Guide for the Safe Handling of Fluoropolymer Resins

3rd edition : June 2005
ACKNOWLEDGEMENT

This guide has been developed by the members of the Fluoropolymers Committee of the PlasticsEurope, the professional representative body for the European polymer producers. The Association has over 50 members representing more than 90% of the Western European plastics manufacturing capability.

PlasticsEurope wishes to acknowledge the Fluoropolymers Division of the USA Society of the Plastics Industry (SPI) for permission to use extracts from the SPI Guide to the Safe Handling of Fluoropolymer Resins.

Disclaimer
The information presented in this brochure is provided free of charge and submitted in good faith and is correct to the best of PlasticsEurope’s present knowledge.

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

Brussels, June 2005.
INTRODUCTION

Chapter I: Fluoropolymer Resins Types and Properties

1 Resins types ........................................................................................................................................................................... 5
2 Thermal properties ..................................................................................................................................................................... 5

Chapter II: Potential Health Effects

1 Polymer General Toxicology ..................................................................................................................................................... 7
2 Health hazards during hot processing and toxicity of decomposition products ............................................................... 7
3 Specific hazards of compounds containing pigments and fillers ...................................................................................... 8

Chapter III: Processing Hazards and Precautions

1 Sintering ........................................................................................................................................................................... 8
2 Melt processing .................................................................................................................................................................. 9
3 Paste extrusion ................................................................................................................................................................. 9
4 Coating/Impregnation ..................................................................................................................................................... 9
5 Machining ........................................................................................................................................................................ 10
6 Welding ......................................................................................................................................................................... 10
7 Soldering, Welding and Melt Stripping of Metals coated with Fluoropolymers ......................................................... 10
8 Cleaning and Maintenance of Process Equipment ........................................................................................................ 10
9 Spillage ........................................................................................................................................................................ 10

Chapter IV: Occupational Hygiene

1 Ventilation .................................................................................................................................................................... 10
2 Personal Protective equipment ........................................................................................................................................... 11
3 Personal hygiene .......................................................................................................................................................... 11

Chapter V: Fire and Explosion Hazards

1 Ignition characteristics .................................................................................................................................................... 11
2 Extinguishing agents ....................................................................................................................................................... 12
3 Fire and explosion protection ............................................................................................................................................ 12
4 Fire and combustion toxicity ........................................................................................................................................... 12
5 Specific hazards of fluoropolymers with powdered materials ...................................................................................... 13

Chapter VI: Environmental Information, Recycling and Disposal

1 Environmental Information ................................................................................................................................................ 13
2 Recycling and Disposal .................................................................................................................................................. 13
3 Recycling of Packaging ................................................................................................................................................ 14

Chapter VII: Food Contact

...................................................................................................................................................................................... 14

Chapter VIII: Medical Applications .......................................................................................................................................... 15

APPENDIX A

ADDRESSES OF FLUOROPOLYMER PRODUCERS IN PLASTICS EUROPE ........................................................................ 15

APPENDIX B

PLASTICS EUROPE STATEMENT ON TFE MONOMER TOXICOLOGY-EFFECT ON FLUOROPOLYMERS SAFETY IN USE .................................................................................................................. 16

APPENDIX C

SAFE HANDLING OF FLUOROPOLYMER DISPERSIONS ........................................................................................................ 16

APPENDIX D

THE INHALATION TOXICITY OF COMBUSTION PRODUCTS OF PTFE AND SIMILAR FLUOROPOLYMERS ......................................................................................................................... 18

APPENDIX E

ADDRESSES OF RECYCLING COMPANIES ...................................................................................................................... 19
Fluoropolymer resins are produced and sold worldwide by several manufacturers. They have found application in nearly every field of modern industrial, technological, and scientific endeavour.

Due to the general inertness of the fluoropolymer resins, they are not listed as hazardous materials by European transport regulations and by EU Council Directive 67/548/EEC and subsequent amendments relating to the Classification, Packaging and Labelling of dangerous substances.

Of the many properties that characterise fluoropolymer resins, one of the most important is the 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 natural or synthetic material overheating or combustion of these resins can produce toxic effluents.

This guide includes information on the safe handling, processing and use of the materials identified in Chapter I. Although compounded fluoropolymers or resins in the form of micropowders or lubricant powders will not be dealt with in detail, due to the variety and number of formulations, some general comments will be included in this guide.
CHAPTER I

1. FLUOROPOLYMER RESINS TYPES

The main resin types covered by this document are shown below. Some companies may offer other specialist fluoropolymers which are not included in this guide. Reference should be made to the supplier for specific information on the handling of these polymers.

**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 forms a clear coalescable gel at 335°C+/-15°C. Once processed, the gel point (often referred to as the melting point) is 10°C lower than that of the virgin resin. PTFE is sold as a granular powder, a coagulated dispersion/fine powder, or an aqueous dispersion. Each is processed in a different manner.

**FEP**

FEP fluorocarbon resin is a copolymer 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 245°-280°C and is melt processible. It is supplied in the form of translucent pellets, powder, or as an aqueous dispersion.

**PFA**

PFA fluorocarbon resin is a copolymer 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 perfluoralkoxy group. PFA melts at 280°C minimum and is melt processible. Some grades are chemically stabilised. It is available in the form of translucent pellets, powder, and as an aqueous dispersion.

**ETFE**

ETFE is a copolymer consisting mainly of ethylene and tetrafluoroethylene, having the formula \([(\text{CF}_2-\text{CF}_2)_x-(\text{C}_2-\text{C}_2)_y]_n\), often modified with a small percentage of a third monomer. Depending on the molecular structure the melting range is 215°C to 270°C. It is melt processible and is supplied in the form of pellets, powder, and dispersions.

