

Contents

Acknowledgment	V
Preface	VII
Contents	IX
1 Introduction	1
2 Flame Retardants in Commercial Use or Development for Polyolefins	3
2.1 Introduction	3
2.2 Generalizations	4
2.3 Endothermic Additives (Mainly Metal Hydroxides)	4
2.3.1 Alumina Trihydrate (Aluminum Trihydroxide, ATH; Mineral Name: Bauxite)	4
2.3.2 Properties of ATH	5
2.3.3 ATH Modifications	5
2.3.4 Synergists and Adjuvants with ATH	6
2.3.5 Magnesium Hydroxide (Magnesium Dihydroxide, MDH)	6
2.3.6 Synergism of MDH with Zinc Borate	7
2.3.7 Other Synergistic MDH Combinations	7
2.3.8 Ultracarb® (Huntite-Hydromagnesite Mixture)	8
2.3.9 Talc	8
2.4 Halogenated Flame Retardants	8
2.4.1 Chloroparaffins	9
2.4.2 Dechlorane Plus®	10
2.4.3 Brominated Additives	11
2.5 Antimony Trioxide	15
2.6 Phosphorus Additives	16
2.6.1 Intumescent Phosphorus-Based Additive Systems	16
2.6.2 Red Phosphorus	19
2.6.3 Other Phosphorus Additives	19
2.7 Expandable Graphite	19
2.8 Co-Additives; Hindered Amines	20
2.9 Nanocomposites	20

2.10	Polymer Modifications	21
2.11	Blends of Polyolefins with Char-Forming Polymers	21
2.12	Silicone Synergists	21
2.13	Silicone Modification of Polyolefins by Addition or Copolymerization	22
2.14	Layered Polymer Approach	22
2.15	Specific Applications	22
2.15.1	Wire and Cable Insulation	22
2.15.2	Wood-Polyolefin Blends	23
2.16	Flame Retardant Elastomers	23
2.16.1	General Comments	23
2.16.2	Diene Elastomers	24
2.16.3	Chloroparaffins in Elastomers	25
2.16.4	Zinc Borates in Elastomers	26
2.16.5	Bromine Compounds in Elastomers	26
2.16.6	Phosphorus Compounds in Elastomers	27
2.16.7	ATH and MDH in Elastomers; Low Smoke Formulations	27
2.16.8	Clays in Elastomers	28
2.16.9	(Poly)chloroprene and other Halogen-Containing Elastomers	29
2.16.10	Chlorinated and Chlorosulfonated Polyethylenes	29
2.17	Future Trends	30
3	Polystyrenes and Thermoplastic Styrene Copolymers	35
3.1	Introduction	35
3.2	General Comments on the Fire Properties of Styrenic Polymers	35
3.3	Crystal Polystyrene	36
3.4	Expandable Polystyrene and Extruded Polystyrene Foam	36
3.4.1	Hexabromocyclododecane (HBCD)	36
3.4.2	Tetrabromocyclooctane	37
3.4.3	Dibromoethyldibromocyclohexane	37
3.4.4	Other Bromine Flame Retardants	38
3.4.5	The Flammability Effect of the Expanding Agent	38
3.4.6	Synergists with Brominated Additives in Polystyrene Foam	38
3.4.7	Phosphorus-Bromine Combinations in Polystyrene Foam	39
3.4.8	Non-Bromine Systems in Polystyrene Foam	39
3.4.9	The Recommended Fire-Safe Use of Extruded Polystyrene Insulation	40
3.5	High Impact Polystyrene	41
3.5.1	Bromine-Containing Flame Retardants for HIPS	41

