFE	ALLIED SIGNAL DAIKIN AMERICA, INC. 3M	"ACLON" "NEOFLON" "KEL F"
PFA	AGA CHEMICALS, INC. AUSIMONT USA, INC. DAIKIN AMERICA, INC. DUPONT FLUOROPRODUCTS DYNEON LLC	"AFLON" PFA "HYFLON" "NEOFLON" "TEFLON" "HOSTAFLON"

APPENDIX C

TRADE NAME CROSS REFERENCES

PTFE	AUSIMONT USA, INC.	"ALGOFLON"
	DAIKIN AMERICA, INC.	"DAIKIN-POLYFLON"
	DUPONT FLUOROPRODUCTS	"TEFLON"
	DYNEON LLC	"HOSTAFLON"
	ICI FLUOROPOLYMERS	"FLUON"
PVDF	AUSIMONT USA, INC.	"HYLAR"
	DAIKIN AMERICA, INC.	"NEOFLON"
	ELF ATOCHEM NORTH AMERICA, INC.	"KYNAR"
	SOLVAY ADVANCED POLYMERS, INC.	"FORAFLON"
		"SOLEF"
THV	DYNEON LLC	"DYNEON"

◇ ◇ ◇

Fluoropolymer Coating Materials

See the FPD *Fluoropolymer Coatings Glossary* (SPI publication BP-104) or www.customcoaters.org for a list of fluoropolymer coating trade names.

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 LC₅₀ 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 nonflaming 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 effected 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.

REFERENCES

- Clarke, F. B., H. van Kuijk, R. Valentine, G. T. Makovec, W. C. Seidel, B. B. Baker, D. Kasprzak, G. J. Marovec, J. K. Bonesteel, M. Janssens, and C. H. Herpol, 1990. "The inhalation toxicity of smoke from fires involving perfluoropolymers: Full scale fires." *Proceedings of Interflam '90*, 287-295.
- Clarke, F. B., W. C. Seidel, V. Schere, Jr., D. Clins, A. Olsen, and J. Bonesteel, 1990. "Formation, identify and coagulations of fluoropolymer-derived smoke aerosols. The relationship between aerosol behavior and observed toxicity of fluoropolymer smoke." *Proceedings of Interflam '90*, 297-304.

Fardell, P., 1990. "UK studies of the toxic smoke potential of PTFE in fire." *Proceedings of Interflam '90*, 257-271.

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

Oberdorster, G., J. Ferin, J. Finkelstein, S. Soderholm, and R. Gelein, 1990. "Ultrafine TiO_2 particles as a model for studying overload-related mechanisms." *J Aerosol Med.* 3, 79.

Purser, D. A. 1990. "Recent developments in understanding of the toxicity of PTFE thermal degradation products." *Proceedings of Interflam '90*, 273-286.

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

Catalog No. BP-101
The Society of the Plastics Industry, Inc.
1801 K Street, NW, Suite 600K
Washington, DC 20006-1301
202.974.5200