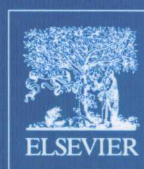


PDL HANDBOOK SERIES



Fluoropolymer Additives

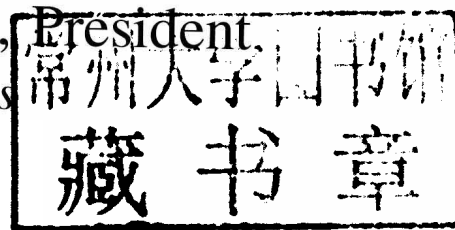
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FLUOROPOLYMER ADDITIVES

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Preface

The aim of the present book, as with the previous volumes in the PDL Fluorocarbon Series, is to compile in one place a working knowledge of the polymer chemistry, physics, and properties of fluoropolymer additives with descriptions of commercial processing and applications techniques.

The book focuses on being a practical guide and data source as well as a reliable reference for learning the basics for the practitioners of applications or research involving fluoropolymer additives. The references listed at the end of each chapter serve as both bibliography and additional reading material. Review papers are helpful as a starting point for finding additional references for concentrated reading in a selected area.

None of the views or information presented in this book reflects the opinion of any of the companies or individuals who have contributed to the book. If there are errors, they are oversight on the part of the authors.

A note indicating the specific errors to the publisher, for the purpose of correction of future editions, would be much appreciated.

The present volume deals with an important but little noticed group of products called fluoropolymer additives. Their use has proliferated in the last three decades because of the unique properties that they impart to the host material to which they are added. We hope this book is useful to those who are in search of information, as we were when we began our fluorine careers some decades ago.

The authors wish to thank all the companies which have generously contributed data and illustrations to this book. Miss Kristin N. Dross is thanked for editing Chapters 1–5.

Sina Ebnesajjad

Richard Morgan

Contents

Preface	xiii
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PART 1 Introduction 1

1 Introduction..... 3

1.1 Introduction	3
1.2 Uniqueness of Fluorine	3
1.3 Fluorine Characteristics	5
1.3.1 Fluorination	6
1.3.2 Reactivity — An Extreme Element.....	6
1.3.3 Preparation of Fluorine	6
1.3.4 Inorganic Chemistry.....	7
1.3.5 Organic Chemistry	8
1.3.6 Fluorine and Nature	9
References.....	9

2 Descriptions of Fluoropolymer Additives..... 11

2.1 Introduction	11
2.2 Polymeric Fluorinated Additives	11
2.2.1 Polytetrafluoroethylene Homopolymer Additives.....	11
2.2.2 Fluoroelastomer Additives (Polymer Processing Additives)	11
2.2.3 Vinylidene Fluoride Polymer Additives (Polymer Processing Additives)	12
2.3 Perfluoropolyether (PFPE) Additives	12
2.4 PTFE-Modified Waxes.....	13
2.5 Fluorinated Graphite	13
2.6 Fluorination	13
References.....	14

PART 2 Manufacturing and Properties 15

3 Manufacturing and Properties of High-Molecular-Weight Fluoropolymer Additives 17

3.1 Introduction	17
3.2 Tetrafluoroethylene (TFE) Preparation.....	17
3.3 Properties of Tetrafluoroethylene.....	19
3.4 Polymerization of Tetrafluoroethylene	20
3.5 Tetrafluoroethylene Polymers	20
3.5.1 Ammonium Perfluorooctanoate (APFO, also C8)	21
3.6 Polymerization Mechanism.....	22