**ECTFE**

ECTFE is a copolymer of ethylene and chlorotrifluoroethylene having the formula \([(\text{CH}_2-\text{CH}_2)_x-(\text{CFCl-CF}_2)_y]_n\). It is often modified with a small percentage of a third monomer. Depending on the molecular structure, the melting range is 190-240°C. It is available in the form of translucent pellets and as a fine powder.

**PVDF**

PVDF is a homopolymer of vinylidene fluoride having the formula \([(\text{CH}_2-CF_2)_x]_n\) or a copolymer of vinylidene fluoride and hexafluoropropylene having the formula \([(\text{CF}(\text{CF}_3)-\text{CF}_2)_x(\text{CH}_2-CF_2)_y]_n\). PVDF polymers melt at 160° C, are melt processible, and are supplied in the form of powder, pellets, and dispersions.

**MFA**

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

**THV**

THV is a terpolymer of tetrafluoroethylene, hexafluoropropylene, and vinylidene fluoride with the formula \([(\text{CF}(\text{CF}_3)-\text{CF}_2)_x(\text{CF}_2-\text{CF}_2)_y(\text{CF}_2-CF_2)_z]_n\).

THV is melt processable with melting points from 120° to 230° C depending on grade. It is available as pellets, agglomerates or aqueous dispersions.

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

2. THERMAL PROPERTIES

Although fluoropolymers are amongst the most thermally stable polymers known, they will start to decompose slowly when heated to elevated temperatures. There is some contradiction in the published literature as to the exact temperature at which decomposition occurs, reflecting the difficulty in analysing trace element emissions. However, significant decomposition occurs only
above the recommended continuous service temperature for the polymer in question. The quantity of effluent evolved remains small until temperatures above the normal processing temperature for the polymer are reached. Rates of thermal decomposition for various fluoropolymers have been determined (Plastics Europe, 2000) using a thermogravimetric analyser. Samples were heated in dry air flowing at a rate of 30 ml/minute. The temperature was increased at 20°C/minute from room temperature to the test temperature. The samples were then held at constant temperature for one hour and the weight loss during the hour was measured (isothermal weight loss). The rate of weight loss was determined for each polymer at a series of three constant temperatures (four for PVDF). The test temperatures used were different for each fluoropolymer and were chosen according to the increasing thermal stability of the polymer. The results are shown in figure 1.

It should be remembered that within any one polymer type, different grades will have different thermal stabilities according to properties such as molecular weight. The data presented in Figure 1 give a general indication of the relative thermal stabilities of each polymer. Reference should be made to the polymer supplier if precise information is required on an individual polymer grade.

Typical melting points, continuous service temperatures and processing temperatures for the different fluoropolymers are given in Table 1.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Typical melting point (°C)</th>
<th>Typical maximum continuous use service temperature (°C)</th>
<th>Typical processing temperature (°C)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTFE</td>
<td>340</td>
<td>260</td>
<td>380</td>
</tr>
<tr>
<td>PFA</td>
<td>305</td>
<td>260</td>
<td>380</td>
</tr>
<tr>
<td>MFA</td>
<td>280</td>
<td>250</td>
<td>370</td>
</tr>
<tr>
<td>FEP</td>
<td>270</td>
<td>205</td>
<td>360</td>
</tr>
<tr>
<td>ETFE</td>
<td>255</td>
<td>150</td>
<td>310</td>
</tr>
<tr>
<td>ECTFE</td>
<td>230</td>
<td>150</td>
<td>280</td>
</tr>
<tr>
<td>PVDF</td>
<td>160</td>
<td>140</td>
<td>230</td>
</tr>
<tr>
<td>THV</td>
<td>120-230</td>
<td>70-130</td>
<td>200-270</td>
</tr>
</tbody>
</table>

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

1. POLYMER GENERAL TOXICOLOGY

Fluoropolymer resins are known for their high chemical stability and low reactivity. These compounds are of low toxicity, demonstrating little if any toxicological activity. Where toxicological studies have been conducted on fluoropolymers no findings of significance for human health hazard assessment have been reported. None of the fluoropolymers is known to be a skin irritant or sensitiser in humans.

Following grossly excessive exposure to fluoropolymer resin dust by inhalation, increases in urinary fluoride were produced. No toxic effects were however observed. Many resins are formulated with additives such as fillers, pigments or surfactants, to provide favourable processing, or other characteristics. These additives may present other hazards in the use of the resins. Some of the additives may have regulatory exposure standards. The Safety Data Sheet provided by the resin suppliers should be consulted for specific health information on the additives used in their products.

2. HEALTH HAZARDS DURING HOT PROCESSING AND TOXICITY OF DECOMPOSITION PRODUCTS

Some fume will be generated even at the temperatures reached during the normal hot processing of fluoropolymers and it is necessary to assume that the resulting fume will present a potential health hazard. It is essential that adequate ventilation is provided to prevent exposure in the workplace. (See Chapter IV). The consequence of over-exposure to the fumes from fluoropolymers decomposing under these conditions is “Polymer Fume Fever” also known as “The Shakes”. This is a temporary, influenza like illness with fever, chills and sometimes a cough which lasts approximately 24 to 48 hours.

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

The three main types of product formed in the decomposition of fluoropolymers are fluoroalkenes, oxidation products and low molecular weight fluoropolymer particulates.

