Jai Prakash Agrawal

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High Energy Materials

Propellants, Explosives and Pyrotechnics

Jai Prakash Agrawal

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This book is dedicated to my revered spiritual teacher
His Holiness Sri Sri Ravi Shankar
Founder, Art of Living and
The International Association for Human Values

Foreword

There are several books dealing with explosives, propellants and pyrotechnics, but much of the latest information on High Energy Materials (HEMs) of recent origin is scattered in the literature as research/review papers. This book is the first of its kind in which the knowledge on materials hitherto accumulated over the past 50 years in the literature has been carefully blended with latest developments in advanced materials, and articulated to highlight their potential from the point of view of end-use.

This book contains six chapters. While chapter one of this book introduces the subject in terms of salient/fundamental features of explosives, additional requirements for military explosives and their applications (military, commercial, space, nuclear & others), chapter 2 highlights the status of current and futuristic explosives in the light of their special characteristics. In addition, the future scope of research in this field has also been brought into focus in this chapter.

Chapter 3 essentially covers the important aspects of processing & assessment of explosives & their formulations. The propellants which are extensively used for various military & space applications are described in chapter 4. The major portion of this chapter is devoted to different aspects of high performance & eco-friendly oxidizers (ADN & HNF), novel binders such as butacene, ISRO Polyol and other state-of-the-art energetic binders [GAP, NHTPB; poly (NiMMO), poly (GlyN), etc.], energetic plasticizers (BDNPA/F, Bu-NENA, K-10, etc.) along with other ingredients which are likely to play a crucial role in augmenting the performance of futuristic propellants for various missions. The inhibition of rocket propellants & insulation of rocket motors along with their recent developments are also included in this chapter. Pyrotechnics which form an integral part of explosive and propellant related missions are discussed in chapter 5 whereas Explosive & Chemical safety which is of vital importance to all those working in the area of High Energy Materials (HEMs) is dealt in chapter 6.

Dr. J. P. Agrawal, who is an internationally acknowledged explosive & polymer scientist of repute, is a great writer with a large number of research publications to his credit. His rich experience and the international knowledge in High Energy Materials written in the book are valuable assets for the new generation of High Energy Materials scientists and rocket technologists.

High Energy Materials: Propellants, Explosives and Pyrotechnics. Jai Prakash Agrawal

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This book is the most comprehensive review of modern High Energy Materials and encompasses their important aspects with special reference to their end-use/applications. The language in the text is very lucid and easy to understand. The readers and researchers will be immensely benefitted by the book.

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Contents

High Energy Materials: Propellants, Explosives and Pyrotechnics. Jai Prakash Agrawal

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Preface

A new term ‘high energy materials’ (HEMs) was coined by the explosives community for the class of materials known as explosives, propellants and pyrotechnics in order to camouflage research on such materials. In other words, HEMs is a generic term used for this class of materials. HEMs, although generally perceived as the ‘devil’ during war and considered as an ‘evil’ during handling, transportation and storage, have proved to be an ‘angel’ due to their tremendous impact on the economy and industries and their innumerable applications in almost all walks of life. There are several books devoted to explosives, propellants and pyrotechnics but most of these either discuss their science in general or concentrate on some specific topic. Also, none of these books deals with recent developments in detail. While a number of excellent reviews have been published to bridge this knowledge gap, there is still no single text available in the literature on the subject, embedded with recent advances and future trends in the field of HEMs. This book, entitled ‘High Energy Materials: Propellants, Explosives and Pyrotechnics’ is a text which covers the entire spectrum of HEMs, including their current status, in a single volume and its objective is to fill this gap in the literature.

The modus operandi of this book is: (i) to provide the current status of HEMs which have been reported in the form of research/ review papers during the last 50 years but are scattered in the literature; (ii) to explore the potential of recently reported HEMs for various applications in the light of additional requirements in the present scenario, that is, cost-effectiveness, recyclability and eco-friendliness; (iii) to identify the likely thrust areas for further research in this area. Thus, the information on HEMs reported during the last 50 years but scattered all over the literature, will be readily available to researchers in a single book. Further, the level at which chemistry is pitched in this book is not as high as in many specialized books focused on a particular aspect of HEMs. Readers interested in better understanding and details of nitration chemistry are referred to the book ‘Organic Chemistry of Explosives’ (J.P. Agrawal and R.D. Hodgson) which provides detailed information on various synthetic routes for a wide range of HEMs and the chemistry involved. By including Chapter 1 on ‘Salient Features of Explosives’ and Chapter 6 on ‘Explosive and Chemical Safety’ along with chapters on Explosives, Propellants and Pyrotechnics, this book will certainly be of interest to both professionals and those with little or no background knowledge of the subject.

High Energy Materials: Propellants, Explosives and Pyrotechnics. Jai Prakash Agrawal

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This book is split into six well-defined chapters: Salient Features of Explosives, Status of Explosives, Processing and Assessment of Explosives, Propellants, Pyrotechnics, and Explosive and Chemical Safety. Further, the book includes an exhaustive bibliography at the end of each chapter (total references cited are more than 1000). It also provides the status of HEMs reported mainly during the last 50 years, including their prospects for military applications in the light of their physical, chemical, thermal and explosive properties. The likely development areas for further research are also highlighted. Accidents, fires and explosions in the explosive and chemical industries may be eliminated or minimized if the safety measures described in this book are implemented.

I hope that this book will be of interest to everyone involved with HEMs irrespective of their background: R&D laboratories, universities and institutes, production agencies, quality assurance agencies, homeland security, forensic laboratories, chemical industries and armed forces (army, navy and air force). This book will also be of immense use to organizations dealing with the production of commercial explosives and allied chemicals.

To sum up, I have endeavored to bring about a refreshing novelty in my approach to the subject while writing this volume and tried my best to include all relevant information on HEMs which could be of interest to military as well as commercial applications. However, it is just possible that a few interesting HEMs or some relevant information might have been overlooked unwittingly, for which I apologize. Readers are requested to inform me or the publisher about such omissions which would be greatly appreciated and included in the next edition of this book.

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Acknowledgments

During the course of writing this book, I have found the books and reports or reviews given under ‘Further Reading’ very interesting and invaluable. The writing of this book would have been difficult if it had not been for the text of these books and reports or reviews by pioneers of HEMs. I wish to express my sincere thanks to the authors and publishers of the books, reports and reviews listed under the heading ‘Further Reading’ at the end of this section.

The Department of Science and Technology (DST), Government of India sponsored a project to me under Utilization of Scientific Expertise of Retired Scientists Scheme to write this book, for which I am grateful to them. I would like to thank Dr. A. Subhananda Rao, Director, HEMRL for providing the office and library facilities. I acknowledge with thanks the help and support provided by all officers and staff of the Technical Information Resource Center, HEMRL during the entire period of this project. I also thank Dr. A.L. Moorthy, Director, Defence Scientific Information and Documentation Centre (DESIDOC), Delhi and his colleagues for providing library support.

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High Energy Materials: Propellants, Explosives and Pyrotechnics. Jai Prakash Agrawal

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respectively, followed by technical discussions. The support in terms of providing literature on SFIO by Dr. B.M. Kosowski, MACH I, USA and Butacene 800 by Dr. B. Finck, SNPE, France is also acknowledged with thanks. I thank Mr. M.C. Uttam, Ex.-Dy. Director, VSSC for providing some details about space applications of explosives. I would also like to thank Professor J.E. Field, Dr. S.M. Walley, University of Cambridge, UK, Dr. R.D. Hodgson, Health and Safety Laboratory, UK, Mr. M. Anbunathan, Ex-Chief Controller of Explosives, Nagpur, Dr. S.M. Mannan, Controller of Explosives and Dr. R.P. Singh, Scientist, NCL for providing valuable information and support from time to time.

