NON-HALOGENATED FLAME RETARDANT HANDBOOK

Edited by
Alexander B. Morgan and Charles A. Wilkie

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Contents

Preface xv
List of Contributors xvii

1 The History and Future Trends of Non-halogenated Flame Retarded Polymers 1
   James W. Mitchell
   1.1 Introduction 2
      1.1.1 Why Non-Halogenated Flame Retardants? 2
   1.2 Key Flame Retardancy Safety Requirements 6
   1.3 Geographical Trends 8
   1.4 Applications for Non-halogenated FRP’s 11
   References 14

2 Phosphorus-based FRs 17
   Sergei Levchik
   2.1 Introduction 17
   2.2 Main Classes of Phosphorus-based FRs 18
   2.3 Polyolefins 20
   2.4 Polycarbonate and Its Blends 27
   2.5 Polyphenylene Ether Blends 32
   2.6 Polyesters and Polyamides 34
   2.7 Thermoplastic Elastomers (TPE) and Thermoplastic Polyurethanes (TPU) 38
   2.8 Epoxy Resins 39
   2.9 Unsaturated Polyesters 43
   2.10 PU Foams 45
   2.11 Textiles 50
   2.12 Conclusions and Further Trends 55
   References 56
3 Mineral Filler Flame Retardants

Reiner Sauerwein

3.1 Introduction 75

3.2 Industrial Importance of Mineral Flame Retardants 76

3.2.1 Market Share of Mineral FRs 77

3.2.2 Synthetic Mineral FRs Within the Industrial Chemical Process Chain 78

3.2.3 Natural Mineral FRs 80

3.3 Overview of Mineral Filler FRs 81

3.3.1 Mineral Filler Flame Retardants by Chemistry 81

3.3.2 Classification by Production Process 82

3.3.2.1 Crushing and Grinding 82

3.3.2.2 Air Classification 84

3.3.2.3 Precipitation and Their Synthetic Processes 84

3.3.2.4 Surface Treatment 87

3.3.3 Physical Characterisation of Mineral FRs 89

3.3.3.1 Particle Shape/Morphology/Aspect Ratio 89

3.3.3.2 Particle Size Distribution 90

3.3.3.3 Sieve Residue 91

3.3.3.4 BET Surface Area 92

3.3.3.5 Oil Absorption 92

3.3.3.6 pH-value/Specific Conductivity 93

3.3.3.7 Bulk Density and Powder Flowability 94

3.3.3.8 Thermal Stability/Loss on Ignition/Endothermic Heat 94

3.3.4 General Impact of Mineral FRs on Polymer Material Properties 96

3.3.4.1 Optical Properties 96

3.3.4.2 Mechanical Properties 97

3.3.4.3 Water Uptake and Chemical Resistance 97

3.3.4.4 Thermal Properties 100

3.3.4.5 Electrical Properties 100

3.3.4.6 Rheological Properties 101

3.4 Working Principle of Hydrated Mineral Flame Retardants 101

3.4.1 Filler Loading, Flammability and Flame Propagation 103

3.4.2 Smoke Suppression 105

3.4.3 Heat Release 107
3.5 Thermoplastic and Elastomeric Applications 109
  3.5.1 Compounding Technology 109
  3.5.2 Compound Formulation Principals 111
  3.5.3 Wire & Cable 113
  3.5.4 Other Construction Products 121
  3.5.5 Special Applications 123
  3.5.6 Engineering Plastics for E&E Applications 125
3.6 Reactive Resins/Thermoset Applications 127
  3.6.1 Production Processes for Glass Fibre Reinforced Polymer Composite 129
     3.6.1.1 Paste Production 129
     3.6.1.2 Hand Lamination/Hand-lay-up 130
     3.6.1.3 SMC and BMC 130
     3.6.1.4 Pultrusion 131
     3.6.1.5 RTM/RIM 131
  3.6.2 Formulation Principles 132
  3.6.3 Public Transport Applications of GFRP 133
  3.6.4 E & E Applications 134
  3.6.5 Construction and Industrial Applications 136
3.7 Summary, Trends and Challenges 137
References 138

4 Nitrogen-based Flame Retardants 143
  Martin Klatt
  4.1 Introduction 143
  4.2 Main Types of Nitrogen-based Flame Retardants 144
  4.3 Ammonia-based Flame Retardants 144
     4.3.1 Ammonium Polyphosphate 145
     4.3.2 Other Ammonia Salts (Pentaborate, Sulfamate) 148
  4.4 Melamine-based Flame Retardants 149
     4.4.1 Melamine as Flame Retardant 150
     4.4.2 Melamine Salts 152
     4.4.3 Melamine Cyanurate 152
     4.4.4 Melamine Polyphosphate 155
     4.4.5 Melamine Condensates and Its Salts 157
  4.5 Nitrogen-based Radical Generators 159
  4.6 Phosphazenes, Phospham and Phosphoroxynitride 162
  4.7 Cyanuric Acid-based Flame Retardants 164
  4.8 Summary and Conclusion 165
References 165
5 Silicon Based Flame Retardants

