



Guide for the Safe Handling of Fluoropolymer Resins

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Acknowledgement

This guide has been developed by the members of the Fluoropolymers Committee of PlasticsEurope (the Association of Plastics Manufacturers in Europe), the professional representative body for the European polymer producers. The association has more than 100 member companies, producing over 90% of all polymers across the EU27 member states plus Norway, Switzerland, Croatia and Turkey.

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Introduction

Fluoropolymer resins are produced and sold world-wide by several manufacturers. They have found application in nearly every field of modern industrial, technological, and scientific endeavour. In applications ranging from power generation to emission controls on vehicles to semiconductor manufacture to aerospace, fluoropolymers provide superior performance in products that contribute to increased safety in offices, homes, industries and communities. 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. The combination of resistance to a broad range of fuels, solvents and corrosive chemicals, heat resistance and excellent dielectric stability means fluoropolymer resins yield an extremely versatile family of engineering

materials. These unique properties may provide certain essential performance characteristics needed in the event of fire, in fluid containment or exclusion, electrical overload and similar emergencies.

Due to the general inertness of the fluoropolymer resins, they fall outside all definitions of hazardous materials within European transport regulations and Regulation (EC) No 1272/2008 on classification, labelling and packaging of substances and mixtures. As with any natural or synthetic material, overheating or combustion of these resins can produce toxic effluents. Additives used with fluoropolymers may also present certain hazards. This guide includes information on the safe handling, processing and use of the materials identified in Chapter II. Although compounded fluoropolymers or resins in the form of micro-powders or lubricant powders will not be dealt with in detail, due to the variety and number of formulations, some general comments will be included in this guide.

Chapter I

Fluoropolymer Resins Types and Properties

1 – 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 $330^\circ\text{C} \pm 15^\circ\text{C}$. 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 260°C - 270°C and is melt processible. It is supplied in the form of translucent pellets, powder or as an aqueous dispersion.

PFA

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

ETFE

ETFE is a copolymer consisting mainly of ethylene and tetrafluoroethylene, having the formula $[(\text{CF}_2-\text{CF}_2)_x(\text{CH}_2-\text{CH}_2)_y]_n$ often modified with a small percentage of a third monomer. Depending on the molecular structure the melting range is 210°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 $[(\text{CH}_2-\text{CH}_2)_x(\text{CFCl}-\text{CF}_2)_y]_n$. It is often modified with a small percentage of a third monomer. Depending on the molecular structure, the melting range is 190°C - 240°C . It is available in the form of translucent pellets and as a fine powder.

PVDF

PVDF is a homopolymer of vinylidene fluoride having the formula $[\text{CH}_2-\text{CF}_2]_n$ or a copolymer of vinylidene fluoride and hexafluoropropylene having the formula $[(\text{CF}(\text{CF}_3)-\text{CF}_2)_x(\text{CH}_2-\text{CF}_2)_y]_n$. PVDF homopolymers melt at 160°C - 175°C , copolymers from 135°C - 170°C , are melt processible, and are supplied in the form of powder, pellets, and dispersions.

THV

THV is a terpolymer of tetrafluoroethylene, hexafluoropropylene, and vinylidene fluoride with the formula: $[(\text{CF}(\text{CF}_3)-\text{CF}_2)_x(\text{CF}_2-\text{CF}_2)_y(\text{CH}_2-\text{CF}_2)_z]_n$. THV is melt processible with melting points from 120°C to 230°C depending on grade. It is available as pellets, agglomerates or aqueous dispersions.

