

Jai Prakash Agrawal

High Energy Materials

Propellants, Explosives and Pyrotechnics



**WILEY-
VCH**

WILEY-VCH Verlag GmbH & Co. KGaA

Contents

	Preface	<i>XIX</i>
	Acknowledgments	<i>XXI</i>
	Abbreviations	<i>XXIII</i>
1	Salient Features of Explosives	1
1.1	Introduction	1
1.2	Definition	2
1.2.1	Evolution of Heat	3
1.2.2	Rapidity of Reaction	3
1.3	Classification	4
1.3.1	Military Explosives	6
1.3.1.1	Detonating or High Explosives	6
1.3.1.2	Deflagrating or Low Explosives	7
1.3.1.3	Pyrotechnics	9
1.3.2	Civil Explosives	9
1.3.2.1	Permitted or Permissible Explosives	9
1.3.2.2	Non-permitted Explosives	11
1.4	Fundamental Features	14
1.4.1	Compatibility and Stability	14
1.4.2	Oxygen Balance (OB)	17
1.4.3	Sensitivity and Sensitiveness	19
1.4.3.1	Sensitivity to Impact	20
1.4.3.2	Sensitivity to Friction	20
1.4.3.3	Sensitivity to Shock	20
1.4.3.4	Sensitivity to Spark	20
1.4.3.5	Sensitivity to Heat	20
1.4.4	Heat of Formation	24
1.4.5	Heat of Explosion and Gaseous Products	27
1.4.6	Velocity of Detonation (VOD)	30
1.4.7	Detonation Pressure (DP or P_{C1})	31
1.4.8	Explosive Power or Strength	32
1.4.9	Brisance	32

1.5	Additional Requirements for Military Explosives	33
1.5.1	Volatility	34
1.5.2	Toxicity	34
1.5.3	Hygroscopicity	34
1.5.4	Density	35
1.5.5	Life	35
1.5.6	Availability, Cost and Demilitarization or Recycling	35
1.5.7	Eco-friendliness	36
1.6	Applications of Explosives	37
1.6.1	Military Applications	38
1.6.1.1	Shells	39
1.6.1.2	Bombs	40
1.6.1.3	Grenades	40
1.6.1.4	Torpedoes	40
1.6.1.5	Shaped Charges	41
1.6.1.6	Warheads	41
1.6.2	Commercial Applications	43
1.6.2.1	Coal Mining	43
1.6.2.2	Tunneling	44
1.6.2.3	Quarrying	44
1.6.2.4	Other Mining	45
1.6.3	Military Explosives and Devices for Commercial Applications	45
1.6.3.1	Detonators	45
1.6.3.2	Pilot Seat Ejection System	45
1.6.3.3	High Altitude Fuel	46
1.6.3.4	Air Re-generating Composition	46
1.6.3.5	Metal Cladding and Welding	47
1.6.3.6	Metal Working	48
1.6.3.7	Explosive Forming	48
1.6.3.8	Explosive Cutting	49
1.6.4	Space Applications	49
1.6.4.1	Solid and Liquid Rockets for Space Applications	49
1.6.4.2	Various Indian Satellite Launch Vehicles	51
1.6.4.3	Explosives, Propellants (Oxidizers, Binders and Plasticizers) and Pyrotechnics for Satellite Launch Vehicles	52
1.6.5	Nuclear Applications	54
1.6.5.1	Types of Nuclear Weapons	54
1.6.5.2	Assembly	55
1.6.5.3	Fissile Materials and Explosive Lenses	56
1.6.5.4	Explosives and Binders for Nuclear Weapons	58
1.6.6	Miscellaneous Applications	58
1.6.6.1	Agriculture	58
1.6.6.2	Medical Industry	61
1.6.6.3	Food Industry	61
1.6.6.4	Civil Engineering	62
1.6.6.5	Automobile Industry	62