3.7	Suspension Polymerization of Tetrafluoroethylene	23
3.7.1	Finishing Technologies of Granular PTFE.....	25
3.8	Emulsion Polymerization of Tetrafluoroethylene.....	27
3.8.1	Dispersion Products	28
3.8.2	Fine Powder (Coagulated Dispersion) Products.....	28
3.9	Characterization of Polytetrafluoroethylene	29
3.9.1	Granular PTFE Resins	29
3.9.2	Fine Powder PTFE Resins	31
3.9.3	Dispersions of PTFE.....	32
	References.....	34
4	Manufacturing and Properties of Low-Molecular-Weight Fluoropolymer Additives	37
4.1	Introduction	37
4.2	Molecular Weight Reduction	37
4.3	Degradation of Polytetrafluoroethylene.....	37
4.4	Production Methods	39
4.4.1	Production of Fluoroadditives by Thermal Cracking (Pyrolysis).....	39
4.4.2	Production of Fluoroadditives by Electron Beam Irradiation.....	39
4.4.3	Grinding Irradiated PTFE	42
4.5	Direct Polymerization	43
4.5.1	Dispersion Polymerization (Fine Powder)	43
4.5.2	Suspension Polymerization (Granular).....	46
4.6	Other Manufacturing Methods.....	51
4.7	Commercial Products	51
	References.....	51
5	Manufacturing and Properties of Fluoroelastomer-Based Additives	53
5.1	Introduction	53
5.2	Manufacturing Process.....	53
5.3	Emulsion Polymerization.....	54
5.3.1	Continuous Emulsion Polymerization	55
5.3.2	Semibatch Emulsion Polymerization.....	55
5.4	Suspension Polymerization	56
5.5	Development of Polymeric Process Additives	58
5.6	Commercial Products.....	64
	Acknowledgment.....	65
	References.....	65
PART 3	Applications.....	67
6	Applications of Fluorinated Additives for Lubricants.....	69
6.1	Introduction.....	69
6.2	Friction.....	69
6.3	Wear Processes	69

6.4 Fluorinated Additive Types	70
6.5 Lubrication Processes	70
6.6 Lubricant Base Oils	71
6.7 Lubricant Additives – General	72
6.8 Comparison of Solid Lubricant Additives	72
6.9 Polymeric Fluorinated Additives.....	73
6.9.1 PTFE.....	73
6.9.2 Low-MW Fluorinated Additives	75
6.10 Lubricant Application Categorization.....	75
6.11 Low-Viscosity Lubricants.....	75
6.11.1 Test Methods for Low-Viscosity Lubricants	76
6.11.2 Literature Studies of Low-Viscosity Oil with PTFE Addition.....	77
6.11.3 Dry-Film Lubricants.....	79
6.11.4 Release Agents	81
6.12 Engine Oil.....	82
6.12.1 Classification	82
6.12.2 Engine Oil Anti-Wear Additives.....	84
6.12.3 Development History of Use of PTFE in Motor Oil.....	88
6.13 Grease	90
6.13.1 Grease Compositions and Characterization	90
6.13.2 Technical Studies of Grease with Fluorinated Additives	93
6.13.3 Grease Patent History.....	94
6.14 Suppliers of Lubricants Containing Fluorinated Additives	96
6.14.1 DuPont™ Company Products.....	96
6.14.2 3M™/Dyneon™ Products.....	98
6.14.3 Daikin™ Industries Ltd/Daikin America Inc.....	98
6.14.4 Solvay Solexis	99
6.14.5 Asahi Glass.....	100
6.14.6 Other Suppliers.....	100
References.....	102
7 Fluorinated Additives for Plastics	107
7.1 Introduction.....	107
7.2 Types of Fluorinated Additives	107
7.3 Friction and Wear Processes	108
7.3.1 Friction Processes.....	109
7.3.2 Wear Processes	110
7.3.3 Countersurface Effects	113
7.4 Friction and Wear of High- and Low-MW PTFE	113
7.5 Role of PTFE Manufacturing Process and Particle Size on Wear and Friction of Plastics.....	116
7.6 Development of Fluoroaddivive Use for Friction/Wear Enhancement of Thermoplastics	116
7.7 Plastic Wear Under Water	118
7.8 Types of Non-Fluorinated Anti-Friction and Anti-Wear Additives	118