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Abbreviations

AA	Adipic acid
AAT	Ammonium azotetrazolate
ADN	Ammonium dinitramide
ADNBF	7-Amino-4,6-dinitrobenzofuroxan
ADPA	American Defense Preparedness Association (now part of National Defense Industrial Association)
AFX	Air force explosive
AIAA	American Institute of Aeronautics and Astronautics
AMCOM	(US Army) Aviation Missile Command
AMM	Activated monomer mechanism
AMMO	3-Azidomethyl-3-methyloxetane
AN	Ammonium nitrate
ANFO	Ammonium nitrate–Fuel oil
ANTA	3-Amino-5-nitro-1,2,4-triazole (French abbreviation ANT)
AP	Ammonium perchlorate
APC	Ammunition protective coating
APP	Aerospace propulsion products
ARC	Atlantic Research Corporation
ARDE	Armament Research & Development Establishment
ARDEC	(US Army) Armament Research & Development and Engineering Center
ARX	Australian research explosive
ASA	Azide-styphnate-aluminum formulation (based on lead azide, lead styphnate & Al powder)
ASLV	Augmented satellite launch vehicle
ASTM	American Society for Testing & Materials
AT	5-Aminotetrazole
A/T	Anti-tank (missile)
ATCP	Aquotetramine cobalt perchlorate
ATEC	Acetyl triethyl citrate
AWRE	Atomic Weapons Research Establishment, UK
BA	Bonding agent
BAEA	Bis (2-azidoethyl) adipate

High Energy Materials: Propellants, Explosives and Pyrotechnics. Jai Prakash Agrawal

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BAM	Bundesanstalt fur Materialprufung, Germany
BAMO	3,3- Bis (azidomethyl) oxetane
BCEA	Bis(2-chloroethyl) adipate
BCMO	3,3-Bis(chloromethyl) oxetane
BDNPA	Bis (2,2-dinitropropyl) acetal
BDNPF	Bis (2,2-dinitropropyl) formal
BDNPA/F	Bis (2,2-dinitropropyl) acetal/formal
BDO	1,4-Butanediol
B-GAP	Branched-glycidyl azide polymer
BLA	Basic lead azide
BLASA	Basic lead azide-styphnate-aluminum formulation (based on BLA, lead styphnate & Al powder)
BLS	Basic lead salicylate
BNCP	Tetraamine-cis-bis(5-nitro-2H-tetrazolato-N^2) cobalt perchlorate
BoE	Bureau of Explosives
BoM	Bureau of Mines
BRM	Burn-rate modifier
BS	Bond strength
BSS	British sieve size
BTAs	Bitetrazole amines
BTATNB	1,3-Bis(1,2,4-triazolo-3-amino)-2,4,6-trinitrobenzene
BTDAONAB	*N,N′*-Bis(1,2,4-triazol-3-yl)-4,4′-diamino-2,2′,3,3′,5,5′,6,6′-octanitroazobenzene
BTTN	1,2,4-Butanetriol trinitrate
Bu-NENA	Butyl-*N*-(2-nitroxyethyl) nitramine
BX	Booster explosive
CA	Cellulose acetate
CAB	Cellulose acetate butyrate
CAP	Cellulose acetate propionate
CC	Copper chromite
CCCs	Combustible cartridge cases
CE	Composition exploding
CHDI	1,4-Cyclohexyl diisocyanate
CL-20	2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane(HNIW)
CMC	Carboxy methylcellulose
CN	ω-chloroacetophenone
CNAD	Conference of National Armament Director
CNSL	Cashew nut shell liquid
CNTs	Carbon nanotubes
CO	Coconut oil or Castor oil
CP	1-(5-Cyanotetrazolato)pentaamine cobalt(III) perchlorate chloropolyester
CPB	Chloropolyester blend
CPM	Chloropolyester based on mixed glycols

CPX-413	UK's Extremely Insensitive detonating composition (EIDC) based on NTO, HMX, Poly(NIMMO) & K-10 plasticizer
CR	Dibenz(b,f)-1,4-oxazepine
CS	*O*-chlorobenzylidene malononitrile
CTCN	Carbonato tetraamine cobalt(III) nitrate
CTPB	Carboxy-terminated polybutadiene
CV	Closed vessel
CVC	Chemical vapor condensation
CVD	Chemical vapor deposition
CVF	Continuously variable filter
DAAT$_z$	Diamino azobistetrazine
DAC	Defense Ammunition Centre
DADE/DADNE	1,1-Diamino-2,2-dinitroethylene (FOX-7)
DADNBF	5,7-Diamino-4,6-dinitrobenzofuroxan
DADNPO	3,5-Diamino-2,6-dinitropyridine-*N*-oxide
DANPE	1,5-Diazido-3-nitrazapentane
DANTNP	5-Nitro-4,6-bis(5-amino-3-nitro-1H-l,2,4-triazole-l-yl) pyrimidine
DATB	1,3-Diamino-2,4,6-trinitrobenzene
DB	Double-base
DBP	Dibutyl phthalate
DBTDL	Dibutyl tin dilaurate
DC	Direct current
DCBs	Ditch-cum-bunds
DDM	4,4′-Diaminodiphenyl methane
DDNP(Dinol)	Diazo dinitrophenol
DDS	4,4′-Diaminodiphenyl sulfone
DDT	Deflagration-to-detonation transition
DEAPA	Diethyl aminopropylamine
DEG	Diethylene glycol
DEGDN/DEGN	Diethylene glycol dinitrate
DEP	Diethyl phthalate
DERA	Defence Evaluation Research Agency, UK
DHT$_z$	Dihydrazino tetrazine
DINA	*N*-Nitrodiethanolamine dinitrate
DINGU	1,4-dinitroglycoluril
DIPAM	3,3′-Diamino-2,2′,4,4′,6,6′-hexanitrodiphenyl
DLA	Dextrinated lead azide
DMAZ	2-(Dimethylamino) ethyl azide
DMF	Dimethyl formamide
DMSO	Dimethyl sulfoxide
DNAF/DDF	4,4′-Dinitro-3,3′-diazenofuroxan
DNAN	2,4-Dinitroanisole
DNBF	4,4′-Dinitro-3,3′-bifurazan
DNNC	1,3,5,5-Tetranitro hexahydropyrimidine (French abbreviation)

DNP	Dinitropiperazine
DNPA	Dinitropropyl acrylate
DNPOH	2,2-Dinitropropanol
DNT	Dinitrotoluene
DOA	Dioctyl adipate
DoE	Department of Energy
DOP	Dioctyl phthalate
DOS	Dioctyl sebacate
DP/P_{CJ}	Detonation pressure
DPA	Diphenyl amine
DPO	2,5-Dipicryl-l,3,4-oxadiazole
DRA	Defence Research Agency, UK
DRDO	Defence Research & Development Organization, India
DREV	Defence Research Establishment Valcartier, Canada
DSC	Differential scanning calorimetry
DTA	Differential thermal analysis
	Diethylene triamine
DTG	Derivative thermogravimetric analysis
E	Elongation
Ea	Activation energy
EA	Edgewood Arsenal, MD
EBW	Exploding bridge wire
EC	Ethylcellulose
ECH	Epichlorohydrin
E_D	Explosion delay/Induction period
EDC	Explosive development composition
EED	Electro-explosive devices
EEW	Electro-explosion of wire
EFP	Explosively formed projectiles
EGA	Evolved gas analysis
EGBAA	Ethylene glycol bis(azidoacetate)
EGDN	Ethylene glycol dinitrate
EIDC	Extremely insensitive detonating composition
EIDS	Extremely insensitive detonating substance
EIR	Extreme infrared
EMs	Energetic materials
EO	Ethylene oxide
EP	Elastopolyester
EPA	European Production Agency
EPDM	Ethylene-propylene-diene monomer
E-PS	Epoxy resin-liquid polysulfide(blend)
EPX	A nitramine plasticizer
ERA	Explosive reactive armor
ERDE	Explosives Research & Development Establishment
ERDL	Explosives Research & Development Laboratory, India