3.5.2	Non-Halogen Flame Retardants for HIPS	47
3.6	Flame Retarded Acrylonitrile-Butadiene-Styrene Copolymers (ABS)	47
3.6.1	Brominated Flame Retardants Used in ABS	48
3.6.2	Chlorinated Additives for ABS or HIPS	50
3.6.3	Non-Halogen Flame Retardants for ABS	51
3.7	Flammability Requirements and Tests	51
3.8	Mechanistic Considerations as a Guide for Flame Retardation of Styrenics ..	51
3.8.1	Vapor Phase Mechanisms in Styrenics and Some Implications	52
3.8.2	The Smoke Problem with Styrenics	52
3.8.3	Condensed Phase Mechanisms in Styrenics	53
3.9	Summary and Future Trends	53
4	Flame and Smoke Retardants in Vinyl Chloride Polymers –	
	Commercial Usage and Current Developments	59
4.1	Introduction	59
4.2	Plasticized (Flexible) PVC	60
4.3	Antimony Oxide and Related Products	61
4.4	Halogenated Phthalate Plasticizers	62
4.5	Chlorinated Paraffins	63
4.6	Inorganic Flame Retardants, Synergists and Smoke Suppressants	64
4.6.1	Alumina Trihydrate (Aluminum Hydroxide, ATH)	64
4.6.2	Magnesium Hydroxide and Related Magnesium Minerals	66
4.6.3	Molybdenum Compounds	67
4.6.4	Copper Compounds	68
4.6.5	Zinc Borates; Barium Borate	68
4.6.6	Zinc Stannates	69
4.6.7	Zinc Sulfide	69
4.6.8	Calcium Carbonate	70
4.6.9	Smoke Suppressants – General Comments	70
4.7	Low Flammability Plasticizers: Phosphate Esters	70
4.7.1	Triaryl Phosphates	71
4.7.2	Low Temperature Alkyl Diphenyl Phosphate Plasticizers	73
4.7.3	Comparison of Some Flame-Retardant and Non-Flame-Retardant Plasticizers	73
4.7.4	Comparison of Various Combinations of Plasticizers and Other Additives	73
4.8	Formulating for Specific Applications	74
4.8.1	Calendered Vinyls	74
4.8.2	Plenum Wire and Cable	76

4.8.3	Coated Textile Applications	79
4.8.4	Vinyl Flooring	79
4.9	PVC from a Safety and Environmental Point of View	79
5	Current Practice and Recent Commercial Developments in Flame Retardancy of Polyamides	85
5.1	Introduction	85
5.2	Additives for Polyamide 6 and 66 in Engineering Thermoplastic Applications	86
5.2.1	Chlorinated Additives	86
5.2.2	Brominated Additives	88
5.3	Melamine Cyanurate	91
5.3.1	Other Melamine Additives	94
5.4	Inorganic Hydrates	95
5.4.1	Magnesium Hydroxide	95
5.4.2	Alumina Monohydrate	95
5.5	Phosphorus Additives	96
5.5.1	Red Phosphorus	96
5.5.2	Aluminum Dialkylphosphinates	97
5.5.3	Hypophosphite Salts	98
5.6	Drip Retarding Additives	98
5.7	Treated Glass Fiber Reinforcement	99
5.8	Textile Fiber Applications	99
6	Flame Retardants for Thermoplastic Polyesters in Commercial Use or Development	105
6.1	Introduction	105
6.2	Polyethylene Terephthalate	105
6.2.1	Textile Fiber Flame Retardance by Melt-Spinning Additives	105
6.2.2	Dihydrooxaphosphaphenanthrene Reactant in Polyethylene Terephthalate	106
6.2.3	Phosphinate Structure in PET Backbone	108
6.2.4	Mode of Action of Phosphorus Flame Retardants in Polyethylene Terephthalate Fabrics and Materials which Interfere with this Action	108
6.2.5	Bromine-Containing FR in PET Fibers	108
6.2.6	Flame Retarding Polyethylene Terephthalate Fabric by a Thermosol Finishing Process	109
6.2.7	Flame Retarding Polyethylene Terephthalate Molding Resin by an Aromatic Diphosphate	110