7.9 Plastic Types	118
7.9.1 Polyamides (Nylons)	119
7.9.2 Polyacetals	121
7.9.3 Polycarbonates	123
7.9.4 Polyesters (PEs)	124
7.9.5 Polyetheretherketone (PEEK)	125
7.9.6 Polyphenylene Sulfide (PPS)	128
7.9.7 Epoxy Resins	128
7.9.8 Miscellaneous Thermoplastics	129
7.10 Fluorinated Additives for Improved Melt and Mechanical Properties	129
7.11 Additives to Alter Plastic Surface Properties	131
7.11.1 Theory and Background	131
7.11.2 Type of Fluorinated Additives for Surface Tension Reduction	132
7.11.3 Permeation	134
7.11.4 Surface Properties of Irradiated PTFE	134
7.12 Fluoropolymer Additives to Inhibit Melt Dripping in Fire Situations	134
7.12.1 Characterization of Fire Retardancy	135
7.12.2 Processes for Mixing High-MW PTFE into Other Resins	137
7.12.3 Commercial PTFE Products for Fire Retardants	138
7.13 Compounding of Fluorinated Additives into Thermoplastics	138
7.13.1 Compounding with High-MW PTFE (Dispersion-Polymerization)	138
7.13.2 Compounding with Low-MW PTFE (and High-MW Suspension-Polymerized PTFE)	140
7.13.3 Extrusion Compounding with PTFE Powders	141
7.13.4 Other Fluorinated Additives	142
References	143
8 Addition of Fluoropolymers to Printing Ink	149
8.1 Introduction	149
8.2 Printing Processes	149
8.3 Inks	151
8.4 Fluoropolymer Addition to Ink	151
8.4.1 Types of PTFE	152
8.4.2 Particle Size	152
8.5 Abrasion/Rub Resistance of Prints	153
8.6 Blocking	154
8.7 Commercial Suppliers of Fluorinated Additives to the Ink Market	154
References	155
9 Use of Fluorinated Additives in Coatings	157
9.1 Introduction	157
9.2 Purposes of Addition of Fluoropolymer Additives to Coatings	157
9.3 Thermoplastic Coatings	159

9.4 Thermosetting Coating Parameters.....	159
9.4.1 Carriers.....	159
9.4.2 Resin Binder or Chemistry	160
9.4.3 Crosslinking or Curing.....	161
9.5 Coating Processes.....	162
9.5.1 Preparing the Coating Formulation	162
9.5.2 Application of Coating	162
9.5.3 Drying/Baking of Coating	162
9.6 Fluoropolymer Types Used in Coatings.....	162
9.6.1 Perfluorinated Semi-Crystalline Resins.....	162
9.6.2 Partially Fluorinated Semi-Crystalline Resins	166
9.6.3 Amorphous Fluoropolymers	167
9.7 Perfluoropolymer/Metal Coatings by Electrolytic or Electroless Processes.....	168
9.8 Prevention of Staining of a Coating	168
9.9 Commercial Fluoroaddivitive Products	170
References.....	171
10 Fluorinated Additives for Rubber.....	175
10.1 Introduction	175
10.2 Rubber Compositions and Compounding.....	175
10.3 Characterization of Rubbers	177
10.4 Fluorinated Additive Types.....	179
10.4.1 High-MW PTFE (Unmodified).....	179
10.4.2 Modified High-MW PTFE.....	180
10.4.3 Melt-Processable Fluorinated Copolymers	181
10.4.4 Low-MW PTFE Additives.....	182
10.4.5 Miscellaneous Fluorinated Additives	184
10.5 Silicone and Fluorosilicone Rubbers.....	184
10.6 Addition of Fluorinated Additives to Fluoroelastomers	185
10.7 Addition of Fluorinated Additives to EPDM Rubber	186
10.8 Commercial Fluoroaddivitive Products for Elastomers	189
References.....	189
11 Applications of Processing Aid Additives.....	193
11.1 Introduction	193
11.2 Low-Molecular-Weight Processing Aids.....	193
11.2.1 Stearates (Release Agents)	193
11.2.2 Polymer Processing Additives (High MW).....	194
11.2.3 Advantages of PPAs.....	194
11.2.4 Melt Fracture.....	194
11.2.5 Die Drool	195