ERL	Explosives Research Laboratory
ESA	European Space Agency
ESCA	Electron spectroscopy for chemical analysis
ESD	Electrostatic discharge
Estane-5703	Polyurethane binder of B.F. Goodrich Company, USA
ESTC	Explosives Storage & Transport Committee
E_T	Explosion temperature
ETPE	Energetic thermoplastic elastomer
EURENCO	European Energetics Corporation
F	Force constant (in gun propellant)
FAEs	Fuel–air explosives
FCPM	Flexible chloropolyester based on mixed glycols
FIR	Far Infrared
FLSCs	Flexible linear shaped charges
FM	Symbol for titanium tetrachloride (CWA-Chemical Warfare Agent)
FOI	Swedish Defence Research Agency (old Swedish name is FOA)
F of I	Figure of Insensitivity
FOL	Fuels, oils & lubricants
FOX-7	1,1-Diamino-2,2-dinitroethylene(DADE/DADNE) [FOI eXplosive]
FOX-12	*N*-Guanylurea dinitramide(GUDN) [FOI eXplosive]
f.p.	Freezing point
FPC-461	Copolymer of vinyl chloride & chlorotrifluoroethene
FR	Fuel-rich(propellant)
FS	US design for smoke-producing liquid mixture of SO_3 and SO_3HCl(CWA)
FSAPDS	Fin stabilized armor piercing discarding sabot
GAM	Gelatin, azide, molybdenum disulfide
GAP	Glycidyl azide polymer
GAT	Guanidinium azotetrazolate
GlyN	Glycidyl nitrate
GO	Groundnut oil
GP	General purpose
GPC	Gel permeation chromatography
GSLV	Geo-synchronous satellite launch vehicle
GTO	Geo-synchronous transfer orbit
GUDN	*N*-Guanylurea dinitramide (FOX-12)
HAAP	Holston Army Ammunition Plant, USA
HAB	Hexakis(azidomethyl) benzene
HAF	High altitude fuel
HAN	Hydroxyl ammonium nitrate
HAT	1,4,5,8,9,12-hexaazatriphenylene
HAZAN	Hazard analysis

HAZOP	Hazards and operability
HBIW	2,4,6,8,10,12-Hexabenzyl-2,4,6,8,10,12-hexaazaisowurtzitane
HBX	High blast explosive (Torpex type explosives)
HCB	Hexachlorobenzene
HCE	Hexachloroethane
HD	Hazard Division
HDT	Heat deflection temperature
HE	High explosive
HEAT	High explosive anti-tank
HEI	High explosive incendiary
HEMs	High energy materials
HEMRL	High Energy Materials Research Laboratory (Ex-ERDL), India
HESH	High explosive squash head
HHTPB	Hydrogenated hydroxy terminated polybutadiene
HMDI/HDI	Hexamethylene diisocyanate
HMX	High melting explosive or Her Majesty's explosive
HNAB	2,2′,4,4′,6,6′-Hexanitroazobenzene
HNC	Hexanitrocubane
HNC-HEMs	High nitrogen content – high energy materials
HNDPA	Hexanitrodiphenylamine
HNF	Hydrazinium nitroformate
HNIW	2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane(CL-20)
H-NMR	Hydrogen(proton) nuclear magnetic resonance
HNS	Hexanitrostilbene
HNTCAB	Hexanitrotetrachloroazobenzene
HP	Halopolyester
HpNC	Heptanitrocubane
HTA	A formulation based on HMX, TNT & Al powder
HTD	High temperature decomposition
HTNR	Hydroxy-terminated natural rubber
HTPB	Hydroxy-terminated polybutadiene
HyMMO	3-Hydroxymethyl-3-methyloxetane
Hytrel	Thermoplastic elastomer manufactured by Du Pont,USA
IBR	Inverse burning rate
ICT	Fraunhofer Institut Chemische Technologie, Germany
IDP	Isodecyl pelargonate
IGC	Inert gas condensation
IHEs	Insensitive high explosives
IM	Insensitive munitions
IMADP	Insensitive Munitions Advanced Development Programme
INSAT	Indian National Satellite
IPA	Isophthalic acid
IPDI	Isophorone diisocyanate
IPS	International Pyrotechnic Seminar

IQD	Inside quantity-distance
IR	Infrared
I-RDX	Insensitive (low sensitivity) RDX
IRFNA	Inhibited red fuming nitric acid
IRS	Indian Remote Sensing
ISAT(A)	Intensified Standard Alternating Trials (different temperatures, & relative humidities and time cycles)
ISAT(B)	
I_{sp}	Specific impulse
ISRO	Indian Space Research Organization
J	Joule
JANNAF	Joint Army-Navy-NASA-Air Force
JASSM	Joint air-to-surface stand-off missile
JSG	Joint Services Guide
K-10	Energetic plasticizer, a mixture of 2,4-dinitroethylbenzene and 2,4,6-trinitroethylbenzene (also known as Rowanite 8001)
Kel-F800	Copolymer of vinylidene and hexafluoropropylene or chlorotrifluoroethylene (Trade name of 3M Company)
LA	Lead azide
LANL	Los Alamos National Laboratory
L/D	Length/diameter(ratio)
LGP	Liquid gun propellant
LLNL	Lawrence Livermore National Laboratory
LOVA	Low vulnerability ammunition
LOX	Liquid oxygen
LPRE	Liquid propellant rocket engine
LS	Lead-2,4,6-trinitroresorcinate(Lead styphnate)
LTD	Low temperature decomposition
LTPB	Lactone-terminated polybutadiene
LX-19	CL-20 based formulation analog of LX-14(HMX/Estane) formulation
MAn	Maleic anhydride
MAPI	Mine anti-personnel inflammable
MAPO	Tris[1-(2-methylaziridinyl) phosphine oxide]
MAPP	Mixture of methyl acetylene, propadiene and propane
MATB	Monoamino-2,4,6-trinitrobenzene
MDF	Mild detonating fuse
MDI	4,4′-Methylenediphenyl diisocyanate
ME	Military explosive
MEK	Methyl ethyl ketone (peroxide as a catalyst)
Methyl Tris-X	Methyl analog of Tris-X
MF	Mercury fulminate
MIC	Metastable Intermolecular Composites
MIR	Mid infrared
mJ	milliJoule

MK	Marked
MMH	Monomethyl hydrazine
MMW	Millimeter wave
$\overline{M}_n$	Number average molecular weight
MNT	Mercuric-5-nitrotetrazole Mononitrotoluene
m. p.	Melting point
MPD	*m*-phenylenediamine
MSIAC	Munitions Safety Information Analysis Center
MTN	Metriol trinitrate
MTV	Magnesium, Teflon, Viton (based decoy flares)
MURAT	Munitions a risques attenues (French)
MV	Muzzle velocity
$\overline{M}_w$	Weight average molecular weight
MW	Multi-walled (carbon nanotubes)
NASA	National Aeronautics and Space Administration, USA
NATO	North Atlantic Treaty Organization
NAWC	Naval Air Warfare Center, USA
NB	Nitramine-base (propellant)
NBC	Nuclear, biological & chemical (warfare)
NC	Nitrocellulose
NDI	1,5-Naphthalene diisocyanate
2-NDPA	2-Nitrodiphenylamine
NENA	Nitroxyethyl nitramine
NEQ	Net explosive quantity
NG	Nitroglycerine
NGB	Nitroglycerine ballistite (ballistite propellant containing high NG)
NHN	Nickel hydrazine nitrate
NHP	Non-halopolyester
NHTPB	Nitrated hydroxy-terminated polybutadiene
Nif	Nitrofurazanyl
NIMIC	NATO Insensitive Munitions Information Center, USA (now MSIAC)
NIR	Near infrared
NMs	Nanomaterials
NMP	1-Methyl-2-pyrrolidinone (*N*-methyl pyrrolidinone)
NMR	Nuclear magnetic resonance
NOL	Naval Ordnance Laboratory, USA
NONA	2,2′,2″,4,4′,4″,6,6′,6″-Nonanitroterphenyl
NP	Nitronium perchlorate
NR	Natural rubber
NSWC	Naval Surface Warfare Center, USA
NT	Nitrotetrazole
NTO	3-Nitro-1,2,4-triazol-5-one