In the case of PTFE there are many studies in the published literature and these report a wide variety of results for the reasons outlined above. The general pattern, however, is that the monomer, tetrafluoroethylene, is the principal gaseous product at the gel point of the polymer (330°C). As the temperature increases to around 450°C, in the presence of air, carbonyl fluoride and hydrogen fluoride become the main products. Also some carbon monoxide may be formed. Carbonyl fluoride hydrolyses rapidly in the presence of moist air to hydrogen fluoride and carbon dioxide. Small amounts of hexafluoropropylene may also be found at these temperatures. The highly toxic perfluoroisobutylene has been detected as a minor product at temperatures above 475°C. When the temperature reaches about 800°C tetrafluoromethane begins to form.

There is a similar decomposition pattern for other fluoropolymers. Decomposition products tend to form at lower temperatures to a degree which depends on the type and amount of comonomer in the fluoropolymer. Health hazards of these products are as follows:

Hydrogen fluoride: The odour threshold of hydrogen fluoride is significantly less than the occupational exposure limits which are typically of the order of 1ppm. Inhalation of hydrogen fluoride at higher concentration will give rise to symptoms of choking, coughing and severe eye, nose and throat irritation. In severe cases, and possibly following a symptomless period, fever, chills, difficulty in breathing, cyanosis, and pulmonary oedema may develop which may lead to death. Acute overexposure to hydrogen fluoride can result in injury to the liver and kidneys.

Carbonyl fluoride: Effects following inhalation, ingestion, or skin or eye contact with carbonyl fluoride may initially include: skin irritation with discomfort or rash; eye corrosion with corneal or conjunctival ulceration; irrita-
HAZARDS AND PRECAUTIONS

1. SINTERING

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 door is opened. Ovens must be regularly maintained and, in particular, gases from the oven must be kept from leaking into the work area.

Temperatures in excess of the normal sintering range must be avoided. To assist in this, ovens should be equipped with an independent high temperature cut-off, triggered by an increase of 10-30°C higher than the desired sintering temperature, in addition to the normal control system. Both systems need to be calibrated at regular intervals. It is important that an interlock is provided which cuts off the heating if the forced ventilation is interrupted. If the oven temperature exceeds the high temperature cut-off setting, the heaters must be switched off and the oven must be cooled to ambient temperature and properly vented before the door is opened. Compounds containing fillers may be

3. SPECIFIC HAZARDS OF COMPOUNDS CONTAINING PIGMENTS AND FILLERS

Filled and pigmented fluoropolymers are in widespread use. The normal precautions for handling fluoropolymers need to be observed. Users need to note any additional hazards arising from the fillers or pigments themselves. Although many of the commonly used fillers and pigments have low toxicity, some are abrasive, and may cause irritation in contact with the skin. Avoid skin contact with filled or pigmented fluoropolymers, or inhalation or ingestion of filled or pigmented fluoropolymer dust. Refer to the sections of Fire and Explosion Protection and Specific Hazards with Powdered Materials. (Chapter V). Contact your supplier prior to using filled and/or pigmented fluoropolymers for specific safety recommendations. Before a user mixes pigments, fillers or other materials with fluoropolymers, health and safety information must be obtained from the vendors of the added materials and the compatibility with the fluoropolymer must be checked.

CHAPTER III

PROCESSING HAZARDS AND PRECAUTIONS

PROCCESSING HAZARDS AND PRECAUTIONS

tion of the upper respiratory passages; or temporary lung irritation effects with cough, discomfort, difficulty in breathing, or shortness of breath. Respiratory symptoms may be delayed for several hours.

**Carbon monoxide:** An odourless gas which reduces the oxygen carrying capacity of the blood, resulting in a decreased capacity for exertion, increased load on the heart and with severe exposure, unconsciousness and death.

**PFIB (perfluoroisobutylene):** PFIB is highly toxic by acute inhalation, and exposure to concentrations above 1ppm for any significant period can be fatal.

**TFE (tetrafluoroethylene):** Tetrafluoroethylene is a colourless, odourless and flammable gas that is very poorly soluble in water. Tetrafluoroethylene has a very low toxicity after acute exposure and has no cardiac sensitisation potential and it has no genotoxic potential in vitro and in vivo. When administered for a long period, it may cause toxic effect primarily to the kidney. In a 2-year bioassay in rats and mice, tetrafluoroethylene caused various kinds of tumours in the kidney, liver and the haematopoietic system. These effects were seen at high dosages. Studies comparing human and animals metabolism suggested that the risk to human to developing some of the tumours is low for humans. The current TLV/TWA value is 2 ppm (ACGIH 2001). Further studies to understand the whole mechanism are still under evaluation. A multicentre epidemiology study involving the major producers of TFE is ongoing. The implications on fluoropolymers safety in use is dealt with in Appendix B.

**HFP (hexafluoropropylene):** Hexafluoropropylene is a colourless, odourless gas that is very poorly soluble in water. Hexafluoropropylene has a low toxicity after acute exposure. The genotoxicity of the compound was considered overall negative. When administered for a long period it may cause toxic effects primarily to the kidney. No official TLV/TWA has been established by ACGIH. The producers have set a provisional internal OEL value of 0,5 ppm.

3. SPECIFIC HAZARDS OF COMPOUNDS CONTAINING PIGMENTS AND FILLERS

Filled and pigmented fluoropolymers are in widespread use. The normal precautions for handling fluoropolymers need to be observed. Users need to note any additional hazards arising from the fillers or pigments themselves. Although many of the commonly used fillers and pigments have low toxicity, some are abrasive, and may cause irritation in contact with the skin. Avoid skin contact with filled or pigmented fluoropolymers, or inhalation or ingestion of filled or pigmented fluoropolymer dust. Refer to the sections of Fire and Explosion Protection and Specific Hazards with Powdered Materials. (Chapter V). Contact your supplier prior to using filled and/or pigmented fluoropolymers for specific safety recommendations. Before a user mixes pigments, fillers or other materials with fluoropolymers, health and safety information must be obtained from the vendors of the added materials and the compatibility with the fluoropolymer must be checked.

