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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.

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Introduction

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

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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 ($Ca_5(PO_4)_3F$ or $3Ca_3(PO_4)_2.CaF_2$) 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 °C, and a melting point of −219.6 °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. Selectfluor™, 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.

Table 1.3 Basic facts about fluorine

Natural abundance
Earth's crust: 950 ppm
Important minerals: Fluorspar CaF_2; Apatite $Ca_5(PO_4)_3F$; 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: CH_3–F 1.39 Å (CH_3–Cl 1.77 Å)
Bond dissociation energy from C: CH_3–F 116 kcal/mol (CH_3–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: $T_{1/2} = 109.8$ min; $\beta^+ = 1.655$ MeV
Application in positron emission tomography (PET)

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,