*Mert Kilinc*

5.1 Introduction 169
5.2 Basics of Silicon Chemistry 170
5.3 Industrial Applications of Silicones 172
5.4 Silicones as Flame Retardant Materials 175
  5.4.1 Inorganic Silicon Based Flame Retardants 176
    5.4.1.1 Silicon Dioxide (SiO₂) (Silica) 176
    5.4.1.2 Wollastonite 178
    5.4.1.3 Magadiite 179
    5.4.1.4 Sepiolite 179
    5.4.1.5 Kaolin 179
    5.4.1.6 Mica 180
    5.4.1.7 Talc 180
    5.4.1.8 Halloysite 181
    5.4.1.9 Layered Silicate Nanocomposites 182
    5.4.1.10 Silsesquioxane 185
  5.4.2 Organic Silicone-based Flame Retardants 186
    5.4.2.1 Polyorganosiloxanes 186
    5.4.2.2 Silanes 188
  5.4.3 Other Silicone-based Flame Retardants 189
5.5 Mode of Actions of Silicone-based Flame Retardants 190
  5.5.1 Silicon Dioxide 190
  5.5.2 Silicate-based Minerals 190
  5.5.3 Silicones 191
5.6 Toxicology and Environmental Effects of Silicones 191
5.7 Future Trends in Silicone-based Flame Retardants 194
5.8 Summary 195
References 196

6 Boron-based Flame Retardants in Non-Halogen-based Polymers

*Kelvin K. Shen*

6.1 Introduction 201
6.2 Major Functions of Borates in Flame Retardancy 202
6.3 Major Commercial Boron-based Flame Retardants and Their Applications 202
  6.3.1 Boric Acid [B₂O₃·3H₂O/B(OH)₃] and Boric Oxide (B₂O₃) 205
    6.3.1.1 Plastics/Coatings 205
    6.3.1.2 Cellulose/Cotton/Wood 206
6.3.2 Alkali Metal Borates 209
6.3.2.1 Borax Decahydrate (Na$_2$O$\cdot$2B$_2$O$_3$$\cdot$10H$_2$O) and Borax Pentahydrate (Na$_2$O$\cdot$2B$_2$O$_3$$\cdot$5H$_2$O) 209
6.3.2.2 Anhydrous Borax (Na$_2$O$\cdot$2B$_2$O$_3$) 211
6.3.2.3 Disodium Octaborate Tetraborate (Na$_2$O$\cdot$4B$_2$O$_3$$\cdot$4H$_2$O) 211
6.3.3 Alkaline Earth Metal Borates 211
6.3.3.1 Calcium Borate (xCaO$\cdot$yB$_2$O$_3$$\cdot$zH$_2$O) 211
6.3.3.2 Magnesium Borate (xMgO$\cdot$yB$_2$O$_3$$\cdot$zH$_2$O) 212
6.3.4 Transition Metal Borates and Miscellaneous Metal Borates 212
6.3.4.1 Zinc Borates (xZnO$\cdot$yB$_2$O$_3$$\cdot$zH$_2$O) 212
6.3.4.2 Miscellaneous Metal Borates 224
6.3.5 Nitrogen-containing Borates 224
6.3.5.1 Melamine Diborate [(C$_3$H$_8$N$_6$)O$\cdot$B$_2$O$_3$$\cdot$2H$_2$O]/(C$_3$H$_6$N$_6$$\cdot$2H$_3$BO$_3$) 224
6.3.5.2 Ammonium Pentaborate [(NH$_4$)$_2$O$\cdot$5B$_2$O$_3$$\cdot$8H$_2$O)] 225
6.3.5.3 Guanidinium Borate [x[C(NH$_2$)$_3$]$\cdot$O$\cdot$yB$_2$O$_3$$\cdot$zH$_2$O] 226
6.3.5.4 Boron Nitride (BN) 226
6.3.6 Phosphorus-containing Borates 227
6.3.6.1 Boron Phosphate (BPO$_4$) 227
6.3.6.2 Metal Borophosphate 228
6.3.7 Silicon-containing Borates 228
6.3.7.1 Borosilicate, Borosilicate Glass and Frits 228
6.3.7.2 Borosiloxane 229
6.3.8 Carbon-containing Borates 231
6.3.8.1 Boric Acid Esters [B(OR)$_3$] 231
6.3.8.2 Boric Acid Ester Salts [M$^+$ B(OR)$_4$] 231
6.3.8.3 Boronic Acid [ArB(OH)$_2$] 231
6.3.8.4 Boron Carbide (B$_4$C) 233
6.4 Mode of Actions of Boron-based Flame Retardants 233
6.5 Conclusions 234
References 235
7 Polymer Nanocomposites: A nearly Universal FR Synergist