11.3	Important Applications of PPAs	195
11.3.1	Blown and Cast Film	195
11.3.2	Cable and Tubing Extrusion	195
11.3.3	Blow Molding	196
11.3.4	Fiber Extrusion.....	196
11.3.5	Fluoropolymer PPAs	196
11.3.6	How PPAs Work	196
11.4	Select Applications of PPAs	198
11.4.1	Blow Molding	198
11.4.2	Film Manufacturing	201
	References.....	208

PART 4 Compliance and Economics 211

12	Compliance with Regulations and Standards	213
12.1	Introduction	213
12.2	Food Contact and Medical Applications	213
12.3	FDA Requirements for Polytetrafluoroethylene Resins for Food Contact	213
12.3.1	Paragraph (d) Specifications	213
12.3.2	Paragraph (e) Limitations	213
12.3.3	Scope of ASTM D 4754-98 (2003).....	214
12.3.4	Special Requirements of Polytetrafluoroethylene Micropowders.....	214
12.4	Compliance of Commercial Micropowder Products.....	214
12.4.1	Articles Intended to Contact Food (Reference: 21 CFR 177.1550 Perfluorocarbon Resins).....	215
12.4.2	Processing Aids for Polyolefins (Reference: 21 CFR 177.1520 Olefin Polymers).....	215
12.4.3	Components of Resinous and Polymeric Coatings (Reference: 21 CFR 175.300 Resinous and Polymeric Coatings).....	215
12.4.4	Components of Paper and Paperboard (Reference: 21 CFR 176.170 Components of Paper and Paperboard in Contact with Aqueous and Fatty Foods).....	215
12.4.5	Lubricant for Rubber Articles (Reference: 21 CFR 177.2600 Rubber Articles Intended for Repeated Use).....	216
12.4.6	Components of Adhesives (Reference: 21 CFR 175.105 Adhesives)	216
12.4.7	Housewares Exemption (Reference: Food Drug Cosmetic Law Journal, Vol. 42, No. 1, January 1987, p. 45)	216
12.5	Standards	217
	References	217

13 Safety, Health, Environment, Disposal, Recycling, and Economics 219

13.1	Introduction	219
13.2	Toxicology of Fluoropolymers	219
13.3	Thermal Properties of PTFE.....	219
13.4	Emission During Processing.....	220

13.5 Safety Measures	220
13.5.1 Ventilation of Degradation Products	221
13.5.2 Processing and Fabrication	222
13.5.3 Spillage Cleanup	224
13.5.4 Equipment Cleaning and Maintenance.....	224
13.5.5 Protective Clothing	224
13.5.6 Personal Hygiene	224
13.5.7 Fire Hazard.....	224
13.5.8 Material Incompatibility	224
13.6 Fluoropolymer Scrap and Recycling	225
13.7 Environmental Protection and Disposal Methods	225
13.7.1 Packaging Disposal and Recycling	225
13.8 Economics	226
References	226
Appendix 1: Food and Drug Administration	229
Appendix 2: Polytetrafluoroethylene (PTFE)	233
Index	287

PART 1

Introduction

1.1 Introduction

Aside from a short description of additives, this chapter is devoted to describing fluorine properties and preparation, inorganic and organic fluorine chemistry, biologically active compounds, and the natural occurrence of fluorine. Specifically speaking, organic fluorine chemistry provides a useful background for fluorinated additives, particularly fluoropolymer additives. Some readers may rightfully feel that the author has gone overboard in discussing fluorine and its chemistry. Yet, this introductory chapter is not a prerequisite for understanding the rest of this book. Each chapter can be studied independently of others.

A typical dictionary defines an *additive* as “a substance added in small amounts to something else to improve, strengthen, or otherwise alter it”. There are vast numbers of additives incorporated in materials to enhance and modify their performances or characteristics and render them more useful. Table 1.1 shows a lengthy, though probably incomplete, list of additive types. Generally, the modifying effect of additives is either chemical or physical. For example, adding a few parts of a laser marking additive, such as titanium dioxide, to a plastic, catalyzes the incident laser beam, and the plastic substrate is carbonized according to a printed pattern. A matting additive, such as silica powder, when added to a plastic film, can drastically decrease its gloss. Laser marking additives has a chemical impact whilst silica acts physically.