NUP	Novel unsaturated polyester
NQ	Nitroguanidine
OAC	Octaazacubane
OB	Oxygen balance
OB_{100}	Oxidant balance
ONC	Octanitrocubane
ONTA	Oxynitrotriazole
OQD	Outside quantity-distance
PA	Picatinny Arsenal, USA
PADNT	4-Picrylamino-2,6-dinitrotoluene
PAPI	Polyaryl polyisocyanate
PAT	5-Picrylamino-1,2,3,4-tetrazole
PAThX	CL-20 based explosive formulations which are more powerful than the analogous HMX formulations ,developed by Picatinny Arsenal, USA
PATO	3-Picrylamino-1,2,4-triazole
PAVA	Pelargonic acid vanillylamide
PAX	Picatinny Arsenal explosive
PB	Polybutadiene
PBAN	Poly(butadiene-acrylic acid-acrylonitrile)
PBNA	*N*-Phenyl-β-naphthylamine
PBX	Plastic bonded explosive
P_{CJ}	Chapman–Jouguet pressure
PDDN	1,2-Propanediol dinitrate
PECH	Poly(epichlorohydrin)
PEG	Polyethylene glycol
PETN	Pentaerythritol tetranitrate
PETRIN	Pentaerythriol trinitrate
PGDN	1,2-Propylene glycol dinitrate
P&I	Process & Instrumentation
PL-1	2,4,6-Tris(3,5-diamino-2′,4′,6′-trinitrophenylamino)-1,3,5-triazine
PNC	Pentanitrocubane
p-NMA	para-nitromethylaniline
PNP	Polynitropolyphenylene
PO	Propylene oxide
PPG	Poly(propylene glycol)
POL	Petrol, oils & lubricants
Poly(AMMO)	Poly(3-azidomethyl-3 methyloxetane)
Poly(BAMO)	Poly[3,3-bis(azidomethyl) oxetane]
Poly(CDN)	Nitrtated cyclodextrin polymers
Poly(GlyN)	Poly(glycidyl nitrate)
Poly(NiMMO)	Poly(3-nitratomethyl-3-methyloxetane)
POT	Pin oscillographic technique(for VOD determination)
PRA	Probabilistic risk assessment

PS	Polysulfide(rubber)
PSAN	Phase stabilized ammonium nitrate
PSLV	Polar Satellite Launch Vehicle
PTFE	Poly(tetrafluoroethylene)
PU	Polyurethane
PVB	Polyvinyl butyral
PVC	Polyvinyl chloride
PVN	Polyvinyl nitrate
PYX	2,6-Bis(picrylamino)-3,5-dinitropyridine
Q-D	Quantity-distance
RARDE	Royal Armament Research & Development Establishment,UK
R-C	Resistance capacitance
RCC	Reinforced cement concrete
RCL	Recoilless
R&D	Research & development
RDX	Research department explosive
RESS	Rapid expansion of supercritical solution
RFNA	Red fuming nitric acid
RH	Relative humidity
ROWANEX	Royal Ordnance Waltham Abbey New Explosive
RP	Red phosphorus
RS-RDX	Reduced sensitivity RDX
SAT	5,5′-Styphnylamino-1,2,3,4-tetrazole
SB	Single-base
SCB	Semiconductor bridge
SCE	Supercritical extraction
SDRA	Swedish Defence Research Agency
SFIO	Superfine iron oxide
SF_5	Pentafluorosulfonyl
SIN	Substance identification number
SLA	Service lead azide
SLV	Satellite launch vehicle Space launch vehicle
SMS	Site mixed slurry
SNPE	Societe Nationale des Poudres et Explosifs, France
SOP	Safe operating procedures
SR	Secret research
SS	Stainless steel
SSO	Sun-synchronous orbit
STA	Simultaneous thermal analysis
STANAG	Standardization Agreement (of NATO)
Stp	Standard temperature and pressure
SW	Single-walled (carbon nanotubes)
Sym. TCB	Symmetrical trichlorobenzene
T	Absolute temperature
TA	Triacetin

TACOT	Tetranitro dibenzo-l,3a,4,4a-tetraazapentalene
TADAIW	Tetraacetyl diamine isowurtzitane
TADBIW	Tetraacetyl dibenzyl isowurtzitane
TADFIW	Tetraacetyl diformal isowurtzitane
TADNIW	Tetraacetyl dinitroso isowurtzitane
TAGAT	Triaminoguanidinium azotetrazolate
TAGN	Triaminoguanidine nitrate
TATB	1,3,5-Triamino-2,4,6-trinitrobenzene
TATNB	1,3,5-Triazido-2,4,6-trinitrobenzene
TB	Triple-base
TBP	Triphenyl bismuth
TBPAn	Tetrabromophthalic anhydride
TCB	Trichlorobenzene
TCP	Tricresyl phosphate
TCPAn	Tetrachlorophthalic anhydride
TCTNB(Sym.)	1,3,5-Trichloro-2,4,6-trinitrobenzene
TDI	Toluene diisocyanate
TEA	Triethyl aluminum
TEAN	Triethanolamine nitrate
Teflon (PTFE)	Poly(tetrafluoroethylene) (Trade name of Du Pont)
TEG	Triethylene glycol
TEGDN	Triethylene glycol dinitrate
TEM	Transmission electron microscope
TET	Triethylene tetramine
T_g	Glass transition temperature
TGA	Thermogravimetric analysis or thermogravimetry
THF	Tetrahydrofuran
TMD	Theoretical maximum density
TMETN	1,1,1-Trimethylolethane trinitrate
TMHI	1,1,1-Trimethyl hydrazinium iodide
TMOS	Tetramethoxysilane
TMP	Trimethylol propane
TNA	1,3,5,7-Tetranitroadamantane
TNABN	2,5,7,9-Tetranitro-2,5,7,9-tetraazabicyclo [4.3.0] nonane-8-one
TNAD	Trans-l,4,5,8-tetranitro-l,4,5,8-tetraazadecalin
TNAZ	1,3,3-Trinitroazetidine
TNB	Trinitrobenzene
TNC	Tetranitrocubane
	Tetranitrocarbazole
TNDPDS	Tetranitrodiphenyl disulfide
TNGU	1,3,4,6-Tetranitroglycoluril (Sorgunyl, French)
TNO	Tetranitrooxanilide
TNO-PML	TNO-Prins Maurits Laboratory, The Netherlands(now a part of TNO Defence, Security and Safety)
TNPDU	Tetranitro propanediurea
TNPG	Trinitro phloroglucinol

TNT	Trinitrotoluene
TNTO	TNT & NTO based formulations
TOP	Tris(2-ethylhexyl) phosphate
TOP	Total obscuring power
TPE	Thermoplastic elastomer
TPM	N^2,N^4,N^6-Tripicrylmelamine
Tris-X	2,4,6-Tris(2-nitroxyethylnitramino)-1,3,5-triazine
TS	Tensile strength
UDMH	Unsymmetrical dimethylhydrazine
UF	Ultrafine(powder)
UK	United Kingdom
UL	Underwriters Laboratories
UNCOE	United Nations Committee of Experts
UNO	United Nations Organization
USA	United States of America
USSR	Union of Soviet Socialist Republics
UXBs	Unexploded bombs
UXO	Unexploded ordnance
VAAR	Vinyl acetate alcohol resin
Viton-A	Copolymer of vinylidene fluoride and hexafluoropropylene (Trade name of Du Pont)
VNS	Vicarious nucleophilic substitution
VOD	Velocity of detonation
VSSC	Vikram Sarabhai Space Centre
VST	Vacuum stability test
WP	White phosphorus
ZIOC	Zelinsky Institute of Organic Chemistry

Symbols

A	Frequency factor
C_p	Specific heat at constant pressure
C_v	specific heat at constant volume
$\mathbf{g}$	Acceleration due to gravity
I_{sp}	Specific impulse
n	Pressure exponent/index
R	Universal gas constant
Q	Heat of explosion
ρ	Density
η_b	Ballistic efficiency
η_p	Piezometric efficiency
γ	Specific heat ratio i.e C_p/C_v
α, β, γ, δ, $\in$	Polymorphic forms of explosives

1
Salient Features of Explosives

1.1
Introduction

Explosives are thought to have been discovered in the seventh century by the Chinese and the first known explosive was black powder (also known as gunpowder) which is a mixture of charcoal, sulfur and potassium nitrate. The Chinese used it as an explosive, propellant and also for fireworks. Subsequently, with the development of nitrocellulose (NC) and nitroglycerine (NG) in Europe, a new class of explosives viz. low explosives came into existence. As this new class of explosives burn slowly in a controlled manner giving out a large volume of hot gases which can propel a projectile, these low explosives were termed as propellants. The discovery of high explosives such as picric acid, trinitrotoluene (TNT), pentaerythritol tetranitrate(PETN), cyclotrimethylene trinitramine (research department explosive RDX), cyclotetramethylene tetranitramine (high melting explosive HMX) etc. which are more powerful but relatively insensitive to various stimuli (heat, impact, friction and spark), advocated their use as explosive fillings for bombs, shells and warheads etc. Similarly, by following the principle of gunpowder and in order to meet the requirements of military for special effects (illumination, delay, smoke, sound and incendiary etc.), formulations based on fuels, oxidizers, binders along with additives were developed and classified as pyrotechnics.