CHAPTER III

PROCESSING HAZARDS AND PRECAUTIONS

1. SINTERING

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 door is opened. Ovens must be regularly maintained and, in particular, gases from the oven must be kept from leaking into the work area.

Temperatures in excess of the normal sintering range must be avoided. To assist in this, ovens should be equipped with an independent high temperature cut-off, triggered by an increase of 10-30°C higher than the desired sintering temperature, in addition to the normal control system. Both systems need to be calibrated at regular intervals. It is important that an interlock is provided which cuts off the heating if the forced ventilation is interrupted. If the oven temperature exceeds the high temperature cut-off setting, the heaters must be switched off and the oven must be cooled to ambient temperature and properly vented before the door is opened. Compounds containing fillers may be
more sensitive to decomposition than PTFE alone and may require the use of lower temperatures. When opening sintering ovens after overheating, appropriate personal protection is recommended, e.g., protective clothing, a self-contained breathing apparatus, thermally insulating gloves, safety glasses, etc.

2. MELT PROCESSING (EXTRUSION/INJECTION MOULDING)

Melt processing of fluoropolymer resins at excessively high temperatures or exposing them for extended times at processing temperatures can cause decomposition. Such decomposition may produce gases and generate pressures in processing equipment sufficient to “blow back” through the feed port. If no vent is available for these gases, as in some compression moulding equipment, pressures can develop which may rupture metal parts and possibly cause injury to personnel near the processing equipment. Corrosion-resistant materials must be used for processing equipment because of the corrosive properties of the melt at high temperatures. Contact your material suppliers for specific machine information.

If a fluoropolymer resin melt begins to darken, the colour 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 be less than +/- 5°C.

3. PASTE EXTRUSION

Processing PTFE coagulated dispersion/fine powder resins requires extrusion by a special process, commonly known as paste extrusion. This involves mixing the resin with a lubricant, usually volatile petroleum fraction. The use of combustible and flammable liquids of relatively low flash-point is a significant potential fire and explosion hazard. Electrically conductive containers should be used and equipment should be earthed to reduce ignition sources. In addition, solvents often have health hazards due to inhalation and/or skin contact associated with their use. Appropriate precautions must be taken for the safe use, storage and handling of fluoropolymer resins containing solvent-based lubricants. Follow the recommendations of the lubricant supplier.

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

4. COATING/IMPREGNATION

The processing of fluoropolymer aqueous dispersions normally requires a heating process to remove water and surfactant prior to sintering the fluoropolymer. Some surfactants and their degradation products are flammable and may have specific irritant or other adverse affects on health. The oven used to remove these products must be provided with forced ventilation to prevent a hazardous build-up of vapour. Furthermore there may be significant build up of decomposition products in the ovens. Protective equipment should be worn when removing such deposits. Contact your dispersion supplier for specific information.

Some coating systems may contain organic solvents in addition to the fluoropolymer resins. These solvents may be combustible and flammable liquids of relatively low flash-point and therefore present a potential fire and explosion hazard. In addition, the solvents often have
health hazards due to inhalation and/or skin contact associated with their use. Appropriate precautions must be taken for the safe use, storage and handling of fluoropolymer resins containing dispersion medium or additives. Follow the recommendations of the supplier. For specific information on ammonium perfluorooctanoate (APFO) see Appendix C.

5. MACHINING

Grinding, sawing, and machining fabricated shapes of fluoropolymers are performed routinely in fabricators’ shops. All normal high-speed machining techniques can be used provided the tools have sharp cutting edges. Coolants are recommended to improve production rates and quality, and they will serve to control any tendency toward overheating, eliminating the need for special ventilation. Dust generated by machining products manufactured from fluoropolymer resins are generally considered a “nuisance dust”. It is commonly recommended that occupational exposure limits of 10mg/m\(^3\) total dust, 5 mg/m\(^3\) respirable dust be used. However, machining products manufactured from resins which contain fillers, pigments, or other additives may produce hazardous dusts due to the presence of fillers and other additives. Consult the additive supplier or Safety Data Sheets (SDS) for further information on additives.

6. WELDING

Special precautions are necessary when welding fluoropolymer parts to one another. Hydrogen fluoride is generated in copious quantities by the process. Complete skin and eye protection is necessary as well as the appropriate respiratory protection which may include the use of self-contained breathing apparatus.

7. SOLDERING, WELDING AND MELT STRIPPING OF METALS COATED WITH FLUOROPOLYMERS

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

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

8. CLEANING AND MAINTENANCE OF PROCESS EQUIPMENT

Cleaning and maintaining process equipment components (dies, screen packs, screws, etc.,) may involve pyrolysis of residual polymer. Appropriate hoods should be designed to completely exhaust the gases and particulates that are formed. Reference should be made to Chapter IV for additional information on ventilation.