Guenter Beyer and Tie Lan

7.1 Introduction 243

7.2 Inorganic Materials as Candidate for Nanocomposite Formation 244

7.2.1 Carbon Nanotubes (CNT) 244
7.2.2 Tubular Nanoclay-halloysite 246
7.2.3 Graphene (Nano-graphite) 246
7.2.4 Layered Double Hydroxides (LDH) 247
7.2.5 Bentonite Clays or Organoclay 249
7.2.6 3D Nano-Oxide 250
7.2.7 Formation of Polymer Nanocomposite 251
7.2.8 Characterization of Nanocomposite 251

7.3 Nanocomposites as Non-Halogenated Flame Retardation Solutions 252

7.3.1 Polymer Clay Nanocomposites 252
7.3.2 Nanocomposite Structure: Exfoliated or Intercalated 254
7.3.3 FR Mechanism Study: EVA-Clay Nanocomposites 255

7.3.3.1 Structure of EVA-Clay Nanocomposites 256
7.3.3.2 Thermal Stability of EVA/Organoclay-based Nanocomposites 257
7.3.3.3 Flammability Properties of EVA/Organoclay-based Nanocomposites 259
7.3.3.4 NMR Investigation and FR Mechanism of EVA Nanocomposites 262

7.3.4 FR Benefits of TPU-Clay Nanocomposites 264
7.3.5 Fire Retardant Benefits from CNT Nanocomposites 266
7.3.6 Flame Retardation from Nanocomposite Containing Tubular Nanoclay Halloysite 268

7.4 Combinations of Nanocomposite with Traditional Flame Retardants 271

7.4.1 Organoclay in LSOH Wire and Cable Compounds 271
7.4.2 Halloysite in LSOH in Wire and Cable Compound 278
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.4.3</td>
<td>Organoclay in TPU/Phosphate Ester FR Compound</td>
<td>279</td>
</tr>
<tr>
<td>7.4.4</td>
<td>Organoclay in PP/Ammonium Polyphosphate FR Compounds</td>
<td>281</td>
</tr>
<tr>
<td>7.5</td>
<td>Contribution of Nanocomposites to Achieve New FR Cable Standard (EU CPR)</td>
<td>282</td>
</tr>
<tr>
<td>7.6</td>
<td>New Developments and Outlook</td>
<td>286</td>
</tr>
<tr>
<td></td>
<td>References</td>
<td>289</td>
</tr>
<tr>
<td>8</td>
<td>Intumescent Systems</td>
<td>293</td>
</tr>
<tr>
<td>S. Duquesne and T. Futterer</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.1</td>
<td>Introduction</td>
<td>293</td>
</tr>
<tr>
<td>8.2</td>
<td>The basics of Intumescence</td>
<td>294</td>
</tr>
<tr>
<td>8.3</td>
<td>Intumescent Products and Formulations Used in Thermoplastic and Thermoset Materials</td>
<td>300</td>
</tr>
<tr>
<td>8.3.1</td>
<td>Systems-based on Ammonium Phosphate Salts</td>
<td>300</td>
</tr>
<tr>
<td>8.3.2</td>
<td>Systems-based on Melamine Phosphate Salts</td>
<td>308</td>
</tr>
<tr>
<td>8.3.3</td>
<td>Other Phosphorus-based Formulations</td>
<td>312</td>
</tr>
<tr>
<td>8.3.4</td>
<td>Expandable Graphite</td>
<td>314</td>
</tr>
<tr>
<td>8.3.5</td>
<td>Other Non-phosphorus-based Systems</td>
<td>318</td>
</tr>
<tr>
<td>8.4</td>
<td>Intumescent Systems in Fire Protection</td>
<td>321</td>
</tr>
<tr>
<td>8.4.1</td>
<td>Fire Protection of Steel Structures</td>
<td>321</td>
</tr>
<tr>
<td>8.4.2</td>
<td>Fire Protection of Polymers and Composites via Intumescent Coatings</td>
<td>328</td>
</tr>
<tr>
<td>8.5</td>
<td>Trends and Challenges in Intumescent Systems</td>
<td>329</td>
</tr>
<tr>
<td>8.6</td>
<td>Conclusions</td>
<td>332</td>
</tr>
<tr>
<td></td>
<td>References</td>
<td>333</td>
</tr>
<tr>
<td>9</td>
<td>Other Non-Halogenated Flame Retardant Chemistries and Future Flame Retardant Solutions</td>
<td>347</td>
</tr>
<tr>
<td>Alexander B. Morgan, Paul A. Cusack and Charles A. Wilkie</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9.1</td>
<td>The Periodic Table of Flame Retardants</td>
<td>347</td>
</tr>
<tr>
<td>9.2</td>
<td>Transition Metal Flame Retardants</td>
<td>350</td>
</tr>
<tr>
<td>9.2.1</td>
<td>Vapor Phase Transition Metal Flame Retardants</td>
<td>350</td>
</tr>
<tr>
<td>9.2.2</td>
<td>Condensed Phase Transition Metal Flame Retardants</td>
<td>351</td>
</tr>
<tr>
<td>9.2.2.1</td>
<td>Metal Oxides</td>
<td>352</td>
</tr>
<tr>
<td>9.2.2.2</td>
<td>Metal Complexes</td>
<td>353</td>
</tr>
</tbody>
</table>
9.3 Sulfur-based Flame Retardants 355
9.4 Carbon-based Flame Retardants 356
  9.4.1 Cross-linking compounds – Alkynes, Deoxybenzoin, Friedel-Crafts, Nitriles, Anhydrides 357
    9.4.1.1 Alkynes 357
    9.4.1.2 Deoxybenzoin 359
    9.4.1.3 Friedel-Crafts 359
    9.4.1.4 Nitriles 360
    9.4.1.5 Anhydrides 361
  9.4.2 Organic Carbonates 361
  9.4.3 Graft Copolymerization 363
  9.4.4 Bio-based Materials 364
9.5 Tin-based Flame Retardants 364
  9.5.1 Introduction 364
  9.5.2 Zinc Stannates 365
  9.5.3 Halogen-free Applications 367
    9.5.3.1 Polyolefins 367
    9.5.3.2 Styrenics 368
    9.5.3.3 Engineering Plastics 368
    9.5.3.4 Thermosetting Resins 371
    9.5.3.5 Elastomers 371
    9.5.3.6 Paints and Coatings 371
    9.5.3.7 Textiles 373
  9.5.4 Novel Tin Additives 373
    9.5.4.1 Coated Fillers 374
    9.5.4.2 Tin-modified Nanoclays 377
  9.5.5 Mechanism of Action 378
  9.5.6 Summary 379
9.6 Engineering Non-Hal FR Solutions 380
  9.6.1 Barrier Fabrics 380
  9.6.2 Coatings 381
    9.6.2.1 Inorganic Coatings 382
    9.6.2.2 IR Reflective Coatings 382
    9.6.2.3 Nanoparticle Coatings 383
    9.6.2.4 Layer-by-Layer (LbL) Coatings 383
9.7 Future Directions 385
  9.7.1 Polymeric Flame Retardants and Reactive Flame Retardants 386
  9.7.2 Flame Retardants with Recycling/Sustainability Design 388
    9.7.2.1 Derivation from Sustainable and Alternative Chemical Feedstocks 390
Contents