These three branches of explosives viz. explosives, propellants and pyrotechnics, were developed independently until the early 1990s and during this time, the number of reported explosives increased exponentially. In order to camouflage research on explosives, propellants and pyrotechnics, a new term ‘high energy materials’ (HEMs) was coined by the explosives community for them. Thus all explosives, propellants and pyrotechnics can be referred to as high energy materials (HEMs) or energetic materials (EMs). In other words, the other name of HEMs/EMs is explosives, propellants and pyrotechnics depending on their formulations and intended use. Nowadays, the term HEMs/EMs is generally used for any material that can attain a highly energetic state mostly by chemical reactions [1].

The ancient civilizations all over the globe used to carry out prodigious mining, quarrying and building projects by the use of forced human labor. The following examples are available in the literature in this regard.

High Energy Materials: Propellants, Explosives and Pyrotechnics. Jai Prakash Agrawal

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- War captives were used to hack out hundreds of miles of mines, irrigation canals and for other constructions by the ancient Egyptians.
- The inhabitants of the Aegean Island of Samos tunneled their way through rock for water supply in the sixth century BCE.
- A large number of temples and forts were carved out of the rocks in India and the Far East.
- Hannibal crossed the Alps by hacking out passageways with chisels and wedges.

Explosives provided ways and means to alleviate this drudgery. It was more efficient and economical to bring down rocks or do mining with the use of gunpowder, the first explosive, than by any other previous means. Explosives are generally associated with a destructive role but their important contributions are very often lost sight of. In fact, it was the power of explosives which made the great industrial revolution possible in Europe and also made the mineral wealth of earth available to mankind. Considerable technological progress in the development and applications of explosives has made it possible to move mountains, tame rivers, mine minerals from deep underground and also link continents and countries by roads and rails through difficult and hazardous terrain. Explosives continue to play an overwhelming role in the progress and prosperity of mankind right from the time of invention of black powder or gunpowder several centuries ago. In fact, some of today's fantastic engineering projects and exploration of space would have not been possible without the use of explosives [2].

Explosives, in a nutshell, generally perceived as 'devil' during war and considered as an 'evil' during processing, handling, transportation and storage, have proved to be an 'angel' due to their tremendous impact on economy and industries. Explosives have contributed enormously in improving the economy of many countries and their chemistry forms the basis of many well-known treatises [3–6].

1.2
Definition

A study of the literature suggests that an explosive may be defined in one of the following ways:

1) An explosive is a substance which, when suitably triggered, releases a large amount of heat and pressure by way of a very rapid self-sustaining exothermic decomposition reaction. The temperature generated is in the range of 3000–5000 °C and the gases produced expand 12 000–15 000 times than the original volume. The entire phenomenon takes place in a few microseconds, accompanied by a shock and loud noise.
2) An explosive is a chemical substance or a mixture of chemical substances, which when subjected to heat, percussion, detonation or catalysis, undergoes

a very rapid decomposition accompanied with the production of a large amount of energy. A large volume of gases, considerably greater than the original volume of the explosive, is also liberated.

3) An explosive is a substance or device which produces, upon release of its potential energy, a sudden outburst of gases thereby exerting high pressure on its surroundings.

Thus there are two important aspects of a chemical reaction which results in an explosion.

1.2.1
Evolution of Heat

The generation of heat in large quantities accompanies every explosive chemical reaction. It is this rapid liberation of heat that causes the gaseous products of reaction to expand and generate high pressures. This rapid generation of high pressures of released gases constitutes explosion. It is worthwhile to point out that liberation of heat with insufficient rapidity does not cause an explosion. For example, although a pound of coal yields five times as much heat as a pound of nitroglycerine, coal cannot be described as an explosive because the rate at which it yields this heat is quite slow.

1.2.2
Rapidity of Reaction

Rapidity of reaction distinguishes an explosive reaction from an ordinary combustion reaction and therefore, an explosive reaction takes place with great speed. Unless the reaction occurs rapidly, thermally expanded gases are dissipated in the medium slowly, so that no explosion results. Again an example of wood or coal fire makes it clear. When a piece of wood or coal burns, there is an evolution of heat and formation of gases, but neither is liberated rapidly enough to cause an explosion.

This means that the fundamental features possessed by an explosive are:

1) Potential energy by virtue of its chemical constitution.
2) Rapid decomposition on suitable initiation.
3) Formation of gaseous products with simultaneous release of a large amount of energy.

In other words, investigation of explosives involves a study of these aspects. For example, an investigation of the potential energy involves study of thermochemistry of the chemical compound in question. Further, the power and sensitiveness of an explosive depend on properties such as ‘heat of formation’ and ‘heat of explosion’. An investigation of the feature (2) involves measurement of the rate of propagation of explosion waves and all phenomena in the proximity of detonating mass of the explosive. This rate of decomposition largely determines the pressure developed and is also the criterion for classification of explosives into 'high' and 'low' explosives. Lastly, investigation of feature (3) mentioned above involves study of reactions leading to explosion. The rates of individual reactions at different temperatures and pressures and equilibria established among various decomposition products may also be studied to understand the mechanism.

An explosive may be a solid (trinitrotoluene, TNT), liquid (nitroglycerine, NG) or gas (a mixture of hydrogen and oxygen). Also, it may be a single chemical compound (TNT), a mixture of explosive compounds [a mixture of TNT and ammonium nitrate (AN, NH_4NO_3)] or a mixture of two or more substances, none of which in itself needs be an explosive (gunpowder – mixture of charcoal, sulfur and potassium nitrate). The products of explosion are gases or a mixture of gases and solids or only solids. NG yields only gaseous products whereas black powder yields both gases and solids. On the other hand, all products are solids in the case of cuprous acetylide.

A comparatively fast reaction of a high explosive is called detonation whereas the slower reaction of low explosives is called deflagration or burning. Explosives may undergo burning, deflagration (fast burning: 300–3000 ms^{-1}) or detonation (5000–10 000 ms^{-1}) depending upon the nature of the explosive, mode of triggering, and confinement of the explosive etc. When initiation of decomposition of an explosive is set in by a flame, it simply burns. However, if confined, it burns at a faster rate and the phenomenon may ultimately transform to detonation. The detonation of an explosive can be achieved by the supply of shock energy in a quantum. Combustion is a slow phenomenon. For the combustion to be fast, oxygen should be in close contact with the fuel. A rapid combustion or detonation can be accomplished by close combination of the fuel and oxidizer elements within the same molecule as in the case of NG, TNT and RDX etc. Further, an explosion is considered to be a rapid form of combustion which occurs due to the oxidation of fuels with the participation of oxygen from the air.

1.3
Classification

Explosives are used for constructive as well as destructive purposes for both military and civil applications. There are several ways of classifying explosives and a few important ones are:

- according to their end-use for example, military explosives for military applications whereas civil explosives for commercial purposes;
- according to the nature of explosion for example, mechanical, nuclear or chemical;
- according to their chemical structure that is, the nature of bonds present in an explosive.