9. SPILLAGE

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

CHAPTER IV

OCCUPATIONAL HYGIENE

1. VENTILATION

As with most polymers, minute quantities of residual gases may diffuse from the resins, even at room temperature. Therefore, as a matter of good occupational hygiene practice, resin containers should be opened and used only in
well ventilated areas. Personnel should be instructed to minimize exposure whilst opening and closing containers. Ventilation is required in hot processing operations where fumes may be released, such as drying, extrusion or sintering. In addition it may be required in “cold” operations such as spray coating, blending and high speed grinding or machining to remove aerosols, mists or particulates. Appropriate exhaust ventilation should be selected dependent on the nature of the process involved and local conditions. Proprietary systems may be available for specific activities, eg., spray booths or fume cup boards and where possible these should comply with relevant standards. In other cases local extract ventilation may have to be specifically designed for the process concerned. In either case, ventilation systems should always be designed or supplied by competent extract ventilation specialists. The design of the extraction hood, ducting system and fan should be based on a good understanding of the emissions involved. This may include environmental and process conditions which could affect the emission or cause a secondary emission. It will be necessary to specify the required capture velocity at the point of the emission sufficient to ensure adequate control. This is related to the velocity of the emission and any associated air movements or currents. Good design of the hood (e.g., slots, rim ventilation, annular extraction, booths and cabinets) is important for efficient elimination of off-gases. It should be designed taking into account all the emission characteristics. The most effective hoods are those which enclose or contain the emission. More air is required as the level of containment decreases.

The required extraction volume to give an adequate velocity at the point of emission should be determined. It is possible to calculate this using published formulae. The ducting, fan and air cleaner can then be correctly designed to match the extraction volume requirements. Further ideas on design and information can be obtained from your resin supplier.

2. PERSONAL PROTECTIVE EQUIPMENT

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

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

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

3. PERSONAL HYGIENE

In regular training of personnel it is important to emphasize that tobacco products must not be carried or used in work areas. Smoking tobacco contaminated with even very small amounts of fluoropolymer resin can cause “polymer fume fever” by inhalation of the effluents. See “Health hazards during hot processing” in Chapter II.

To prevent traces of fluoropolymer resin powders being carried out of the work area on clothing, it is advised that personnel should store their work clothing separately from their normal clothing (double locker or separate changing rooms). Personnel should be provided with adequate washing facilities and required to use these regularly.

CHAPTER V

FIRE AND EXPLOSION HAZARDS

1. IGNITION CHARACTERISTICS

The self-ignition temperatures (SIT) of solid PTFE products measured in accordance with ASTM D 1929 are
FIRE AND EXPLOSION HAZARDS

in the range of 500°C to 560°C and hence are far above those of materials capable of sustaining combustion when the ignition source is removed. For comparison the SIT of cellulose containing materials such as wood, paper, board etc is 240°C to 245°C. All fire and flammability tests show that fluoropolymers are amongst the most difficult plastics to set on fire. If a flame is applied to the surface of these polymers it will ignite because of the formation of gaseous decomposition products. However if the flame is removed combustion ceases. During the combustion of fluoropolymers little or no smoke is produced. Care should be taken however to avoid the inhalation of smoke generated by all combusting materials, including fluoropolymers. The exceptionally low flammability of the fully fluorinated fluoropolymers is also indicated by their limiting oxygen index (LOI) measured in accordance with ASTM D 2863. The oxygen index is the minimum concentration of oxygen of a mixture of oxygen and nitrogen that will just support flaming combustion of a material.

The LOI for fully fluorinated polymers such as PTFE, PFA and FEP is greater than 95%. For polymers which are not fully fluorinated, the LOI is between 30 and 60 depending on the molecular structure. This compares with values of around 20 for cellulose products. PTFE does not form flammable dust clouds under normal factory conditions. PTFE and other fluoropolymer powders fall into dust explosion class STO.

2. EXTINGUISHING AGENTS

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

3. FIRE AND EXPLOSION PROTECTION

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

In the event of a fire, the fire service should be warned of the possibility of the presence of toxic and corrosive gases. Self-contained breathing apparatus must always be worn when extinguishing fires or when conducting cleaning up operations in the presence of fire effluent. Suitable measures should be taken to prevent exposure of members of the public. If individuals are exposed, treatment may be required for inhalation of hydrogen fluoride or the other decomposition products or for skin contact with hydrogen fluoride.

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

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

4. FIRE AND COMBUSTION TOXICITY

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

If fluoropolymers are involved in a fire, the hazardous gases and vapours produced include hydrogen fluoride, carbonyl fluoride, carbon monoxide, low molecular weight fluoropolymers and particulates. The toxicology of the combustion product has been investigated extensively, and
it has been shown that particulates have potential, under certain laboratory conditions, to be extremely toxic. A more detailed assessment of the combustion toxicology of fluoropolymers is given in Appendix D. In a real fire situation it is not likely that any fluoropolymers present will contribute to the overall toxicity of the combustion products by virtue of the normally expected thermal degradation products (e.g. hydrogen fluoride) and will not dominate the overall toxicity due to the production of extremely toxic products.

5. SPECIFIC HAZARDS OF FLUOROPOLYMERS WITH POWDERED MATERIALS

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

Other fluoropolymer materials may react at higher or lower temperatures. In addition other materials known to catalyse these reactions include silica, silicon carbide, titanium dioxide, metallic compounds and glass fibres or beads. There may be other materials that can cause such reactions. Contact your materials suppliers for specific information.

CHAPTER VI ENVIRONMENTAL INFORMATION, RECYCLING AND DISPOSAL

1. ENVIRONMENTAL INFORMATION

Neither fluoropolymers themselves, nor any of their decomposition products pose any threat to the ozone layer and, consequently, they are not subject to any form of restrictive regulation under the terms of the Montreal Protocol, the US Clean Air Act Amendments (1993) and its labelling provisions, nor proposed legislative measures within the European Union.

Difluorochloromethane (HCFC22) is used as a feedstock in the production of the principal monomer TFE used in fluoropolymer manufacture. This substance has an ozone depleting potential of less than 1/20th of that of standard trifluorochloromethane (CFC11). The Montreal Protocol and subsequent regulations, which deal with the control of ozone depleting substances, recognises that substances which are used as chemical feedstocks and destroyed in the process are thus removed from the environment. When used in this way the ozone depleting potential is zero. For this reason the Protocol specifically excludes these substances from its regulation.