9.7.2.2 Flame Retardant Durability for Recycling 390
9.7.2.3 Waste-To-Energy/Waste-To-Chemical Processes and Flame Retardants 391
9.7.2.4 Environmental Decomposition and Flame Retardants 392
9.7.3 Experimental Methodology for Flame Retardant Screening 393
Acknowledgements 395
References 395

Index 405
Preface

Over the past 20-30 years, there has been a major change in flame retardant material science as certain chemical additives have been under intense scrutiny for persistence, bioaccumulation, and toxicity (PBT) issues. The class of flame retardants that has taken the brunt of the scrutiny is the oldest and most commonly used modern flame retardants, those based upon halogen (chlorine or bromine). As such, brominated and chlorinated flame retardants have either been banned from use or voluntarily de-selected by end-users as the market and regulations have pushed them out of use. The fire threat has not gone away however as those halogen based flame retardants were deselected, and so flame retardants without halogen content, or broadly named non-halogenated flame retardants, have surged into use and demand. Unlike halogenated flame retardants, which can be widely used in several applications and polymers (but not universally) due to their vapor phase flame retardant mechanism, non-halogenated flame retardants tend to be more restricted to specific polymers and specific fire risk scenarios. Therefore, among material scientists, there has been a clear need for non-halogenated flame retardant understanding in how to use them and in which polymers those flame retardants would be useful. This handbook, one of the first to focus solely on non-halogenated retardants, is a reflection of that market and scientific community need.

The book you are holding is broken down into an introduction on why non-halogenated solutions are needed, several chapters on the specific classes of non-halogenated flame retardants available, and then a conclusion on the unmet needs and future of non-halogenated flame retardants. Industrial experts on the practical use of non-halogenated flame retardants were solicited to write chapters and have done so, along with inputs from key scientific researchers in some chapters. The book is called “handbook” for a reason; it is meant to be a practical distillation of knowledge to capture the scientific literature and comfortable enough to get started on the use of non-halogenated flame retardants, and serve as a quick reference point for when more complex solutions or research, development, testing,
and evaluation (RDT&E) are required. Based upon our many combined decades of flame retardant science and knowledge, we believe this handbook will help the reader understand and utilize non-halogenated flame retardants, and educate them on what is known and still unknown about this wide range of materials. We hope that you will find the book to be of great utility now and in the future.

As with all prefaces, we would like to thank those who helped make this book possible, especially the authors of the individual chapters who have taken time out of their busy lives to write the chapters. We also wish to thank Scrivener for their publishing support. Finally, we would like to thank our wives, Julie Ann Morgan and Nancy Wilkie for their continued support.