6.2.8	Flame Retarding Polyethylene Terephthalate by other Phosphorus-Containing Additives	110
6.3	Polybutylene Terephthalate	110
6.3.1	Polymeric and Oligomeric Brominated Flame Retardants in PBT ..	110
6.3.2	PBT with other Bromine-Containing Additives	113
6.3.3	Polybutylene Terephthalate/Polycarbonate Blends	113
6.3.4	Non-Halogen Flame Retardant Polybutylene Terephthalate – Phosphorus Flame Retardant Additives	113
6.3.5	Non-Halogen Flame Retardant Polybutylene Terephthalate – Phosphinate Salt Additives	114
6.3.6	Non-Halogen Flame Retardant Polybutylene Terephthalate – Aromatic Phosphate Additives	115
6.3.7	Non-Halogen Flame Retardant Polybutylene Terephthalate Using Melamine Cyanurate or Sulfate	116
7	Flame Retardants in Commercial Use or Advanced Development in Polycarbonates and Polycarbonate Blends	121
7.1	Introduction	121
7.2	Bromine-Based Flame Retardancy	122
7.3	Anti-Dripping Additives	123
7.4	Non-Halogen Flame Retardancy – General Comments	124
7.4.1	Phosphates	124
7.4.2	Other Phosphorus Compounds	125
7.4.3	Sulfonate Salts	125
7.4.4	Other Salts	128
7.4.5	Silicone-Based Systems	128
7.5	Polycarbonate-ABS Blends	128
7.5.1	Halogen Additives in PC Blends	129
7.5.2	Phosphorus Compounds in Blends of Polycarbonates and ABS	129
7.5.3	Other Phosphorus Compounds in PC-ABS Blends	132
7.5.4	Other Flame Retardant Systems for PC-ABS Blends	132
7.6	Polycarbonate-Polyester Blends	133
7.7	Other Polycarbonate Copolymers and Blends	133
7.8	Structural Approaches (Laminates)	134
7.9	Modified End Groups	134
7.10	Conclusions	134

8 Commercial Flame Retardancy of Unsaturated Polyester, Vinyl Resins, Phenolics and their Composites	141
8.1 Introduction	141
8.2 Halogen-Containing Unsaturated Resins	141
8.3 Vinyl Ester Resins	143
8.4 Hydrated Mineral Fillers	144
8.4.1 Combination of ATH and Decabromodiphenyl Ether (“Decabrom” or “Deca”)	145
8.5 Low Smoke Polyester Resins	145
8.5.1 Low Smoke Unsaturated Acrylate Oligourethane Resins with Alumina Trihydrate	145
8.6 Phosphorus-Containing Flame Retardant Polyester Resins	146
8.6.1 Phosphorus Reactives in Unsaturated Polyester Resins	147
8.6.2 Phosphorus-Melamine Combinations in Unsaturated Polyester Resins	147
8.7 Borates in Unsaturated Polyester Resins	148
8.8 Phenolic Composites	148
8.9 The Effect of Glass Reinforcement on the Fire Performance of Polymer Composites	149
8.10 Protective Veils	149
9 Flame Retardants in Commercial Use or Advanced Development in Polyurethanes	153
9.1 Introduction	153
9.2 Commercial Flame Retardance of Rigid Foams	153
9.2.1 Additives in Rigid Foams	154
9.2.2 Reactive Flame Retardants – General Comments	156
9.2.3 Reactive Flame Retardants in Rigid Polyurethane Foams	157
9.2.4 Impact of Blowing Agent on Flame Retardancy of Rigid Foams	157
9.2.5 Brominated Alcohols as Reactive Flame Retardants	159
9.2.6 Non-Halogenated Polyols Favorable to Flame Retardancy in Rigid Foams	160
9.2.7 Additives in Isocyanurate Foams	160
9.2.8 The Effect of Catalyst Choice on Flame Retardancy of Rigid Lamination Foams	161
9.3 Flame Retardance of Flexible Foams	161
9.3.1 Additives in Flexible Foams	162
9.3.2 Additives in Flexible Foams – Volatility Considerations (“Fogging”)	163