The classification of explosives is depicted in Figure 1.1 and their brief description is outlined below:

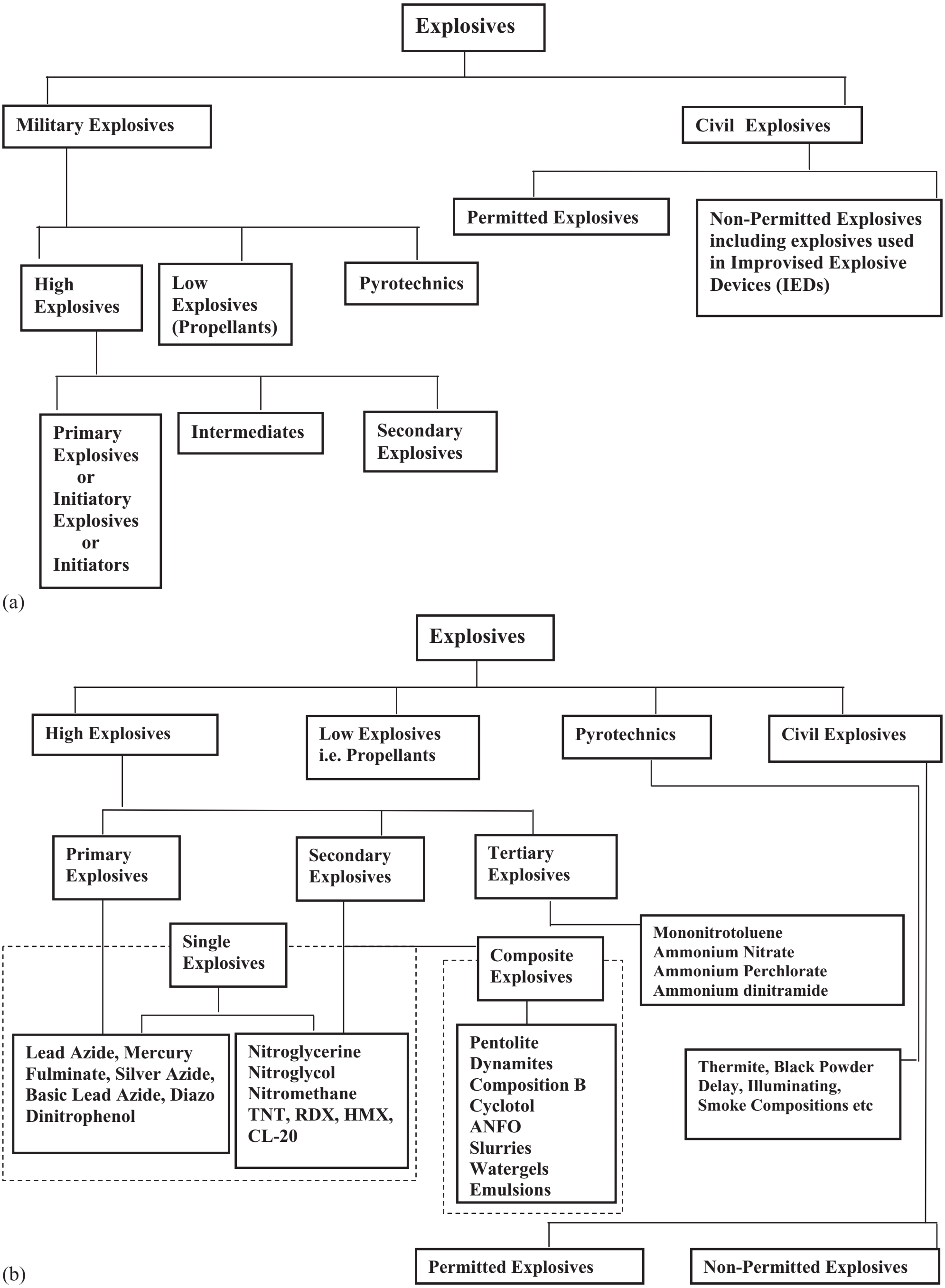


Figure 1.1 (a) Classification of explosives (according to their end-use). (b) Classification of explosives (according to nature of explosive/ingredient).

1.3.1
Military Explosives

Military explosives comprise explosives and explosive compositions or formulations that are used in military munitions (bombs, shells, torpedoes, grenades, missile or rocket warheads). The bulk charges (secondary explosives) in these munitions are insensitive to some extent and are, therefore, safe for handling, storage and transportation. They are set off by means of an explosive train consisting of an initiator followed by intermediates or boosters.

Military explosives must be physically and chemically stable over a wide range of temperatures and humidity for a long period of time. They must be reasonably insensitive to impact, such as those experienced by artillery shells when fired from a gun or when they penetrate steel armor. They are used for a number of applications. They are fired in projectiles and dropped in aerial time bombs without premature explosion. The raw materials necessary to manufacture such explosives must be readily available for production in bulk during wartime.

The chemical explosives are sub-divided into four main types: (i) detonating or high explosives; (ii) deflagrating or low explosives; (iii) pyrotechnics and (iv) civil or commercial explosives.

1.3.1.1 Detonating or High Explosives

These explosives are characterized by very high rates of reaction and generation of high pressures on explosion. They are usually sub-divided into (i) primary or initiatory explosives, (ii) secondary explosives and (iii) tertiary explosives.

(i) **Primary high explosives** are very sensitive materials and are easily exploded by the application of fire, spark, impact, friction etc. They are dangerous to handle and are used in comparatively small quantities. They are generally used in primers, detonators and percussion caps. Examples of primary explosives are lead azide (LA), mercury fulminate (MF), silver azide, basic lead azide(BLA) etc.

(ii) **Secondary high explosives** are explosives which are relatively insensitive to both mechanical shock and flame but explode with greater violence when set off by an explosive shock obtained by detonating a small amount of a primary explosive in contact with it. In other words, secondary high explosives require the use of a detonator and frequently a booster. PETN is often considered a benchmark explosive, with explosives that are more sensitive than PETN being classified as primary explosives.

A major difference between primary and secondary explosives arises from the fact that primary explosives are initiated to detonate by burning whereas secondary explosives are initiated to detonate by shock waves. Therefore, the most important property of a primary explosive is its ability to undergo a fast deflagration-to-detonation transition (DDT). Thus, fast DDT is the strength of primary explosives as well as their weakness. All other parameters being equal, the faster the DDT, the better the primary explosive. At the same time, fast DDT shows a weakness because accidental initiation of deflagration results in detonation.

(iii) **Tertiary explosives (also called blasting agents)** mainly consist of oxidizers such as ammonium nitrate (AN, NH_4NO_3), ammonium perchlorate (AP, NH_4ClO_4), ammonium dinitramide [ADN, $NH_4N\ (NO_2)_2$] and mononitrotoluene (MNT) etc. AN and AP are the prime examples. It is more difficult to initiate tertiary explosives by fire, impact or friction and, if initiated, they have a large critical diameter so that the propagation to mass detonation is much less likely than for secondary explosives. Tertiary explosives are so insensitive to shock that they cannot reliably be detonated by practical quantities of primary explosives and require an intermediate explosive booster of secondary explosive instead. These explosives, in pure form without fuel components, also have low explosion energies, only about a third of that of TNT. For the purpose of commercial transportation and storage, both AN and AP are classified as oxidizers and not as explosives. Contrary to the common belief, tertiary explosives have been the cause of some of the largest accidental explosions in history. The 1921 and 1947 AN explosions in Oppau and Texas respectively and the 1988 AP explosion at Henderson (Nevada) have taken by surprise all those locally involved with the material [7–9].

1.3.1.2 Deflagrating or Low Explosives

Low explosives differ from high explosives in their mode of decomposition. They burn slowly and regularly. The action is therefore less shattering. On combustion, low or deflagrating explosives evolve large volume of gases but in a controllable manner. Examples are black powder, smokeless powder and propellants: single-base (SB), double-base (DB), triple-base (TB), composite, composite modified DB, fuel rich etc. Propellants are combustible materials containing within themselves all the oxygen needed for their combustion and their main function is to impart motion to a projectile or missile. These are used for military applications and space exploration. Propellants only burn and do not generally explode or detonate. Propellants are initiated by a flame or spark and are converted from a solid to gaseous state relatively slowly [10].

In other words, high explosives detonate and hence are ideally suitable as shell and bomb fillers in order to give maximum demolition effect at the target. On the other hand, low explosives burn and are ideally suitable as propellant powders to expel projectiles from weapons. A high explosive would blow up the weapon because of its high reaction rate and shattering effect whereas a low explosive would be ineffective in reducing concrete fortifications or in obtaining proper shell fragmentation. TNT and other high explosives make excellent shell fillers and smokeless powder makes an excellent low explosive in the form of a propellant.