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January 27, 2014. Dayton, Ohio USA

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Professor Sophie Duquesne of the University of Lille researches in the development of new FR formulations for polymeric materials (process and characterization), in particular intumescent systems and nanocomposites and the recycling of polymeric wastes.

Dr. Thomas Futterer has many years’ experience in the development and marketing of flame retardants in polymer and coatings applications. His current position is at Chemische Fabrik Budenheim as Head of Business Development.

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The History and Future Trends of Non-halogenated Flame Retarded Polymers

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Abstract
Non-halogenated flame retardants have emerged as the dominant additive system used in engineering plastics. This is mainly due to new environmental regulations but also due to their ability to meet the end customer requirements without compromising safety. Key fire tests like the UL94 and the glow wire can be passed to the highest safety levels using these additives. Further, unlike traditional halogenated systems they provide a low fume toxicity and density allowing their use in railway and other public transportation systems where ease of escape is a key requirement.

High growth potential is expected in various Asian countries with special attention on China and India. In Europe, applications are moving east into countries like Poland and Bulgaria, while Russia appears to offer future opportunities. North America has re-emerged as a power in engineering plastics due to the revolution in cheap energy coming from shale gas fracking. This new possibility of cheap energy could change the face of the industry over the coming years and will depend highly on political decisions coming from individual states.

While standard electrical protection applications will continue to provide growth it is with new applications that the major growth is expected. LED lighting, photovoltaic parts and both electrical and structural parts in the automotive industry are of particular interest.

Non-halogenated flame retardant use shows little sign of slowing down and will continue as the additive of choice for the considerable future.

Keywords: Non–halogenated flame retardants, engineering plastics, ENFIRO, melamine cyanurate, organo phosphorus, glow wire, UL94, shale gas, photovoltaic, LED

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1.1 Introduction

1.1.1 Why Non-Halogenated Flame Retardants?

During the last 10–15 years there has been a constant trend in Engineering Plastics to move from traditional halogenated “Flame Retarded Polymers” (FRP’s) towards non-halogenated alternatives. Some of the reasons for this are linked to the toxicology, or assumed toxic effects and environmental concerns of the halogenated additives and/or of their synergists (such as antimony trioxide (ATO) and zinc substances) [1–7]. Another reason is that by declaring a “blanket ban” on all halogenated substances, regardless of their chemical nature or supposed link to toxic or environmental problems, the part producers have a much simpler way to manage their purchasing policy. This, of course, can also have a negative effect on both the physicochemical property performance and the robust safety of the end product [8–10]. However, in most cases equivalent performance is achievable by using FRP’s containing non-halogenated substitutes. The Electric and Electronical market (E & E), a major user of FRP’s, by understanding correctly the safety requirements of the end part, has been able to tailor simpler and lower costing formulations than the traditional halogenated based products. One example of these types of products is polyamide flame retarded with melamine cyanurate which dominates production of high volume items like connectors and mini circuit breakers. Even though relatively low cost, in comparison to traditional halogenated systems, these melamine cyanurate FRP’s fully comply with the required safety norms and regulations [11].

The drive to change from halogenated FRP’s, due to toxicology and environmental concerns, came about in the middle of the last decade driven by the introduction of three new regulations, RoHS (Restriction of Hazardous substances) [12], REACH (Regulation on Registration, Evaluation, Authorization and Restriction of Chemicals), specifically SVHC (substances of very high concern) and the WEEE (Waste Electric and Electronical Equipment). These regulations basically pushed the additive suppliers, the compounders and the E & E industry to act, innovate and control the type of additive systems used in their formulations. Today these regulations, or very similar regulations, have circumnavigated the globe, mainly due to the globalisation of major companies and the need to import into Europe, so that in essence all consolidated manufacturing countries now follow to a greater or lesser extent these or like regulations [13]. One of the major benefits of these regulations is the push they have given to the industry to innovate and find new and often better solutions. A
huge amount of investment at manufacturers and universities has occurred
and now for any application requiring FRP’s a suitable non-halogenated
solution is more than often available. That is not to say that all prop-
erties will be equivalent to the halogenated FRP’s. Some properties will be
enhanced while other properties will decrease [14–15]. Halogenated addi-
tives provide an undeniable highly robust flame retardant behaviour over a
myriad of different polymers, tests and applications that a single chemical
type of non-halogenated flame retardant cannot. Therefore, it is necessary
to carefully match the non-halogenated flame retardant to the type of pol-
ymer formulation and the required end part properties. For the E & E and
the Automotive and Consumer Goods markets different flame retardant
additives are used, each displaying either a combination or a single type
of four principle mechanisms to retard the flame [16, 17, 23, 10, 11, 23, 29,
31, 32]. For further needs a number of very good training resources, which
covers this issue in detail, exist and can be found online by simply search-
ing for “Flame Retardant Mechanisms” [18].