9.3.3	Halogen-Free Additives for Flexible Foams	164
9.3.4	Overcoming the “Scorch” Problem in Flexible Foams	164
9.3.5	Reactive Flame Retardants for Flexible Foams	166
9.3.6	Polyols Favorable to Flame Retardancy in Flexible Foams	166
9.3.7	Melamine in Flexible Foams	167
9.3.8	Other Solid Additives in Flexible Foam	169
9.3.9	Silicone Surfactants Favorable to Flame Retardancy in Flexible Foams	169
9.3.10	Effect of Foaming Catalysts on Air Flow, Flame Retardancy and Smoldering Combustion	170
9.3.11	Interaction of Upholstery Fabric on the Flammability of Flexible Foam in Furniture	170
9.3.12	Effect of Fillers on Flame Retardancy of Flexible Foams	171
9.3.13	Rebonded Foam	171
9.3.14	Combinations of Polyurethane and other Foaming Polymers	171
9.3.15	Basic Studies on Flammability and Flame Retardant Action in Flexible Foams	171
9.4	Polyurethane Elastomers and Cast Resins	172
9.5	Reaction-Injection-Molded Products	173
9.6	Urethane Coatings and Sealants	173
10	Current Flame Retardant Systems for Epoxy Resins	179
10.1	Introduction	179
10.2	Electrical and Electronic Applications	179
10.3	Brominated Flame Retardants in PWB	180
10.3.1	A Challenge to Tetrabromobisphenol A	181
10.4	Non-Halogen Alternatives to Tetrabromobisphenol A	183
10.4.1	High Loadings of Metal Hydroxide Fillers	183
10.4.2	Red Phosphorus plus ATH	184
10.4.3	Other Additive Phosphorus Compounds in PWB	185
10.4.4	Reactive Phosphorus Compounds in Epoxy Resins	186
10.4.5	Use of Metal Hydroxide Additive, Char-Favoring Curing System and Char-Promoter	189
10.5	Resin Design for Flame Retardancy	189
10.6	A Multi-Pronged Approach to PWB Formulation – Resin Design, Filler, Interphase Control	190
10.7	Flame Retarding Epoxy Coatings	190

11 Flame Retardants in Commercial Use or Development for Textiles	197
11.1 General Background	197
11.1.1 A Brief Review of the History of Flame Retardant Textiles	197
11.1.2 Flammability of Textiles (General Comments)	198
11.1.3 Modes of Action	198
11.1.4 Detrimental Effects on Flammability	198
11.2 Non-Durable Treatments	199
11.2.1 Non-Durable Treatments of Cotton and other Cellulosics	199
11.2.2 Non-Durable Treatments for Polyester	200
11.2.3 Semi-Durable Treatments for Cotton	200
11.2.4 Further Development of the Phosphorylation of Cellulose	201
11.3 Backcoating with Phosphorus-Containing Formulations	202
11.4 Durable Finishes	203
11.4.1 THPX Finishes for Cellulosics and Blends	203
11.4.2 Improvements and Recent Developments in the THPX Type of Finish	205
11.4.3 New Products Using the Proban Treatment	205
11.4.4 THPX Processes not Using Gaseous Ammonia	206
11.4.5 Pyrovatex® CP and Similar Competitive Products	206
11.4.6 Other Durable Finishes for Cotton	207
11.5 Thermosol Flame Retardant Treatment of Polyester Fabric	208
11.6 Nylon Topical Finish	209
11.7 Wool	210
11.8 Processes with Broad Application for Synthetics and Blends	210
11.9 Coating with Bromine-Containing Emulsion Polymers	211
11.10 Backcoating of Carpets; Metal Hydroxide Fillers	211
11.11 Melt Processable Additives in Polypropylene	212
11.12 Melt Processable Additives in Polyester Fibers	212
11.13 Inherently Flame Retardant Fibers	213
11.13.1 Rayon	213
11.13.2 Polyester Fibers	213
11.13.3 Polyamides; Aramids	214
11.13.4 Polyimide Fibers	215
11.13.5 Melamine Fibers	215
11.13.6 Glass Fabric	215
11.13.7 Basalt Fibers	215
11.13.8 Silicic Acid-Containing Rayon Fibers (Visil®)	216
11.13.9 Halogen-Containing Fibers	216