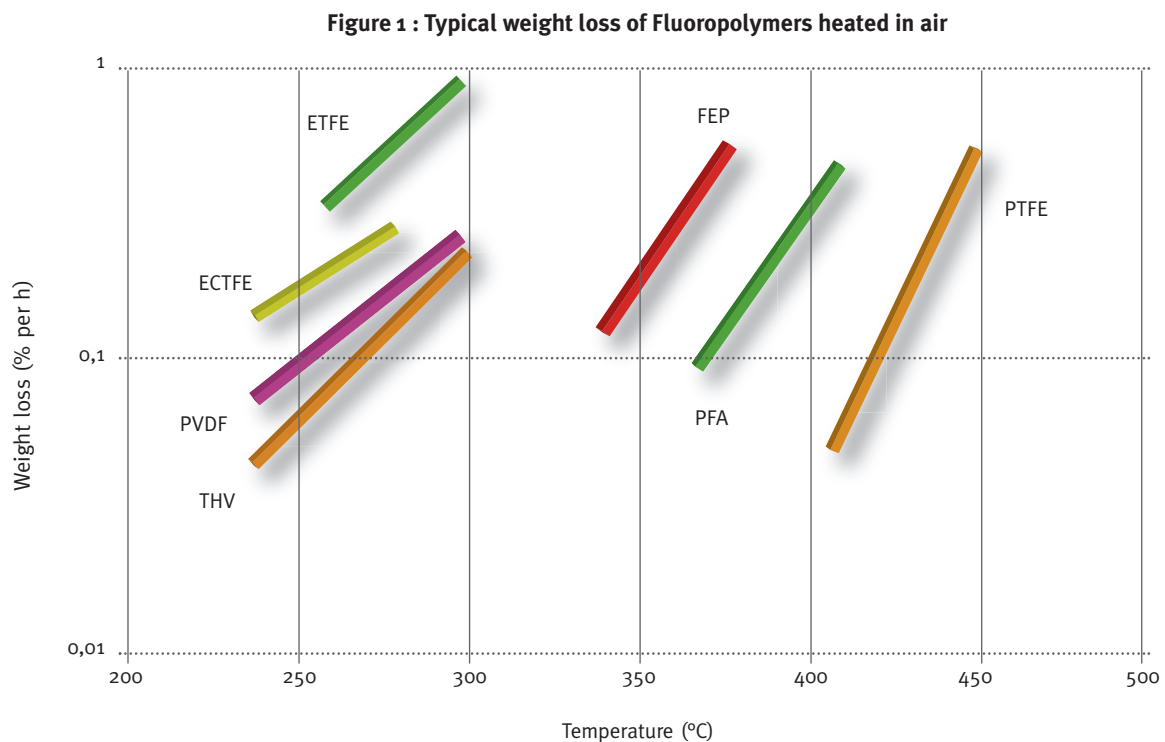
The suppliers of the above materials and their addresses are listed in Appendix A. Many different grades or classes of each type of fluoropolymer resin are available. Individual suppliers should be contacted for specific product information.

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

Polymer	Typical melting point (°C)	Typical maximum continuous use service temperature (°C)	Typical processing temperature (°C)*
PTFE	340	260	380
PFA	265-310	225-260	360-380
FEP	250-270	205	360
ETFE	210-270	150	310
ETFEECTFE	230	150	280
PVDF	160	140	230
THV	110-230	70-130	200-270

* 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 observed, however. Many resins are formulated with additives such as fillers, pigments or surfactants, to provide favourable processing, or other characteristics. These additives may present other hazards in the use of the resins. Some of the additives may have regulatory occupational exposure standards. The 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

During the hot processing of fluoropolymer resins, some fume will be generated, even at the temperatures reached during normal hot processing, 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 to the fume in the workplace. (See Chapter IV). The potential consequence of overexposure to the fumes from fluoropolymers decomposing under these conditions is “Polymer Fume Fever”. This is a temporary, influenza-like illness with fever, chills and sometimes

a cough which lasts approximately 24 to 48 hours. Onset of symptoms may not be apparent for up to 24 hours. As a precaution, any person thought to be suffering from polymer fume fever should seek medical attention.