The presence of fluorine in any compound sets it apart from all others. F_2 is not only the most reactive halogen, but also, arguably, the most reactive element on the periodic table, combining with all other elements, except the lighter noble gases, He, Ne, and Ar [1]. Fluorine is unique because of its electronic structure and for being the most electronegative of all elements. Indeed, there is a healthy range of research and development activities aimed at the development of new fluorine compounds. The singular nature of the fluorine atom, combined with the unique physical and chemical properties that the fluorine substituent

imparts to compounds that contain it, is responsible for the importance of the field and for its constant “reinvention”. Thus, in spite of the immense contributions of fluorine chemistry to various technologies of the last century, the current period, i.e., the beginning of the 21st century, can authentically be considered a “renaissance” period for the field of fluorine chemistry, where renaissance, in particular, is defined as “a period characterized by vigorous activity along literary, artistic, or other lines” [2].

After reading this chapter, the reader should be equipped with a working knowledge of fluorine compounds, including fluoropolymers, disregarding all prior knowledge of the subject. Even though the scope of the coverage of fluorinated materials has been limited to fluoropolymers in this book, every fluorinated compound is potentially an additive. The nature of possible applications may be unknown at present but the potential use exists.

1.2 Uniqueness of Fluorine

What sets fluorine apart from other halogens? Technically speaking, the term “halogen” provides little descriptive value in scientific and technological discussions. The common characteristic of halogens is that they all have seven electrons in the outer shell of their atomic structure. They all have a valence of -1 in their reactions with hydrogen and metals. The reactivity of halogens decreases from the top (fluorine) to the bottom of the column. The *McGraw-Hill Encyclopedia of Chemistry* [3] describes the differences among halogens: “Although halogens generally undergo the same types of reactions, the extent and ease with which these reactions occur vary markedly. Fluorine in particular has the usual tendency of the lightest member of a family of elements to exhibit reactions not comparable to the other members.”

Fluorine forms an extremely strong bond with other elements, such as carbon, because it is the most electronegative of all elements. The carbon–fluorine

Table 1.1 List of Additive Types

Acid scavenger
Adhesion promoter
Antifoaming agent (foam suppressant)
Antifogging agent
Antioxidant
Antiozonant
Antislip agent
Antistatic agent
Antitack (antiblock) agent
Biocide/antibacterial agent
Blowing/foaming agent
BOPP film modifier
Carbon black
Chain extender
Chelating agent/complexing agent
Clarifying agent
Cling agent
Coupling agent/compatibilizer
Crosslinking catalyst/accelerator/initiator
Crosslinking or curing agent/hardener
Defoamer
Deodorant
Desiccant
Dispersing agent
Emulsifier
Fibers (extender reinforcer)
Filler/fiber conductive
Fillers (reinforcer/extender)
Flame retardant/smoke suppressant
Flatting (gloss control) agent
Flexibilizer
Fluorescent whitening agent
Fragrance
Fresh keeping agent

Continued

Table 1.1 List of Additive Types—cont'd

Gel inhibitor
Heat stabilizer
Hydrophilic agent
Impact modifier
Infrared filter
Inhibitor
Laser marking additive
Leveling agent
Light stabilizer/UV absorber
Lubricants & waxes
Matting/gloss agent
Melt strength enhancer
Metal deactivator
Nucleating agent
Organic pigment
Oxygen absorber
Peptizer
Photoinitiator
Photoselective agent (agriculture)
Plasticizer
Polymerization inhibitor
Polymerization initiator
Processing aid
Release agent
Slip agent
Solvent
Styrene suppressant
Tackifier
Thickening agent
Thixotropic agent
Titanium dioxide
Viscosity modifier
Vulcanizing agent
Wetting agent

bond (C—F) is the fundamental reason that polytetrafluoroethylene is one of the most stable and inert plastics known to man. Yet, tetrafluoroethylene is highly explosive, adding to the diversity of the fluorine effect. A key point is made in the *McGraw-Hill Encyclopedia of Chemistry* about the stability of halogenated compounds: “Organic halogen compounds generally show progressively increased stability in the order iodine, bromine, chlorine and fluorine.”