- 1.6.6.6 Oil and Gas Industry 62
- References 63

- 2 Status of Explosives 69**
- 2.1 Historical Aspects 69
- 2.2 Status of Current and Future Explosives 70
- 2.2.1 Black Powder 71
- 2.2.2 Trinitrotoluene 71
- 2.2.3 Tetryl 72
- 2.2.4 Nitroglycerine 72
- 2.2.5 Dynamite 73
- 2.2.6 Pentaerythritol Tetranitrate 73
- 2.2.7 Nitrocellulose 74
- 2.2.8 Polyvinyl Nitrate 75
- 2.2.9 Mercury Fulminate 76
- 2.2.10 Lead Azide 76
- 2.2.11 Picric Acid, Lead Picrate and Ammonium Picrate 78
- 2.2.12 Lead Styphnate (Lead-2,4,6-trinitroresorcinate) 79
- 2.2.13 Diazodinitrophenol 79
- 2.2.14 Tetrazene 80
- 2.2.15 Mercuric-5-nitrotetrazole 81
- 2.2.16 Research Department Explosive 81
- 2.2.17 High Melting Explosive (or Her Majesty's Explosive) 82
- 2.2.18 'Heat-Resistant' or 'Thermally Stable' Explosives 83
- 2.2.18.1 General Approaches for the Synthesis of TATB, HNS, PATO etc. 84
 - Salt Formation 84
 - Introduction of Amino Groups 84
 - Introduction of Conjugation 89
 - Condensation with Triazole Ring/s 91
- 2.2.18.2 3,3'-Diamino-2,2',4,4',6,6'-hexanitrodiphenyl 93
- 2.2.18.3 N^2, N^4, N^6 -Tripicryl melamine or 2,4,6-Tris(picrylamino)-1,3,5-triazine Series of Explosives 93
- 2.2.18.4 Tetranitrodibenzo-1,3a,4,4a-tetraazapentalene 95
- 2.2.18.5 2,6-Bis(picrylamino)-3,5-dinitropyridine 95
- 2.2.18.6 2,5-Dipicryl-1,3,4-oxadiazole 96
- 2.2.18.7 2,2',2'',4,4',4'',6,6',6''-Nonanitroterphenyl 96
- 2.2.18.8 3,5-Diamino-2,6-dinitropyridine-*N*-oxide 97
- 2.2.18.9 *N, N'*-Bis(1,2,4-triazol-3-yl)-4,4'-diamino-2,2',3,3',5,5',6,6'-octanitroazobenzene 97
- 2.2.19 High Performance (High Density and High VOD) Explosives 99
- 2.2.19.1 General Synthetic Approaches for High Performance Explosives (HNIW/CL-20 etc.) 100
 - Replacement of the Nitro Group by Furoxano Group 100
 - Introduction of SF₅ Groups into Nitro Compounds 102
 - Strained and Cage Compounds 103