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

The four main types of product formed in the decomposition of fluoropolymers are fluoroalkenes, hydrogen fluoride, oxidation products and 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 formed 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. (Recent studies indicate the formation of PFIB at

temperatures from 360° C for some types of FEP). Health hazards of the most significant decomposition products are as follows:

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

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

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 of time can be fatal. The US ACGIH has ascribed a TLV – Ceiling level of 0.01ppm to PFIB.

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. TFE has been found to

be carcinogenic in animal studies and under the REACH regulation EC/1907/2006, industry has agreed TFE is a category 2 (GHS Cat.1b) carcinogen A multi-centre epidemiology study to study the carcinogenic impact of TFE in humans, if any, involving the major producers of TFE, is ongoing. The US ACGIH has established a TLV of 2.0ppm (8-hour TWA) for TFE. 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. HFP is generally considered to be non-gentoxic. Repeated or prolonged exposure to HFP may cause toxic effects to the kidney. The US ACGIH has established a TLV of 0.1ppm (8-hour TWA) for HFP.

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 approximately 5% of the desired sintering temperature, in addition to the normal control system. Both systems need to be calibrated at regular intervals. It is important that an interlock is provided which cuts off the heating if the forced ventilation is interrupted. If the oven temperature exceeds the high temperature cut-off setting, the heaters must be switched off and the oven must be cooled to ambient temperature and properly vented before the door is opened. Compounds containing fillers may be more sensitive to decomposition than PTFE alone and may require the use of lower temperatures. When opening sintering ovens after overheating, appropriate personal protection is recommended, e.g., protective clothing, a self-contained breathing apparatus, thermally insulating gloves, safety glasses, etc.

2 – Melt processing

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. It is considered bad practice to stand in front of an extruder for this reason. The exhaust from the vacuum pump used to control the length of the melt cone during extrusion is likely to contain decomposition products from the fluoropolymer and should be discharged outside the workplace.

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 $\pm 5^{\circ}\text{C}$.

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 flashpoint is a significant potential fire and explosion hazard. Electrically conductive containers must be used for

the solvents 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 effects 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, following the recommendations of the supplier. Fluoropolymer dispersions are made using fluoropolymer processing aids (FPA). In most cases the levels of FPA have been reduced to trace amounts.

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/m³ total dust, 5 mg/m³ 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 significant 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. As much polymer as possible should be removed (e.g. with a brass brush) before finally burning off. Appropriate hoods should be designed to completely exhaust the gases and particulates that are formed. Reference should be made to Chapter IV for additional information on ventilation.

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

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 minimise 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.

As described elsewhere in this guide toxic gasses may be generated during the processing of fluoropolymer resins. Processors are advised to allow sufficient degassing of the product prior to further handling of the finished article.

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 emphasise that tobacco products must not be carried or used in work areas. Smoking tobacco contaminated with even very small amounts of fluoropolymer resin can cause “polymer fume fever” by inhalation of the effluents.

See “Health hazards during hot processing” in Chapter II. To prevent traces of fluoropolymer resin powders 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. Further guidance on the handling of dispersion products can be found in Appendix C.

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 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 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.

3 – Extinguishing agents

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

4 – Fire fighting

Fluoropolymers are difficult to ignite and will not themselves sustain a flame so will make no contribution to the start or spread of fires. However if they are involved in a fire they can decompose and may contribute to the toxicity of the fire gases formed. Chapter II and Appendix 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. It is imperative that firefighters and their equipment are thoroughly decontaminated with a water wash down after fire and smoke exposure.

5 – Explosion protection

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

Similarly with 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.

6 – 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 European Regulation on substances that deplete the ozone layer (Regulation (EC) No 1005/2009 of 16th September 2009) allows the use of HCFC as feedstock agents with no limitations (article 7). 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

Recycling options are available for all fluoropolymers. Where separation from other materials is not practical, landfill options may be considered as fluoropoly-

mers are inert. Incineration of fluoropolymers should only be carried out using 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 environmentally 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 solids may 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.