It is clear that fluorine is a special element beyond all others. It is relatively easy to substitute fluorine for hydrogen (and other elements) in organic compounds because of its extreme affinity for grabbing electrons. Substituting fluorine for hydrogen in a chemical compound gives rise to a variety of unique and useful effects. Examples include increased polarity, decreased polarity, chemical activity, chemical neutrality, increased biological activity for pharmaceuticals and agrochemicals, greater thermal and oxidative stability, and increased chemical resistance.

An interesting example is fluorination of polyolefin film surface. Slight fluorination renders the neutral surface of a polyolefin film polar. Further increases in the fluorine content of the surface result in total neutrality of the film surface. In practice, slight fluorination of polyolefin surfaces is used to make them adherable. The inside surface of plastic pesticide and herbicide bottles is fluorinated extensively to prevent permeation of agents, which could result in loss of material and unsafe conditions. Sometimes, fluorine is mixed with the blow molding gas in order to combine the bottle fabrication and fluorination steps.

A number of partially and fully fluorinated polymers have been developed because of the unique effect of fluorine on their properties. Some of the common polymer chemistries include polyolefins, fluorinated elastomers, polymethyl siloxane, acrylic and methacrylic polymers, and perfluorether polymers. The impact of *increasing* the fluorine content of olefinic polymers on their properties is listed in Table 1.2.

One can simply conclude that fluorinated compounds have varied and unusual properties, a number of which are quite useful to the development of commercial materials for a broad range of applications, including plastics, electronics, agriculture, pharmaceuticals, and medicine.

Table 1.2 Effect of Increase in Fluorine Content of Polymers

Property	Impact
Chemical resistance	Increases
Melting point	Increases
Coefficient of friction	Decreases
Thermal stability	Increases
Dielectric constant	Decreases
Dissipation factor	Decreases
Volume and surface resistivity	Increase
Mechanical properties	Decrease
Flame resistance	Increases
Resistance to weathering	Increases

1.3 Fluorine Characteristics

Fluorine ranks 13th in abundance among the Earth's rocks, present at an average concentration of 0.1% by weight [4]. Fluorine abundance is 0.08%, compared to 0.05% in the Earth's lithosphere [5]. Fluorine is considered the most dominant halogen when the whole Earth is considered.

The most abundant natural sources of fluorine are fluorspar (CaF_2) and cryolith (also called cryolite (Na_3AlF_6)). The enamel of teeth is very hard, and mechanically strong, and has long-term durability, mainly because of fluoroapatite ($\text{Ca}_5(\text{PO}_4)_3\text{F}$ or $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2$) and hydroxyapatite being its major components. Fluoride is considered a trace element because only small amounts are present in the body (about 2.6 g in adults), and because the daily requirement for maintaining dental health is only a few milligrams a day. About 95% of the total body fluoride is found in bones and teeth. Fluoride's primary function in the human body is to strengthen the bones and it is known to prevent tooth decay. Experts contend that fluoride strengthens the teeth's enamel by strengthening the mineral composition of the teeth themselves [6,7].

About 40% of fluorspar [4] is used as metallurgical flux in the steel industry, some of which is recovered as synthetic fluorspar. The highest grade of fluorspar (>97% CaF_2) is reacted with sulfuric acid for the production of HF, which is the starting point of organic fluorinated compounds. Some fluorspar is consumed in uranium processing, petroleum alkylation, and stainless steel pickling [8].

Fluorine is a gas with a green–yellow color, a boiling point of $-188.1\text{ }^{\circ}\text{C}$, and a melting point of $-219.6\text{ }^{\circ}\text{C}$ [9]. Its pungent odor is perceptible at a concentration of 10 parts per million. Fluorine is highly toxic, corrosive, and oxidizes nearly every element, including noble gases xenon and krypton. In contrast to HF, dry fluorine does not etch glassware but reacts with hot platinum and gold. To reduce its reactivity and hazard, fluorine is diluted with nitrogen; a 10% F_2 in nitrogen can be stored and transported in passivated steel bottles.