2.2.19.2	1,3,4,6-Tetranitroglycoluril	106
2.2.19.3	Tetranitropropanediurea	106
2.2.19.4	1,3,5,5-Tetranitrohexahydropyrimidine	107
2.2.20	Melt-Castable Explosives	108
2.2.20.1	Tris-X and Methyl Tris-X	108
2.2.20.2	1,3,3-Trinitroazetidine	109
2.2.20.3	4,4'-Dinitro-3,3'-bifurazan	110
2.2.21	Insensitive High Explosives	110
2.2.21.1	Oxynitrotriazole or Nitrotriazolone	112
2.2.21.2	Dinitroglycoluril	113
2.2.21.3	Aminonitrotriazole	114
2.2.21.4	Trans-1,4,5,8-tetranitro-1,4,5,8-tetraazadecalin	114
2.2.22	Energetic Binders and Plasticizers	115
2.2.22.1	Energetic Binders	115
2.2.22.2	Energetic Plasticizers	117
2.2.23	Energetic Materials Synthesized Using Dinitrogen Pentoxide	117
2.2.24	Newly Reported Explosives	118
2.2.25	Important Formulations Based on TATB, CL-20 and NTO	120
2.2.25.1	TATB-based Formulations	120
2.2.25.2	CL-20-based Formulations	122
2.2.25.3	NTO-based Formulations	124
2.2.26	Insensitive Munitions and Some New Insensitive Explosives/ Formulations	125
2.2.26.1	ROWANEX Class of PBXs	126
2.2.26.2	SNPE's PBXs	127
2.2.26.3	FOI's Explosives	129
	FOX-7	129
	FOX-12	130
2.2.26.4	American Formulations	130
2.2.27	Basic Lead Azide	131
2.2.28	Hexakis(azidomethyl) Benzene	134
2.2.29	Tetraamine-cis-bis(5-nitro-2H-Tetrazolato-N ²) Cobalt (III) Perchlorate	134
2.2.30	Octanitrocubane	137
2.2.31	Nickel Hydrazine Nitrate	139
2.2.32	Furazan-, Furoxan- and Tetrazine-Based Explosives	140
2.2.33	High Nitrogen Content-High Energy Materials	141
2.2.34	Fuel-Air Explosives	144
2.3	Future Scope for Research	147
2.3.1	High Performance, Thermally Stable and Insensitive Explosives	147
2.3.2	Melt-Castable Explosives	148
2.3.3	Energetic Binders and Plasticizers	148
2.3.4	Particle Size of Explosives	148
2.3.5	Eco-Friendly Production Processes and Explosives	149
	References	150

3	Processing and Assessment Techniques for Explosives	163
3.1	Processing Techniques for Explosives	163
3.1.1	Casting	164
3.1.1.1	Melt-casting	164
3.1.1.2	Normal Casting	165
3.1.1.3	Vibration or Sedimentation Casting	166
3.1.1.4	Squeeze or Pressure Casting	166
3.1.2	Extrusion	166
3.1.3	Pressing	166
3.1.3.1	Unidirectional Pressing	167
3.1.3.2	Double Action Pressing	167
3.1.3.3	Incremental Pressing	167
3.1.3.4	Hydrostatic Pressing	168
3.1.3.5	Isostatic Pressing	168
3.2	Formulation Fundamentals	170
3.2.1	Current Formulations	170
3.2.2	Aluminized Explosive Formulations	171
3.2.3	Sheet Explosives	171
3.2.4	Plastic Bonded Explosives	173
3.3	Assessment of Explosives	175
3.3.1	Determination of Compatibility and Stability of Explosives	176
3.3.1.1	Vacuum Stability Test	177
3.3.1.2	Heat Test	179
3.3.1.3	Impact Sensitivity Test	179
3.3.2	Sensitivity of Explosives to Heat, Impact, Friction, Spark and Shock	180
3.3.2.1	Determination of Heat Sensitivity	180
	Explosion Delay	180
	Explosion Temperature	181
	Activation Energy	182
	Thermal Analysis	183
3.3.2.2	Determination of Impact Sensitivity	188
3.3.2.3	Determination of Friction Sensitivity	195
3.3.2.4	Determination of Electric Spark Sensitivity	197
3.3.2.5	Determination of Shock Sensitivity	197
3.3.3	Determination of Detonation Velocity	198
3.3.3.1	Pin Oscillographic Technique	198
3.3.3.2	Dautriche Method	202
3.3.4	Determination of Detonation Pressure	203
3.3.5	Determination of Strength	204
	References	205
4	Propellants	209
4.1	Classification of Propellants	209
4.2	Liquid Propellants	209