3 – Recycling of Packaging

Containers and drums used for the supply of solid grades of fluoropolymer resins may be re-used within their safe working limits 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 fluoropolymer 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.

In Europe the framework regulation (EC) No 1935/2004 covers all materials and articles intended to come into contact with food. This regulation requires that Materials and articles shall be manufactured in compliance with good manufacturing practice so that, under normal or foreseeable conditions of use, they do not transfer their constituents to food in quantities which could: Endanger human health, bring about an unacceptable change in the composition of the food, or bring about deterioration in the organoleptic characteristics. Plastic Materials and Articles coming into contact with food are regulated by the Regulation (EC) No 10/2011 and its amendments, known as the Plastics Implementing Measure (PIM). Under this Regulation plastic articles and materials intended to come into contact with food shall have all their monomers or starting substances, as well as their additives listed in the European Union list of authorised substances, given in Annex I of Commission Regulation (EC) No 10/2011 and are required to comply with an overall migration limit and specific migration limits for the authorised substances used in the production of the polymer. It is the responsibility of the supplier of the finished article to ensure compliance with these limits. (Note that from 1 January 2010 the list of additives in Directive 2002/72/EC relating to plastic materials and articles intended to come into contact with foodstuffs became a positive list.) Commission Regulation (EC) No 10/2011 is applicable from the 1st of May 2011 and repeals the Plastic Directive 2002/72/EC and its amendments.

The present Regulation is not applicable to coatings on non-plastic substances. There are only a few countries (Germany, 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 subject to frequent review. 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, food contact notification, 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 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 fluoropolymer producers in PlasticsEurope

AGC CHEMICAL EUROPE, LIMITED

Hillhouse Int., P.O. Box 4
Thornton Cleveleys
Lancashire
FY5 4QD
United-Kingdom
Tel: +44 (1253) 861975
Fax: +44 (1253) 861950
Web: www.agcce.com
Email: Info@agcce.com

ARKEMA

Rue d' Estienne d'Orves
92705 Colombes CEDEX
France
Tel: +33 (1) 49 00 80 80
Fax: +33 (1) 49 00 83 96
Web: www.arkema.com

Guest member:

DAIKIN CHEMICAL EUROPE

Immermannstrasse 65D
40210 Düsseldorf
Germany
Tel: +49 211 179 22 50
Fax: +49 211 164 0732
Web: www.daikinchem.de
www.daikin.com

DUPONT DE NEMOURS INTERNATIONAL

2, Chemin du Pavillon
P.O. Box 50 CH-1218
Le Grand-Saconnex (Genève)
Switzerland
Tel: +41 (22) 717 51 11
Fax: +41 (22) 717 51 09
Web: www.dupont.com

DYNEON GmbH

Industrieparkstrasse 1
84508 Burgkirchen
Germany
Tel: +49(0)8679-74709
Fax: +49(0)8679-3992
Web : www.dyneon.com
www.dyneon.eu

HEROFLON S.R.L.

Via A de Gasperi 4
25060 Colleberato (Brescia)
Italy
Tel: +39 030 25 20 211
Fax: +39 030 25 11 495

SOLVAY SPECIALTY POLYMERS ITALY S.p.A

Via Lombardia 20
20021 Bollate (Milano)
Italy
Tel: +39 (02) 38 35 1
Fax: +39 (02) 38 35 26 14
Web: www.solvaysolexis.com

Appendix B

PlasticsEurope statement on TFE monomer toxicology – Effect on fluoropolymer safety in use

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. 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.

Tests on solid fluoropolymers sold by PTFE manufacturers to processors have failed to detect TFE. Aqueous dispersions may contain traces (less than 1 ppm) of residual TFE.

High temperature processing of fluoropolymers may generate low levels of TFE. However effective ventilation, which is currently required to prevent acute health problems such as polymer fume fever or exposure to HF, is sufficient to prevent any potential exposure to TFE. Analysis of fabricated articles shows no detectable TFE: this applies to articles made from both solid fluoropolymers and aqueous dispersions processed under recommended conditions.