1. Poisoning: It is mainly due to the action of gases which are
heavier and denser than oxygen. In this case the flame can-
not be fed by the carburant and so it is choked. Furthermore
the presence of radical scavengers in the gas phase helps to
inhibit flame propagation. Examples of additives using this
action are below.

- Red Phosphorous (Phosphine production)
- Halogens + synergistic agents (HBr, HCl, with heavy
metal halides)
- Melamine Cyanurate ($N_2$, $NH_3$)

2. Dilution: It is linked to endothermic reactions which “cool”
the flame temperature in the gas phase.

- $\text{Al(OH)}_3 \rightarrow \text{Al}_2\text{O}_3 + 3 \text{H}_2\text{O}$ $1.2 \text{kJ/g (280 cal/g)}$ (starts at
$230^\circ\text{C}$)
- $\text{Mg(OH)}_2 \rightarrow \text{MgO} + \text{H}_2\text{O}$ $1.4 \text{kJ/g (328 cal/g)}$ (starts at
$330^\circ\text{C}$)

Water in the gas phase helps to keep oxygen away and to
extinguish the flame. Furthermore the heavy oxides create a
non-burning layer (char) which insulate the specimen from the
heat source.

*Magnesium and Aluminium Hydroxides are the additives which
use the dilution action.*
3. **Char formation:** This is due to the action of substances which are able to reticulate the burning substrate and to create a charring insulating layer.

*Zinc and Boric oxides (Zinc Borates as synergistic agents)*
*Aluminium and Magnesium oxides*
*Phosphorus compounds, including Red Phosphorus (in PA66)*

4. **Intumescence:** It is the mechanism that is able to create a foamed charring structure which forms a barrier to prevent the flame and oxygen reaching the substrate. To enable a good intumescence three distinct actions are required;

- A **charring source** *(a carbon-rich organic substrate containing functional groups; e.g. \(-\text{OH}; \ -\text{NH}_2; \ -\text{COOH}\)).*
- A **char promoter** *(an inorganic acid liberated by heating a compound which contains it; e.g. ammonium polyphosphate).*
- A **foaming agent** *(a chemical agent which liberates gas if heated; e.g. melamine or ammonium compounds).*

*Melamine polyphosphate is a good example of an additive displaying intumescence.*

These modes of actions help the fire scientist/formulation engineer to select the correct additive system for the given application of the end product. Four such examples of commonly used flame retardants are shown below,

- **Melamine Cyanurate or other melamine salts**
  - Excellent for passing the glow wire and UL94 test for E & E applications like circuit breakers and electrical connectors.
  - Low fume production, so very good for public transportation needs.
  - Low addition requirement means the FRP maintains a good level of ductility, excellent for “snap fit” connectors and covers.

- **Organophosphorus compounds**
  - Mainly used for glass reinforced UL94 V0 products such as electrical contactors or higher voltage circuit breakers.
  - Excellent colourability enabling light colours (greys and whites) required for circuit breakers.
- Can be used for a variety of polymer types with slight modifications. Enables halogen free PBT for the electronics industry.

**Red phosphorus**
- Where UL94 V0 is required on glass fibre reinforced parts such as contactors.
- Used mainly on black or very dark parts due to its inherent dark red colouring.
- Mainly reserved for use on PA66 Glass Reinforced parts due to the need of having PA66 to produce a proficient char.

**Aluminium and Magnesium oxides**
- Used extensively in cables to provide low smoke toxicity and corrosion for buildings and public transportation, tunnels, etc.
- High addition requirements minimise its use in engineering applications as parts tends to be quite brittle in nature.
- Excellent low warpage properties for planer items means that for large flat casings with limited mechanical needs it can be the material of choice.

All of these additives have peculiarities in how they provide flame retardancy and they all have positive and negative points related to their usage [19]. Therefore, picking the correct type of flame retardant additive to use in FRP’s is both difficult and requires a broad range of experience and knowledge. It is in the author’s opinion that the development of a new type of FRP’s is only successful when there is clarification and full cooperation from the part producer, the compounder/manufacturer and the additive supplier. These three parties each have a very important and essential role to play in order that the new FRP meets the need of the end consumer in terms of safety and performance. In the past, the type of additives and the FRP’s themselves were considered more a black art than actual chemical/material engineering. However, there has emerged a much greater transparency and cooperation between these three parties over the last few years which is helping improve FRP’s performance allowing a wider flexible in terms of part design and cost.

Some concerned parties think that a complete ban on flame retardants is the way to actually proceed [20–21]. However, FRP’s are both expensive
and can negatively affect the physico-mechanical properties of part in which they are used. This is in a sense a self-regulation and will, with the onset of tighter toxicological studies and environmental concerns and knowledge, self-govern their use to a “just-as-necessary” scenario in the future [22].