4.3	Solid Propellants	213
4.3.1	Homogeneous Propellants	213
4.3.1.1	Single-Base Propellants	213
4.3.1.2	Double-Base Propellants	214
4.3.1.3	Triple-Base Propellants	214
4.3.2	Heterogeneous Propellants	214
4.3.2.1	Composite Propellants	214
4.3.2.2	Composite Modified Double-Base Propellants	215
4.3.2.3	Fuel-Rich Propellants	215
4.4	Hybrid Propellants	217
4.5	Thixotropic Propellants	217
4.6	Performance of Propellants	218
4.6.1	Gun Propellants	218
4.6.1.1	Force Constant	218
4.6.1.2	Burning Rate Coefficients	219
4.6.1.3	Vivacity	219
4.6.1.4	Muzzle Velocity	219
4.6.1.5	Efficiencies of Gun System and Charge	220
4.6.2	Rocket Propellants	220
4.6.2.1	Burn Rate	221
4.6.2.2	Thrust	222
4.6.2.3	Specific Impulse (I_{sp})	222
4.6.2.4	Chamber Pressure	223
4.6.2.5	Characteristic Velocity (C^*)	223
4.6.2.6	Temperature Sensitivity	224
4.7	Formulation of Gun Propellants	226
4.8	Ingredients of Gun Propellants	227
4.8.1	High Energy Propellants	228
4.8.2	Low Vulnerability Gun Propellants	228
4.8.2.1	Ingredients of LOVA Gun Propellants	229
4.8.3	Liquid Gun Propellants	231
4.8.3.1	Hydroxyl Ammonium Nitrate Liquid Gun Propellants	231
4.8.3.2	DMAZ Liquid Gun Propellants	233
4.9	Ingredients of Solid Rocket Propellants	234
4.9.1	Oxidizers	234
4.9.1.1	Ammonium Nitrate	235
4.9.1.2	Ammonium Dinitramide	237
4.9.1.3	Hydrazinium Nitroformate	239
4.9.2	Binders	243
4.9.2.1	Characteristics of Binders	243
4.9.2.2	Polyurethanes as Binders	244
4.9.2.3	Novel Binders	249
	Inert or Non-Energetic Binders	249
	Energetic Binders	252
4.9.3	Metal Fuels	265
4.9.4	Plasticizers	267

- 4.9.4.1 Classification of Plasticizers 267
- 4.9.4.2 Characteristics of Plasticizers 268
- 4.9.4.3 Functions of Plasticizers 268
- 4.9.4.4 Migration of Plasticizers 268
- 4.9.4.5 Novel Plasticizers 271
 - Nitroxyethyl Nitramine Plasticizers 271
 - Polynitro Aliphatic Plasticizers 272
 - Rowanite 8001 or K-10 Plasticizer 273
 - Azido Plasticizers 273
 - Energetic Oligomeric Plasticizers 274
 - Nitrate Ester Plasticizers 275
- 4.9.5 Bonding Agents 275
- 4.9.6 Stabilizers 277
- 4.9.7 Burn-Rate Modifiers 280
 - 4.9.7.1 Burn-Rate Modifiers for DB Propellants 281
 - 4.9.7.2 Less Toxic and Non-Toxic Burn-Rate Modifiers for DB Propellants 284
 - 4.9.7.3 Burn-Rate Modifiers for CMDDB Propellants 284
 - 4.9.7.4 Burn-Rate Modifiers for Composite Propellants 284
 - Metallic Oxides 284
 - Ferrocene Derivatives 287
 - Butacene 287
- 4.10 Inhibition of Rocket Propellants 289
 - 4.10.1 Characteristics of Inhibitors 291
 - 4.10.2 Testing of Inhibitors 291
 - 4.10.3 Ballistic Evaluation of Inhibited Propellants 292
 - 4.10.4 Materials for Inhibition 293
 - 4.10.5 Techniques of Inhibition 294
 - 4.10.5.1 Sleeve Technique 294
 - 4.10.5.2 Tape-Winding Technique 294
 - 4.10.5.3 Casting Technique 295
 - 4.10.5.4 Thread-Winding Technique 295
 - 4.10.5.5 Inhibitor Sleeve Technique 296
 - 4.10.6 Inhibition of Double-Base Propellants 298
 - 4.10.6.1 Tailoring of Properties of Unsaturated Polyesters 300
 - 4.10.6.2 Recent Trends 301
 - 4.10.7 Inhibition of Composite Propellants 302
 - 4.10.7.1 Chemistry of Epoxy Resins 302
 - Epoxy Resins 304
 - Novolac Epoxy Resins 304
 - Synthesis 305
 - Curing Agents for Epoxy Resins 306
 - Cure Mechanism 308
 - 4.10.7.2 Novel Systems 308
 - 4.10.7.3 Plasticizer Migration in Composite Propellants 308
 - 4.10.8 Inhibition of CMDDB Propellants 308