The new European Regulation on substances that deplete the ozone layer (Reg EC N° 2037/2000 of 29/6/2000) allows the use of HCFC as feedstock agents with no limitations (article 5). The feedstock substance is defined as “any controlled substance or new substance that undergoes chemical transformation in a process in which it is entirely converted from its original composition and whose emissions are insignificant”.

2. RECYCLING AND DISPOSAL

Like other materials all fluoropolymers can be recycled, landfilled or incinerated in approved incinerators (see below).

Polymer scrap resulting from the processing of fluoropolymer resins should be recycled where possible. This can be done by the processor himself or on a large scale mainly by specialist multinational recycling companies. At present compounds containing fillers such as glass fibre, carbon or bronze are recyclable to a more limited extent than unfilled fluoropolymers but outlets for recycled compounds are being developed. A list of some of the recycling companies is given in Appendix E.

As fluoropolymers are used predominantly in small components of larger finished products it is usually impractical to separate, decontaminate and reclaim the small amounts of fluoropolymers used. The presence of fluoropolymers is not a barrier to recycling the main component. For example steel articles containing small amounts of a fluoropolymer article may be re-smelted and the metal recovered. Industrial fluoropolymer waste may be landfilled in accordance with local regulations. Fluoropolymers are environ-
FOOD CONTACT

mentally neutral and are particularly suitable for landfill as they are inert, resistant to high thermal load, do not contain harmful elements which can leach out and do not emit gases. The preferred option for disposal of fluoropolymer aqueous dispersions is to separate solids from liquid by precipitation and decanting or filtering. The dry solids may again be landfilled or incinerated according to local regulations. The liquid filtrate may be discharged to a waste water system in accordance with local regulations or permits. Industrial fluoropolymer waste containing additives such as solvents, primers or thinners must be regarded as special waste. Companies should contact their local waste disposal authorities for details of the relevant waste disposal regulations.

Fluoropolymers can be incinerated in special waste incinerators, at a minimum temperature of 800°C. Control measures, such as wet scrubbing with alkaline solutions, may be necessary to maintain the emission of hydrogen fluoride below that specified by National or local regulation. Typical emission limits of hydrogen fluoride are 1 to 2mg/m³. This method of disposal is most relevant to disposal where the fluoropolymer is a component of a larger article. Incineration may not be suitable for some compounds as there are frequently strict limits on the emissions of heavy metals from incinerators.

3. RECYCLING OF PACKAGING

Containers and drums used for the supply of solid grades of fluoropolymer resins may be re-used for other products but it is essential to ensure that there is no trace of fluoropolymer powder left in the container. Otherwise there is the risk that someone re-using the container could transfer powder onto tobacco products and subsequently suffer “polymer fume fever” (see health hazards during hot processing in Chapter II).

Containers used for the supply of fluoropolymer aqueous dispersions may also be re-used but must be carefully washed out to remove all traces of fluoro-polymer dispersion. The washings from the container may be discharged to a waste water system in accordance with local regulations and permits.

Collection and recycling schemes exist for both plastic and fibreboard containers. Contact your fluoropolymer supplier for details.

CHAPTER VII

FOOD CONTACT

The inertness of sintered fluoropolymers and their resistance to high temperatures have made them a good candidate material for articles to be used in contact with foodstuffs. At present, in Europe, plastic materials coming into contact with food are regulated by EC Directive 2002/72 and its amendments. Under this directive plastic articles intended to come into contact with food shall have all their monomers or starting substances listed in the above mentioned Directive and are required to comply with an overall migration limit and specific migration limits for the monomers used in the production of the polymer. It is the responsibility of the supplier of the finished article to ensure compliance with these limits.

The present directive covers incompletely additives, for which one should still refer to national legislations. The present directive is also not yet applicable to coatings on non-plastic substances. There are only a few countries (Germany, France, The Netherlands and the USA) which have specific regulations or recommendations for coatings with fluoropolymer resins. In both cases the compliance with the regulations depends on the polymer family and on the grade used. Consequently, users should contact their suppliers to obtain information.

This is a very complex area of European legislation which is moreover changing rapidly. It is important that suppliers of articles intended for food contact seek expert advice to obtain an up-to-date position.
In the case of export to the USA, it should be noted that many fluoropolymers have been cleared by the US 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. However additives that are not an essential part of the polymerisation process must be cleared under an appropriate food additive regulation such as 21 CFR § 175.300 or 21 CFR part 178, or be subject of a prior sanction, or be considered GRAS (generally recognised as safe), or not be reasonably expected to become a component of food. For limitations and details it is necessary to refer once more to your supplier.

CHAPTER VIII

MEDICAL APPLICATIONS

Fluoropolymers have historically been developed for industrial applications. Due to their excellent properties they also have been used over a number of years in a wide range of medical applications. A variety of devices containing fluoropolymers have been evaluated. Various small and bigger PTFE-tubes, different small articles and films are in use mainly for short term applications. However to our knowledge, no fluoropolymer producer has ever developed a fluoropolymer product for specific medical use. There is no general regulatory approval of a fluoropolymer resin for medical uses. Each specific type of medical product must be submitted to appropriate regulatory authorities for approval. Manufacturers of such articles or devices should carefully research medical literature, test and determine whether the fluoropolymer is suitable for the intended use. They must obtain all necessary regulatory agency approvals for the medical product including any raw material components.

Examples of both successful life saving cases and inappropriate devices can be found in the published medical literature. For EU member countries, the European Directive on Medical Devices should be followed as well as any applicable national regulation.