The very latest information regarding the adverse effect of FRP’s and the way in which to minimise such effects over a product life time has been published in the outcome of the ENFIRO project [23]. This research project was sponsored by the European Union and involved concerned parties from every part of the industry even including representatives from the NGO (Non-Government Organisation) Green Peace. Although the emphasis of the LCA (Life Cycle Analysis) results is on many different aspects than just hazardous flame retardant chemicals, they do also confirm that substitution of brominated FRPs by non-halogenated FRP’s leads to a reduction of (eco) toxicological impacts. In research projects focusing on the substitution of hazardous chemicals, LCA analyses produce valuable complementary information which allows a more complete evaluation of the viability and sustainability of alternatives. One of the most important findings of the ENFIRO project was that improper disposal of FRP’s lead to the worse LCA results. If disposed of correctly or recycled the negative effect of FRP’s is very much minimized [23].

1.2 Key Flame Retardancy Safety Requirements

There has been many papers published over the last twenty or so years by many fire scientists regarding the use of the cone calorimeter as the tool to use to measure the performance of FRP’s. To a great extent the cone and different measurements of heat release has helped us to understand better the overall science of fires [24–29]. However, for everyday use of testing and development of FRP’s, the tried and tested methods, for better or worse, still dominate the industry. The UL94 test is perhaps the best known of these and whilst the idea of the UL94 flame measurement is quite simple, in practice it is highly complicated test requiring a great deal of skill and investment to do correctly. The glow wire flammability index is a test much used in the E & E industries and one that can be tested by all parties on the end product. This test is one of the most prevalent in the low voltage electrical protection applications that are governed mainly by the IEC regulations. With an important update to the standard UL1077 the switch to halogen free engineering plastics in the USA and South America should now be a real possibility and should enable a change from traditional thermoset based products to more flexible and multifunctional thermoplastic
The appliance industry introduced the IEC 60335-2 regulation in 2003 with the main outcome being that everybody, additive supplier, compounder, part manufacturer had to become expert in glow wire testing. The main determining factor for these parts is the ability to pass a glow wire “no flame” test on the end part at a temperature above 750°C. This test however, is very sensitive to variations between operators, test apparatus and the method used and so results have been found to vary by up to 150°C on the same product. This uncertainty led to materials being certified as meeting the IEC 60335-2 at major electrical test certification houses like the VDE (the Association for Electrical, Electronic & Information Technologies) and Underwriters Laboratory (UL). Below is a list of the most common types of measurements used to measure the flammability performance of FRP's [31–32].

- **UL 94** – Rating of the ability to self-extinguish after ignition by a naked flame.
- **Glow wire flammability Index (GWFI IEC 60995-2-12)** – Measures the materials ability to self-extinguish after the application of a hot (glow) wire.
- **Glow wire ignition temperature (GWIT IEC 60995-2-13)** – Measures the material’s ability to resist ignition from a hot (glow) wire.
- **Hot wire ignition (HWI UL746A)** - Measure material ability to resist to ignition by a hot wire wrapped around a sample.
- **Limiting oxygen index (LOI ISO 4589)** – Measures the material’s ability to self-extinguish as function of the percentage of O₂ required.
- **Cone Calorimeter** – a bench scale apparatus that can simulate real fire scenarios and measures the material response such as rate of heat release, time to ignition or smoke release rate

One of the latest regulations to be introduced is the EN 45545-2 for railways. This regulation harmonises various country regulations into an application and hazard rated testing of products. The current widely used European standards, such as the French NF F 16-101, the German DIN 5510 and British BS 6853, have had a massive impact on the railway sector for many years through quantifying the impact of a fire regarding fumes emission (toxicity, opacity) and ease of ignition. The new European standard EN 45545-2 that has been published in April 2013 will supersede the national standards by March 2016. Even though
national and European standards will coexist for 3 years, it is key to prepare the phase-out [33].

This new European standard keeps the same objective of minimizing the probability of a fire starting and to control its development, but also highlights the importance of allowing the evacuation of passengers and staff in satisfying conditions. Therefore, like several national standards, EN 45545-2 covers two aspects of the fire risk

- the material behaviour during and after ignition
- the opacity and the toxicity of the fumes

However, the structure of this standard is unique. Hazard levels (HL1, HL2; HL3) have been created depending on the vehicle type (e.g. sleeping wagon, double deck trains,), but also its operating environment (tunnels). Depending on the usage of the part, technical requirements (R1 to R26) are defined and must be evaluated according to a list of testing methods (T1 to T17). The combination provides the classification of the material.