- 4.11 Insulation of Rocket Motors 313
 - 4.11.1 Characteristics of Insulators or Insulating Materials 313
 - 4.11.2 Materials for Insulation 314
 - 4.11.3 Process for Insulation of Motors 315
 - 4.11.4 Future Materials for Insulation 315
- References 316

- 5 Pyrotechnics 331**
 - 5.1 Introduction 331
 - 5.2 General Features of Pyrotechnics 332
 - 5.3 Ingredients of Pyrotechnic Formulations 333
 - 5.3.1 Fuels 333
 - 5.3.2 Oxidizers 334
 - 5.3.3 Binders 334
 - 5.3.4 Coolants 335
 - 5.3.5 Retardants 335
 - 5.3.6 Dyes 335
 - 5.3.7 Color Intensifiers 335
 - 5.3.8 Moderators 335
 - 5.4 Important Characteristics of Ingredients for Pyrotechnic Formulations 336
 - 5.4.1 Density 336
 - 5.4.2 Hygroscopicity 337
 - 5.4.3 Melting and Boiling Points and Decomposition Temperatures 338
 - 5.4.4 Oxygen Content of Oxidizers 339
 - 5.4.5 Thermal Conductivity of Fuels and Containers 339
 - 5.4.6 Nature of Combustion Products 339
 - 5.4.7 Toxicity of Ingredients 340
 - 5.5 Types of Pyrotechnic Formulations 341
 - 5.5.1 Illuminating Formulations 341
 - 5.5.1.1 Chemical Nature of Fuel and Oxidizer, Their Proportions and Particle Size 342
 - 5.5.1.2 Formulations of Tracers 346
 - 5.5.1.3 Photoflash Formulations 347
 - 5.5.1.4 Signal Formulations 347
 - 5.5.1.5 Infrared Flare Formulations 348
 - 5.5.1.6 Some Resins for Illuminating Formulations 351
 - Liquid Polysulfides 351
 - Epoxy-Liquid Polysulfide Blends 352
 - Vinyl Acetate Alcohol Resins 352
 - 5.5.2 Delay Formulations 354
 - 5.5.2.1 Requirements of an Ideal Delay Formulation 355
 - 5.5.2.2 Factors Affecting the Performance of Delay Formulations 355
 - 5.5.2.3 Types of Delay Formulations 356
 - Gas-producing (Slagless) Delay Formulations 356
 - Gasless Delay Formulations 357