It is better to examine this difference between the detonation of a high explosive and the deflagration or burning of a low explosive more closely on a qualitative basis. Consider a point in a high explosive, initiated at one end as shown in Figure 1.2.

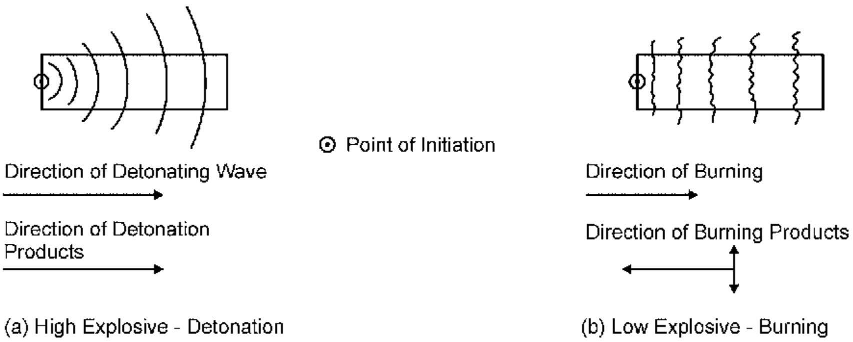


Figure 1.2 Detonation vs. burning for high and low explosives.

The explosive is consumed by the rapid physico-chemical transformation as the detonating wave travels away from the point of initiation. The products of detonation (usually gases) also travel in the same direction, so that there is a tendency to create a low pressure area behind the wave as well as high pressure established by the wave itself. This accounts for the fact that when large quantities of high explosives are detonated, such as are contained in 'blockbusters', the low pressure created may do as much damage as the direct blast effect and windows may break outwards toward the detonation outside of a dwelling. The speed of this detonating wave is called the rate of detonation; it varies from 3000 to 9500 ms^{-1}. The rate of detonation of a high explosive is one of its important properties and partly determines its application. Ordinary cast TNT has a rate of detonation of about 7000 ms^{-1}; many times faster than the velocity of sound. The initiator lead azide has a rate of detonation of about 3800 ms^{-1} whereas 50/50 pentolite has a rate of 7500 ms^{-1}.

Low explosives burn much faster than ordinary combustible materials such as wood or paper, but in much the same manner. Consider a low explosive initiated as in Figure1.2. The direction of burning is also away from the point of initiation, but the products of burning may move in any direction away from the burning surface, and they do not create a low pressure situation, like in detonation. The speed of the deflagration, or the rate of burning, depends upon many factors, such as the degree of confinement, area of the burning surface and composition of the low explosive. At the usual pressures existing in weapons, rate of burning is about 30–50 $cm\,s^{-1}$ or about 1/10 000 of the rate of detonation of high explosives.

Most explosives may deflagrate or detonate and are used in high and low explosive compositions. It means that a propellant can also detonate under extreme conditions. For example, nitrocellulose (NC) deflagrates if ignited but detonates if initiated by a booster. Also, in low or deflagrating explosives (black powder), the explosion propagates through the materials at subsonic speed through an accelerated burning or combustion process. On the other hand, in high explosives (TNT), the explosion propagates by a supersonic 'detonation', driven by the breakdown of the molecular structure of the explosive.

1.3.1.3 Pyrotechnics

Pyrotechnics may be considered as mixtures of materials capable of combustion when suitably initiated to produce a special effect. In most cases, pyrotechnic compositions consist of a fuel and an oxidizer together with a binder to give structural integrity and additives for imparting special effects.

- **Fuels** (Metallic/non-metallic): Aluminum (Al), chromium (Cr), magnesium (Mg), manganese (Mn), titanium (Ti), boron (B), silicon (Si) and sulfur (S) etc.
- **Oxidizers:** Chlorates, chromates, nitrates, oxides and perchlorates etc.
- **Binders:** (i) Natural (beeswax, paraffin wax, shellac and boiled linseed oil etc.) and (ii) man-made (Bakelite resin, polyester resin, polyvinyl chloride (PVC), chlorinated rubber, Thiokol rubber and epoxy resin etc).

The special effects provided by pyrotechnics can be categorized as

Special Effect	**Example**
i) Heat	igniters and incendiaries
ii) Light	illumination, tracking, signaling and decoys
iii) Smoke	signaling and screening
iv) Sound	signaling and distraction.

As shown in Figure 1.1a, depending on whether the explosive consists of a single molecular species or is a mixture of several species, it is called ‘single explosive’ or ‘composite explosive’. The examples of single explosive are LA, MF, NG, TNT, RDX, HMX and CL-20 etc. On the other hand, composite explosive may consist of: (i) a mixture of several single explosives such as pentolite (a mixture of PETN and TNT); (ii) a mixture of one or more single explosive with added fuel or oxidizer such as dynamite or (iii) a mixture of a fuel and an oxidizer such as ANFO (a mixture of AN and fuel oil). Some important characteristics of high explosives, low explosives and pyrotechnics are given in Table 1.1.

1.3.2
Civil Explosives

Civil explosives are also known as commercial or blasting explosives and are typically used for mining, quarrying, construction and tunnel building. They are chemical compositions, which detonate when initiated by high explosive primers or boosters or directly by detonators. They are relatively insensitive to shock, friction or impact.

Civil explosives are further sub-divided into permitted or permissible explosives and non-permitted explosives. Two types of civil explosives namely ammonium nitrate–fuel oil (ANFO) and emulsion explosives dominate the rock blasting scene in the USA.

1.3.2.1 Permitted or Permissible Explosives

A permitted or permissible explosive is one that has been allowed for use in gas- or dust-filled coal mines. These explosives produce strong detonation but

Table 1.1 Some characteristics of high explosives, low explosives (propellants) and pyrotechnics.

Sr No	Characteristics	High explosives	Low explosives (Propellants)	Pyrotechnics
1	Hazard classification			
	H Class	1	1	1
	H Division	1.1	1.3	1.3
	H Sub-Division	1.1.1	1.1.3	1.1.3
2	Method of initiation	Primary: By ignition Secondary: By booster/detonator	By ignition	By ignition
3	Time for complete conversion of explosive to gaseous products	Microseconds	Milliseconds	Microseconds to seconds
4	Velocity of consumption of explosive grains	1.0 to 10 km s^{-1}	04 to 50 mm s^{-1}	(i) Flash Pyros – Extremely high (ii) Illuminating Pyros: 2–5 mm s^{-1} (iii) Delay Pyros: 1–70 mm s^{-1} (iv) Smoke Pyros: 1–2 mm s^{-1}
5	Velocity of Detonation	1.0 to 10 km s^{-1}	Usually do not detonate but may detonate under extreme conditions	
6	Pressure of detonation	3.5–425 kbar	–	–
7	Sensitivity			
	Impact	Primary : Extremely sensitive Secondary: Relatively insensitive	Moderately sensitive	Relatively insensitive to highly sensitive
	Friction	Primary: Extremely sensitive Secondary: Relatively insensitive	Moderately sensitive	Relatively insensitive to highly sensitive
	Spark	Primary: Extremely sensitive Secondary: Moderately sensitive	Moderately sensitive	Relatively insensitive to highly sensitive

Table 1.1 *Continued*

Sr No	Characteristics	High explosives	Low explosives (Propellants)	Pyrotechnics
8	Stability (Under atmospheric conditions)	Primary: Moderately stable Secondary: Very stable	SB, DB and TB Propellants: Moderately Stable and stabilizers are usually added during manufacture Composite Propellants: Very stable	Stable
9	Initiation in gun	Shatter gun	Propel a projectile	Shatter gun
10	Demolition	Excellent	Poor	Poor
11	Uses	Demolition and blasting	As propellants for rockets, missiles and space vehicles	Signaling, screening, tracking, decoying, illumination, delay and ignition etc.
12	Life of processed formulations	Primary: ≈ 10 years Secondary: 20 years	SB, DB, TB Propellants: ≈ 10 years Composite Propellants: ≈ 15 years	≈ 15 years

comparatively little flame of low volume, short duration and low temperature or practically no flame and therefore, they cannot ignite methane gas or coal dust. Some examples of permitted or permissible explosives are:

- **NG-based explosives:** Dynamite (NG, kieselguhr), gelatin (NC, NG, KNO_3, and wood meal);
- **ANFO explosives:** AN and fuel oil;
- **Emulsion explosives:** Water in oil with oxidizers like nitrates;
- **Slurry explosives:** These are the latest additions for commercial applications and consist of the mixtures of inorganic nitrates, gum, water, sensitizing agents etc.