The PlasticsEurope fluoropolymer suppliers have policies restricting sales of their materials for medical applications. Before investing resources in testing and seeking regulatory approval for a medical device that incorporates a fluoropolymer, users should consult their supplier to ensure continued access to the material.

APPENDIX A

ADDRESSES OF PLASTICSEUROPE FLUOROPOLYMERS PRODUCERS

ASAHI GLASS FLUOROPOLYMERS U.K.
Hillhouse Int., P.O. Box 4
Thornton-Cleveleys
GB – LANCASHIRE FY5 4QD
Switchboard: +44 (1253) 86 18 00
Fax number: +44 (1253) 86 19 50
Web site: www.fluoropolymers.com

ARKEMA
4-6 Cours Michelet – La Défense 10
F – 92091 PARIS LA DEFENSE CEDEX
Switchboard: +33 (1) 49 00 80 80
Fax number: +33 (1) 49 00 83 96
Web site: www.atofina.com

SOLVAY SOLEXIS
Via Lombardia 20
I – 20021 BOLLATE (Milano)
Switchboard: +39 (02) 38 35 1
Fax number: +39 (02) 38 35 23 67
Web site: www.solvay.com

DUPONT DE NEMOURS INTERNATIONAL
2, Chemin du Pavillon, P.O. Box 50 CH–1218 Le Grand-Saconnex, GENEVE
Switchboard: +41 (22) 717 51 11 Fax number: +41 (22) 717 51 09 Web site: www.dupont.com

DYNEON
Werk Kelsterbach
D–65444 KELSTERBACH
Switchboard: +49 (6107) 776 162
Fax number: +49 (6107) 776 160
Web site: www.dyneon.com
APPENDIX B

New Assessment of TFE Monomer Toxicology – Effect on Fluoropolymers Safety in Use

PLASTICS EUROPE STATEMENT

Tetrafluoroethylene (TFE) has been shown to cause cancer in rats and mice exposed to relatively high concentrations of TFE vapour for their lifetime. Various types of tumour in kidney, liver and the haematopoietic system were seen. Studies comparing the metabolism of TFE in humans and animals, suggest that the risk for developing some of these tumours is lower for humans than for rats and mice. Further studies to understand the mechanism of the response to TFE are still under evaluation. A multicentre epidemiology study involving the major producers of TFE is ongoing.

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

Solid fluoropolymers sold by PTFE manufacturers to processors do not contain detectable levels of TFE. Aqueous dispersions may contain traces (less than 1 ppm) of residual TFE.

Effective ventilation, which is currently required to prevent acute health problems, such as polymer fume fever or exposure to HF, is sufficient to prevent any potential exposure to TFE. Ventilation is particularly important in melt-processing or sintering of fluoropolymers under normal recommended conditions, where there is a limited weight loss consisting mainly of TFE monomer.

Analysis of fabricated articles show no detectable TFE: this applies to articles made from both solid fluoropolymers and aqueous dispersions processed under recommended conditions.

Brussels, June 2005

APPENDIX C

SAFE HANDLING OF FLUOROPOLYMER DISPERSIONS

1. INTRODUCTION

Fluoropolymer dispersions are an aqueous form of fluoropolymer typically used in metal and glass cloth coating. These dispersions are produced and sold on a global basis by several manufacturers. The purpose of this appendix is to provide safe handling information to dispersion processors, since these products usually contain a fluoropolymer polymerisation aid (FPA) remaining from the manufacture of the dispersion.

These FPAs are surfactants that are members of a class of commercially available perfluorooalkyl carboxylate surfactants (e.g. ammonium and sodium perfluorooctanoate). FPAs are used to suspend and emulsify fluoropolymers during manufacture or industrial use, and are typically used in concentrations less than 0.5%. FPAs may be found in other forms of fluoropolymers, such as formulated coatings.

Ammonium perfluorooctanoate (APFO) is the most commonly used FPA in the production of many fluoropolymers and fluoroelastomers. Because APFO is the best understood from the point of view of toxicology and health effects, it is the main focus of this appendix. The other perfluorocarboxylates are considered chemically and toxicologically similar to APFO.

Since APFO is a perfluorinated chemical, it is extremely stable, degrades slowly and has a long life in the environment. APFO has been found in trace amounts in the blood of workers exposed during manufacturing operations involving its use. However, based on more than thirty years of careful health studies there have been no adverse health effects observed in exposed employees. The American Conference of Governmental Industrial Hygienists (ACGIH) recommends a Threshold Limit Value (TLV) for APFO of 0.01 mg/m³ in air as an 8h TLV/TWA (A3, skin).

Fluoropolymer dispersions that may contain FPAs include PTFE, ETFE, FEP, PFA, MFA, PVDF and THV. Fluoroelastomer dispersions are also available that may contain FPAs. Users should consult their supplier for compositional details of the products they are purchasing.
2. TOXICOLOGICAL INFORMATION AND POTENTIAL HEALTH EFFECTS

The fluoropolymer dispersions may contain ammonium perfluorooctanoate (APFO). APFO is absorbed via the lung, the skin and gastrointestinal tract and is only eliminated slowly from the blood. Studies in animals have shown that APFO causes weight loss and adverse effects on the liver. Ingestion studies in animals have shown that repeated administration for 2 years produces benign tumours in the pancreas, liver and testes. None of these effects are likely to occur in humans provided that the exposure is maintained at or below the occupational exposure limit. Epidemiology studies in workers exposed to APFO have demonstrated persistent levels of organo fluorine in the blood without showing any adverse effects.