5.5.3	Smoke Formulations	358
5.5.3.1	Requirements for Smokes	359
5.5.3.2	Classification of Smokes	359
5.5.3.3	Types of Smoke Agents	360
5.5.3.4	Colored Smokes	362
5.5.3.5	Lachrymatory Smokes	364
5.5.3.6	Non-toxic and Eco-friendly Smokes	364
5.5.3.7	Infrared Screening Smokes	365
5.5.3.8	Chemistry of Phosphorus	367
	Stability of Red Phosphorus	369
	Applications for Red Phosphorus	370
5.5.4	Incendiary Formulations	373
5.5.4.1	Characteristics of Incendiary Materials	374
	Essential Characteristics	374
	Desirable Characteristics	374
5.5.4.2	Liquid Incendiaries	375
5.5.4.3	Solid Incendiaries	376
5.5.4.4	Chemistry of Napalm	379
5.6	Performance Assessment of Pyrotechnic Formulations	381
5.6.1	Ignition Temperature	381
5.6.2	Mechanical Properties	381
5.6.3	Moisture Absorption	381
5.6.4	Heat Output and Gas Volume	382
5.6.5	Luminous Intensity	382
5.6.6	IR Intensity	383
5.6.7	Burning Rate	384
5.6.8	Screening Performance of Smokes	385
5.6.8.1	Total Obscuring Power	385
5.6.8.2	Yield Factor (Y)	386
5.6.8.3	Mass Extinction Coefficient (α)	386
5.6.8.4	Obscuration Effectiveness	387
5.7	Life of Ammunition with Pyrotechnic Devices	387
5.8	Nanomaterials: Various Aspects and Use in HEM Formulations	389
5.8.1	Synthesis of Nanomaterials	390
5.8.1.1	Physical Methods	390
5.8.1.2	Chemical Methods	391
5.8.2	Carbon Nanotubes	393
5.8.2.1	Synthesis of CNTs	393
5.8.2.2	Some Properties and Applications of CNTs	394
5.8.3	Nanosized Fuels	394
5.8.3.1	Nano-Aluminum Powder	394
5.8.3.2	Other Nanometal Powders	396
5.8.4	Nano-oxidizers	397
5.8.5	General Properties of Nanomaterials	398
5.8.6	Nanomaterials for Pyrotechnic Formulations	398
5.8.7	Nanomaterials for Propellant Formulations	400

5.8.8	Nanomaterials for Explosive Formulations	401
5.9	Recent and Future Trends in Pyrotechnics	401
5.9.1	Energetic Binders, Plasticizers and Oxidizers	401
5.9.2	Exotic Salts of Lithium, Rubidium and Caesium and their Formulations	402
5.9.3	Dinitramide Salts of Alkali Metals and Their Formulations	403
5.9.4	Moisture Resistant Coatings for Metal Powders	404
5.9.5	New Fuels as Substitute for Charcoal	405
5.9.6	High Nitrogen Content-High Energy Materials for Pyrotechnic Formulations	406
	References	406
6	Explosive and Chemical Safety	413
6.1	Safety	413
6.2	Explosive Safety	414
6.2.1	UN Classification of Dangerous Goods and Hazardous Chemicals	416
6.2.1.1	Hazard Divisions	417
6.2.1.2	Compatibility Groups for Explosives and Ammunition	420
6.2.1.3	Hazard Classification	422
6.3	Fire Safety	422
6.3.1	Fire Divisions	423
6.3.2	Classes of Fires, Fire Extinguishers and Fire Fighting	424
6.3.2.1	Classes of Fires	425
6.3.2.2	Designations and Ratings of Fire Extinguishers	425
6.3.2.3	Fire-fighting Procedures	425
6.4	Safety Aspects for Transportation of Explosives and Ammunition	427
6.5	Safety Aspects for Storage of Explosives and Ammunition	428
6.6	Safety Aspects for Handling of Explosives and Ammunition	432
6.7	Static Electricity Hazards	433
6.8	Extremely Insensitive Detonating Substances and Ammunition	435
6.9	Hazard and Risk Analysis	438
6.9.1	Hazards and Operability (HAZOP)	438
6.9.2	Hazard Analysis (HAZAN)	439
6.10	Chemical Safety	439
6.11	Prevention and Elimination of Explosions, Accidents and Fires	439
6.11.1	Operations and Organization	440
6.11.2	Honor the Explosives	441
6.11.3	Use of Personal Protective Equipment	442
6.11.4	Cleanliness and Good Housekeeping	443
6.11.5	Waste Collection and Disposal	444
6.11.6	Training	445
	References	446
	Index	449