11.13.10 Polyphenylene Sulfide Fibers	216
11.13.11 Oxidized Polyacrylonitrile Fibers (Pyron)	216
11.14 Technology Related to Mattresses	217
11.14.1 Regulatory Actions Regarding Open-Flame Tests	217
11.14.2 Flame Retardant Facing	217
11.14.3 Boric Acid on Cotton Batting	218
11.14.4 Batting and Nonwoven Fabrics from Combinations of Flame Retardant Fibers	218
11.14.5 Corespun Yarn	219
11.14.6 Mattress Construction	219
11.15 Future Trends	220
12 Comments on Flammability and Smoke Tests	227
12.1 Introduction	227
12.2 The UL 94 Vertical Flame Test	228
12.2.1 Precautions in the UL 94 Test	229
12.2.2 Variants of the UL 94 to Obtain More Quantitative Data	229
12.3 Oxygen Index (Limiting Oxygen Index)	230
12.3.1 Oxygen Index – Correlation to Other Tests and Use in R&D	230
12.4 Glow Wire Test	231
12.5 Hot Wire Index (UL 746C)	232
12.6 Cone Calorimeter	232
12.6.1 Cone Calorimeter Correlation to UL 94	233
12.6.2 Cone Calorimeter Correlation to the E 84 Tunnel Test (Discussed Below <i>per se</i>)	233
12.6.3 Cone Calorimeter Correlation to Other Fire Tests	233
12.7 Steiner (25-Foot) Tunnel Test (ASTM E 84)	234
12.8 NBS Smoke Chamber ASTM E 662	234
12.9 Federal Apparel Test (16 CFR Part 1610)	234
12.10 Federal Children’s Sleepwear Test (CFR Title 16, Parts 1615 and 1616)	235
12.11 Textile Test NFPA 701	235
12.12 Textile Test ASTM D 6413	235
12.12.1 Test Specific to Upholstered Furniture: Cigarette Ignition	235
12.12.2 Tests Specific to Upholstered Furniture: California Technical Bulletin 117	235
12.12.3 Tests Specific to Upholstered Furniture: California Technical Bulletin 133	236
12.12.4 Tests Specific to Upholstered Furniture: British standard	236
12.13 Federal Motor Vehicle Safety Standard 302	236

12.14 French Epiradiateur Test (NF P 92-501) for Building Materials	236
12.15 Carpet Tests: Pill Test and Radiant Panel	237
12.16 Roofing: the Burning Brand Test	237
12.17 Large Scale Tests	237
12.18 Other Specialized Tests	238
12.19 Warning Regarding Interpretation of Fire Tests	238
13 Overview of Modes of Action and Interaction of Flame Retardants	241
13.1 Introduction	241
13.2 Heat Sinks (Heat Capacity Effects and Endotherms)	241
13.3 Heat Sinks in the Vapor Phase	242
13.4 Barrier Effects	242
13.5 Flame Inhibition Effects	245
13.6 Char Formation	246
13.7 Char Formation in Poorly Charrable Polymers	247
13.8 Intumescence and Formation of a Foam Insulation Barrier	247
13.9 Drip Promotion or Drip Suppression	248
13.10 Additivity, Synergism and Antagonism of Flame Retardant Combinations ...	248
13.11 General Comments	250
Appendix 1 Sources of Further Information on Flame Retardancy	253
A1.1 Books	253
A1.2 Conferences	254
A1.3 Journals and Business Periodicals	254
A1.4 Reviews by the Present Authors with More-Inclusive Coverage	256
A1.5 Internet Information Sources	256
Appendix 2 Directory of Flame Retardant Manufacturers, Distributors, and Compounds	259
Subject Index	271