3. HANDLING, STORAGE AND EXPOSURE CONTROL

The primary exposure routes of FPAs are through the skin (dermal) and by inhalation. FPAs are irritating to the eyes. FPAs are released when dispersions are dried or heated. Gloves made from nitrile rubber or neoprene should be worn when handling fluoropolymer dispersions. Eye protection should be worn. If there is significant potential for splashing, the eye protection should be in the form of chemical goggles or face shield and body protection such as overalls or aprons will be required. Good hygiene procedures are essential to control exposure. Hands and exposed skin should always be washed after use of fluoropolymer dispersions and before handling food or applying cosmetics. Contaminated gloves should not be kept in the pockets of clothing. Clean and contaminated clothing should be kept separate. Contaminated clothing and shoes should be thoroughly cleaned before re-use. Laundry arrangements must ensure that no exposure of laundry workers to fluoropolymer dispersions, FPAs or their thermal decomposition products can occur. Eating and drinking must not be allowed in areas where fluoropolymer dispersions have been used. Smoking cigarettes or other tobacco products contaminated with fluoropolymer products is likely to lead to polymer fume fever. Smoking must therefore not be permitted in any fluoropolymer processing facility. Spillages of fluoropolymer dispersions must be cleaned up immediately, as allowing them to dry will lead to the formation of dusts and will greatly increase the likelihood of exposure to FPAs. Work surfaces should be kept clean to prevent inadvertent transfer of dispersions or FPAs to skin. The major health hazard associated with handling fluoro-polymers is the inhalation of thermal decomposition products produced during operations such as sintering and welding. In addition, when handling fluoropolymer dispersions FPAs are released when coatings are dried or heated. Sufficient ventilation must be provided to maintain exposures below recommended limits. If it is not possible to provide adequate exhaust ventilation, use appropriate personal respiratory protection such as an air supplied respirator.

Vapours and gases produced in ovens used for processing fluoropolymer dispersions may condense as solids or liquid solutions in the oven, exhaust duct or stack, or on other cool surfaces. These condensed or solidified fumes can contain hazardous substances. Skin contact with this condensate when cleaning the oven, stack or other equipment must be avoided. Handling such concentrated FPA solutions and solids requires the use of suitable gloves, bodysuits, face shields and respirators. Exposure to FPAs must also be prevented during other equipment maintenance (e.g. cleaning tanks, spray equipment, fans, spray filters, exhaust ducts, etc.). Users should consult their supplier’s Material Safety Data Sheet (MSDS) for more specific information on prevention of exposure.

4. ECOTOXICOLOGICAL AND DISPOSAL CONSIDERATIONS

Do not discharge dispersions to lakes, streams or waterways. Disposal to water will produce a milky appearance. The fluoropolymer component is not toxic. The stabilizing surfactants have varying ecotoxicity profiles, and users should contact their supplier for more detailed ecotoxicological information for their particular product.

Preferred options for disposal are:
- Separate solids from liquid by precipitation and decanting or filtering. Dispose of dry solids in a landfill that is permitted, licensed or registered to manage industrial solid waste. Discharge liquid filtrate to a wastewater treatment system.
- Incinerate only if incinerator operates at 800°C or higher and is capable of scrubbing out hydrogen fluoride and other acidic combustion products. Empty containers should preferably be cleaned and recycled, but failing this should be punctured or otherwise destroyed before disposal. All treatment, storage, transportation, and disposal of this product and/or container must be in accordance with applicable national and local regulations.
APPENDIX D

THE INHALATION TOXICITY OF COMBUSTION PRODUCTS OF PTFE AND SIMILAR PERFLUOROPOLYMERS

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

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

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

The particulate phase of the degradation products is clearly responsible, specifically with regard to the size of the particles evolved. When fumes are generated in a temperature range of approximately 450-800°C the particles generated are extremely fine, typically less than 0.05 microns and in an apparatus such as the NBS chamber, will be confined to a relatively small volume. They will rapidly undergo thermal coagulation producing fume particles of greater size and lower number concentration and which will spread throughout the 200-litre exposure chamber. As they recirculate through the furnace they may undergo 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 relate to free radical production during pyrolysis and indeed relatively stable alkylfluoroperoxy radicals are reported to have been detected (Fardell, 1990). Nonetheless, the most critical factor appears to be the size of the particles when inhaled. This dictates the proportion that will deposit in the alveolar region where damage is seen, but possibly more importantly, the interaction of the particle with the epithelial cells. There is increasing evidence that ultrafine particles of sizes less than approximately 0.05 microns of even highly inert materials such as titanium dioxide are substantially more toxic to the lung compared with larger particles (Oberdorster, 1990) due to direct penetration into or reaction with the epithelial cells. The extreme toxicity of PTFE pyrolysis products is consistent with this picture.

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

ADDRESSES OF RECYCLING COMPANIES

HEROFLON S.R.L.
Via A de Gasperi 4,
I-25060 COLLEBERATO (Brescia), Italy
Switchboard: +39 030 25 20 211
Fax number: +39 030 25 11 495
www.heroflon.com

MIKRO-TECHNIK GMBH & CO
Betriebe KG,
D 63886 MILTENBERG, Germany
Switchboard: +49 9371 4005 92 Fax number: +49 9371 4005 70
www.mikro-technik.com

SHAMROCK TECHNOLOGIES bvba
Heersterveldweg 21
B-3700 TONGEREN, Belgium
Switchboard: +32 12 45 83 30 Fax number: +32 12 45 83 40
www.shamrocktechnologies.com

UNITED POLYMER MIXERS
Ramgaatseweg 14
NL-4941 AM RAAMSDONKVEER, The Netherlands
Switchboard: +31 1625 14 945 Fax number: +31 1625 22 219
www.upmkunststoffen.nl

REFERENCES