A wide majority of small E & E components will need to satisfy R22 (interior) and R23 (exterior) requirements. The tests are the same, only the required performance level varies. In comparison with NF F 16-101, R22/R23 applications require LOI but not glow wire measurements. As far as fume testing is concerned, the smoke density is tested on horizontal plates instead of vertical plates, and toxicity must be evaluated using the widely used NFX 70-100 standard with the quantification of NOx in addition to the gases which were already tested such as monoxide (CO), carbon dioxide (CO2), hydrogen chloride (HCl) and hydrogen bromide (HBr). This new regulation shows that flame testing can be both specific and intelligent to the needs of the part and its risk in use [34–35]. It is the opinion of the author that such regulations could and should be built to improve both safety and pragmatism in other forms of transportation, such as coaches and automobiles, which show much higher death rates as a result of fires, as reported in the NFPA 556 [36].

### 1.3 Geographical Trends

The world of flame retarded plastics and plastics in general is rapidly changing and adjusting to suit different market perspectives. Geographically the market attention has switched, from western mature nations, to the so called BRIC regions of Brazil, Russia, India and China. However, even some of these so called emerging nations are rapidly becoming mature
as wages soar and trade barriers are put in place to try and protect their position. Russia, although laden with risk, and perhaps more importantly India, even though major problems exist with infrastructure, look to be the new growth regions driving the market forward into the next decade. Further major trend changes are likely and already the seeds have been sown in the US with their rapid gain in fuel costs and their near loss of dependency on Middle Eastern energy due to the ‘quantum leap’ of technological advances in shale gas and oil extraction. North America is set to become the largest producer of gas and oil in the near future, with just one site estimated to hold over 3 trillion barrel alone [37–38]! Nations like China, Poland, Russia and the UK are trying hard to put in place similar programmes to ensure their energy needs in the future lie in their own hands. Mainland European nations, like France and Germany, shackled with the inability to come to a consensus decision, look set to miss the boat on energy, which, moving forward, could spell the end of their elite position in plastics and thus the highly attractive flame retardant sector. Politics and material and energy resource policy is quick to change and so these comments must be judged on the current geopolitical situation of each country mentioned.

The flame retardant plastics landscape and battlefield is equally undergoing rapid change in terms of applications and materials offered. Automotive is emerging as a key development area for FR plastics as manufacturers rush to put in place materials for new high electrical resistance applications, such as battery housings, connectors and fuel cell separators. Other structural parts are also being targeted with FR products with large volumes and radical new applications seemingly coming on a daily basis.

India offers a relatively new and exciting playground for flame retardant plastics, in particular for ABS and commonly used engineering plastics like polycarbonate and polyamide. Many companies in both the E & E and transportation industries see the low costs and lessening of taxes, coupled with a young and well educated English speaking population as the ideal mix to drive the industry forward away from the shackles of a difficult European situation. The vision for these mature nations, stuck in a quagmire of indecision and inability to kick start the member states monetary problems, is foggy at best. In India major OEMs are emerging such as Tata, Havells and C & S, while major FR polymer users, such as Schneider Electric, Legrand, Hager, TE connectivity and ABB to name just a few, have carefully established their presence mainly by tactical investments and sound investment in these growth regions. The market in India can be divided roughly into 3 categories;
1. High end parts, for export back to western nations, meeting the required norms and regulation of these mature regions.
2. Middle range products for local high end use,
3. and the majority which is the lower end, high volume-low cost where nearly anything goes!

Given recent disasters in this region caused by fires [39] and the increased need to improve safety in automobile electronics [40] the middle range of just good enough but quality products look to increase rapidly and dominate for the coming years. The major investment into R & D in India also means that it seems likely that they will emerge as a powerhouse in terms of regulations and innovation rather than being just a low cost production zone.

Moving onto China, it is clear that they have undertaken massive strides not only to improve the quality and safety of the parts produced but also by massive investments in innovation. However, China still remains principally a manufacturing zone for the world, meaning it is highly influenced by the on-going crisis in Europe and other zones. Couple this to a rapidly ageing population, a shortage of skilled workers, high inflation and rapidly increasing wages in its major cities and the outlook for China is not so certain. However, the Chinese government has for many years had the ability and means to shape their own destiny and so it remains highly unlikely that anything other than growth will remain for the region with a more sustainable internal, less export oriented, outlook model being followed. With rapidly inflating wages and higher demanding consumers China should move the way of previous low cost countries, such as like Korea and Italy, and move to high quality, highly regulated electrical and electronical parts and end products. A vision of the market for the different types of flame retardant products and how their usage has changed can be found in Table 1.1 and Table 1.2.

Table 1.1 Type and volume of FR additives sold 2007–2015 (KT).

<table>
<thead>
<tr>
<th></th>
<th>2007</th>
<th>2010</th>
<th>2015</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brominated</td>
<td>575</td>
<td>535</td>
<td>595</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>490</td>
<td>440</td>
<td>500</td>
</tr>
<tr>
<td>Red Phosphorus</td>
<td>35</td>
<td>38</td>
<td>45</td>
</tr>
<tr>
<td>Chlorinated</td>
<td>20</td>
<td>25</td>
<td>30</td>
</tr>
<tr>
<td>Alum./Mag. oxides</td>
<td>170</td>
<td>175</td>
<td>180</td>
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</tbody>
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