Some basic facts about fluorine are given in Table 1.3.

1.3.1 Fluorination

For introducing fluorine atoms into particular target molecules, researchers are now well served by a variety of commercially available, easy-to-use, fluorinating agents. SelectfluorTM, developed at the University of Manchester Institute of Science and Technology (UMIST) and manufactured by Air Products in the US [10], is perhaps the best-known electrophilic fluorinating agent. Pharmaceutical researchers routinely use the reagent, for example, when fluorinating steroids. Diethylaminosulfur

trifluoride (DAST) transforms hydroxyl and carbonyl groups into CF and CF_2 moieties, while triethylamine tris-hydrofluoride provides a pH neutral, non-volatile equivalent of hydrogen fluoride and is a source of fluoride ions for various nucleophilic reactions. In addition, trifluoromethyltrimethylsilane, CF_3SiMe_3 , is a useful CF_3 source that reacts with carbonyl systems to give trifluoromethylated alcohol derivatives.

The search for effective and improved fluorinating and perfluoroalkylating reagents is ongoing. At the University of York, the Green Chemistry Group [11] have developed efficient one-pot syntheses of fluorine-containing aromatic systems. Moreover, converting chlorofluorocarbons (CFCs) to useful products is now the focus of much industrial attention.

1.3.2 Reactivity – An Extreme Element

As has often been stated, fluorine is truly a material of extremes [12]. Fluorine is the most reactive element known to man. It reacts with nearly everything, including glass. Noble gases such as xenon, and krypton, and gold and platinum are no exceptions; all react with fluorine. Moissan [13] has been credited with the first synthesis of fluorine. Here is an experiment that he conducted to illustrate the extreme reactivity of fluorine.

Oil of turpentine, in the solid state, is attacked by liquid fluorine. To perform this experiment, a little oil of turpentine was placed at the bottom of a glass tube surrounded by boiling liquid air. As soon as a small quantity of fluorine was liquefied on the surface of the solid, combination took place with explosive force. After each explosion, the current of fluorine gas was kept up slowly, a fresh quantity of liquid fluorine was formed, and the detonations succeeded each other at intervals of 6–7 min. Finally, after a longer interval of about 9 min, the quantity of fluorine formed was sufficient to cause, at the moment of reaction, the complete destruction of the apparatus. In several of these experiments, a little liquid fluorine accidentally fell on the floor; the wood instantly caught fire.

1.3.3 Preparation of Fluorine

Interest in fluorine is literally centuries old, even though its successful preparation is relatively recent. A number of unsuccessful efforts to prepare fluorine were made in the past. In 1529, Georgius Agricola described the use of fluorspar (CaF_2) as a flux. In 1670,

Table 1.3 Basic facts about fluorine

Natural abundance
Earth's crust: 950 ppm
Important minerals: Fluorspar CaF_2 ; Apatite $\text{Ca}_5(\text{PO}_4)_3\text{F}$; Cryolite Na_3AlF_6 (Cl 130 ppm)
Ocean: 1.3 ppm (Cl 18,000 ppm)
Essential element: 0.3–0.5 mg/day for humans; a human body (70 kg) contains 2.6 g fluorine
Bond distance to C: $\text{CH}_3\text{—F}$ 1.39 Å ($\text{CH}_3\text{—Cl}$ 1.77 Å)
Bond dissociation energy from C: $\text{CH}_3\text{—F}$ 116 kcal/mol ($\text{CH}_3\text{—Cl}$ 81 kcal/mol)
Fluorine forms the strongest single bond to carbon (and other elements)
Hammett σ parameters
F: σ_p 0.06; σ_m 0.34
CF_3 : σ_p 0.54; σ_m 0.43
SO_2CF_3 : σ_p 0.96; σ_m 0.83
^{18}F : $T_{1/2} = 109.8\text{ min}$; $\beta^+ = 1.655\text{ MeV}$
Application in positron emission tomography (PET)