Appendix C

Safe handling of fluoropolymer dispersions

The handling hazards for fluoropolymer dispersions are mainly determined by the stabilising surfactant used in the product. Please refer to individual safety data sheets for specific handling information. In general it is advisable to avoid skin and eye contact and ingestion.

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

Preferred options for disposal are discussed in Chapter VI.

Fluoropolymer polymerisation aids (FPAs)

In previous editions of this guide Appendix C covered the safe handling of fluoropolymer dispersions containing FPAs – fluorinated surfactants such as ammonium and sodium perfluorooctanoate.

The member companies of PlasticsEurope have implemented technologies to significantly reduce FPAs in their dispersion products. FPA specific safety measures are therefore no longer required for dispersions supplied by PlasticsEurope members. However, dispersions are offered by producers outside PlasticsEurope that have not implemented these technologies. If those products are used, the suppliers should be contacted for the appropriate safe handling instructions.

Appendix D

The inhalation toxicity of combustion products of PTFE and similar fluoropolymers

A considerable number of studies have been conducted to investigate the toxicity of the combustion/thermal degradation products of PTFE. Prior to 1982 it was considered that the major products, including hydrogen fluoride and carbonyl fluoride, were responsible for the toxic effects seen in rats exposed to the evolved combustion products of PTFE, toxicity being approximately ten times greater than for the combustion products of wood. However, in 1982 Levin et al., using the newly developed National Bureau of Standards small-scale test method for assessing the toxicology of combustion products, reported an unexpectedly high toxicity when testing PTFE. They found an LC₅₀ of 0.045mg/l for PTFE products as compared with 20-40 mg/l for a standard sample of wood (Douglas Fir). This unexpected result could not be explained in terms of the expected combustion products and led to an extensive investigation of this phenomenon by 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 de-aggregation and dispersal, stabilising at the ultrafine particle size and producing extreme toxicity. In a dynamic system such as that described by Warheit et al., (1990), if exposure is 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, Johnston 1996) due to direct penetration into

or reaction with the epithelial cells. The extreme toxicity of PTFE pyrolysis products is consistent with this picture. The toxicity of PTFE pyrolysis products is influencing decisions by regulators on many potential uses of PTFE due to direct extrapolation to real, large scale fire scenarios where humans may be exposed to combustion products. However, caution must be exercised in such extrapolations. The only time that extreme toxicity has been demonstrated has been under closely controlled experimental conditions. It is not inconceivable that such conditions could be reproduced in a real fire but other factors must also be taken into consideration. Firstly, experimental studies have shown effects only when using PTFE or fluoropolymers alone. 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

MIKRO-TECHNIK GMBH & CO Betriebe KG

63886 Miltenberg

Germany

Tel: +49 9371 4005 92

Fax: +49 9371 4005 70

Web: www.mikro-technik.com

SHAMROCK TECHNOLOGIES bvba

Heersterveldweg 21

B-3700 Tongeren

Belgium

Tel: +32 12 45 83 30

Fax: +32 12 45 83 40

Web: www.shamrocktechnologies.com

UNITED POLYMER MIXERS

Ramgatseweg 14

NL-4941 AM RAAMSDONKVEER

The Netherlands

Tel: +31 1625 14 945

Fax: +31 1625 22 219

References

Levin, B.C., et al "Further Development of a Test Method for the Assessment of Acute Inhalation Toxicity of Combustion Products" National Bureau of Standards (US), NBSIR 82-2532 (1982)

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

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

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

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

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

Oberdorster, G, Ferin, J, Finkelstein, J, Soderholm, S and Gelein R. (1990). Ultrafine TiO₂ 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, Seidel, W C, Carakostas, M C and Hartsky, M. (1990). Attenuation of perfluoropolymer fume pulmonary toxicity : effects of filters, combustion methods. and aerosol age. Exp. Mol. Path. 52, 309-329.

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