1.3.2.2 Non-permitted Explosives

Explosives which produce a flash on detonation and create hazards for workers in coal mines are called non-permitted explosives. Basically these explosives include compositions based on aluminum powder and other HEMs with negative oxygen balance.

When classified on the basis of the nature of explosion, there are three types of explosions (a) *Mechanical* (b) *Nuclear* and (c) *Chemical*. The *mechanical explosion* is best illustrated by 'Cardox' used in coal mining. An example of mechanical explosion is the steam explosion which is caused by dumping a molten slag bar into a body of water. A mechanical explosion also occurs due to a physical reaction such as overheating of a whole potato in a microwave oven [11]. In a *nuclear explosion*, the vast amount of energy locked inside the nuclei of atoms is suddenly released, altering the atomic nuclei themselves. The energy released comes from two contrasting nuclear reactions: fission of heavy nuclei and fusion of light nuclei. The energy release in fission is million times larger than that in chemical explosions. In the fission process, nuclei of some heavy elements break-up spontaneously and produce two or more lighter nuclei, often with the emission of protons and neutrons and release of a large amount of energy. An important example of this is U^{235}. A large nucleus like U^{235} absorbs a neutron and changes into an unstable nucleus (U^{236}, a fissile isotope) which then breaks into two or more nuclei as shown in Equation 1.1.

$$\begin{tikzcd} {}_{92}U^{235} + {}_{0}n^{1} \arrow[r] & {}_{92}U^{236} \arrow[d] \\ & {}_{56}Ba^{141} + {}_{36}kr^{92} + 3\ {}_{0}n^{1} + \text{Large amount of energy} \end{tikzcd} \tag{1.1}$$

Another example of a nuclear fission explosion is the explosion of an atomic bomb. Nuclear fission explosions may also take place in a nuclear reactor if a breakdown occurs and a critical mass is achieved.

On the other hand, light atomic nuclei like hydrogen fuse together to form heavier nuclei with the consequent release of energy in the fusion process. Nuclear explosives are the most powerful types and there are different varieties of explosive devices based on the mechanics of the explosion. An important example is Equation 1.2:

$${}_{1}H^{2} + {}_{1}H^{3} \rightarrow {}_{2}He^{4} + {}_{0}n^{1} + \text{Large amount of energy} \tag{1.2}$$

Another example of a nuclear fusion is the reaction that constantly takes place on the surface of the sun, from which the earth receives its energy. In other words, nuclear explosives produce a sustained nuclear reaction and are the most powerful explosives.

In a *chemical explosion*, energy is released by rapid combustion of a chemical fuel. Atoms of the original compounds (reactants) rearrange themselves to form different compounds (products) with consequent release of energy.

Nuclear explosives release their energy much more rapidly than chemical explosives; typically the time in the case of nuclear explosives or devices, is less than 1 μs and that for a chemical explosive is in the range of microseconds. Thus, a nuclear explosive produces a sharper shock wave and as a result, it is somewhat more effective in shattering rocks and somewhat less effective as an earthmover. In terms of physical dimensions, the nuclear charge is much more compact than the chemical explosives leading to a much higher initial energy-density and consequently, to a much higher temperature and pressure after detonation. However, the most important aspect is that this compactness reduces transportation and emplacement costs [12, 13]. This book however, mainly deals with the third variety of explosives, namely chemical explosives.

Another way to classify explosives is based on their chemical structures. Plets proposed a theory of 'explosophores' and 'auxoploses' analogous to Witt's theory of 'chromophores' and 'auxochromes' and to Ehrlich's theory of 'toxophores' and 'autotoxes'. According to this theory, the explosive properties of any given substance depend upon the presence of definite structural groupings, called explosophores. The auxoploses fortify or modify the explosive properties brought about by explosophores. On the basis of this theory, Plets examined all explosives and divided them into eight classes containing following groupings as explosophores [14].

1) $-NO_2$ and $-ONO_2$ in both organic and inorganic compounds such as $C_6H_3(NO_2)_3$, HNO_3 etc.;
2) $-N{=}N-$ and $-N{=}N{=}N-$ in inorganic and organic azides such as $Pb(N_3)_2$ and CH_3N_3 etc.;
3) $-NX_2$ where X = halogen;
4) $-C{=}N-$ group, for example in fulminates $Hg(ONC)_2$ and fulminic acid (HONC);
5) $-OClO_2$ and $-OClO_3$ in inorganic and organic chlorates and perchlorates respectively. For example in $KClO_3$, $KClO_4$, NH_4ClO_4 and certain organic chlorates and perchlorates;
6) $-O-O-$ and $-O-O-O-$ in inorganic and organic peroxides and ozonides respectively;
7) $-C\equiv C-$ in acetylene and metal acetylides;
8) M–C, metal bonded with carbon in some organometallic compounds.

Although this classification is correct in principle, the distinction between the terms 'explosophores' and 'auxoploses' is very vague and is of little value from a practical point of view. The majority of explosives contain oxygen, present in nitro, nitrate, chlorate, perchlorate groups etc., and release their energy by a process of combustion, producing oxides of carbon, water, and nitrogen on explosion. However, oxygen is not essential; for example, the decomposition energy of lead azide results from the rupture of weak linkages between nitrogen atoms which subsequently recombine to form more stable compounds.

While reviewing the developments in the field of HEMs, Agrawal has suggested an altogether different way of classification which is based on the single most important property: thermal stability or high performance or insensitivity etc. [15]. Thus all HEMs or explosives reported so far in the literature have been assigned to the following classes.

1) Heat-resistant or thermally stable explosives.
2) High-performance or high density and high velocity of detonation (VOD) explosives.
3) Melt-castable explosives.
4) Insensitive high explosives (IHEs).
5) Energetic binders and plasticizers for explosives and propellants.
6) Energetic materials synthesized with the use of dinitrogen pentoxide (N_2O_5) technology.

It is evident that this classification facilitated the review of a huge number of HEMs reported in the literature and resulted in a methodical, lucid, and unique review paper published in 1998.

1.4
Fundamental Features

Some of the important characteristics of an explosive which are taken into consideration while selecting it for any application, are:

- compatibility and stability;
- oxygen balance;
- sensitivity and sensitiveness;
- heat of formation;
- heat of explosion and gases evolved;
- velocity of detonation;
- detonation pressure;
- explosive power or strength;
- brisance.

1.4.1
Compatibility and Stability

The knowledge of the compatibility and stability characteristics of explosives is of prime importance before considering their use for any ammunition [16]. Compatibility of materials may be defined as their ability to be stored intimately that is, in close contact, without occurrence of any chemical reaction. Consequently, incompatibility is likely to result in a loss of effectiveness or sometimes may be very hazardous, leading to accidents. For example, chlorate explosives and AN are not compatible (ammonium chlorate which is self-decomposing is formed). The data on compatibility and stability is indicative of safety during transport and storage and reliability in service. Thus the assessment as to whether the properties of explosives, propellants and pyrotechnics are adversely affected by any of the materials used in contact with them, becomes very important. The problem is further complicated not only by the frequent necessity to meet stringent storage and service requirements but also by a variety of non-explosive materials used in the construction of weapon systems. In addition to the study of the stability and mutual compatibility of the ingredients of explosive, propellant and pyrotechnic fillings, it is also necessary to study their compatibility with interior surface coatings that is, sealants, lutings and potting compositions used in assemblies. This also ensures that explosives, propellants and pyrotechnics or their formulations are not adversely affected by any of the materials which surround them, or vice versa. The stability studies are usually supported by compatibility investigations to check the suitability of novel ingredients and also to investigate possible interactions between propellants and inhibitors or adhesives used in their contact. The interaction may be of a chemical nature or may arise as a result of migration and interchange of explosive plasticizer (nitrate ester i.e., NG) [17–20] or non-explosive plasticizers such as triacetin (TA), diethylphthalate (DEP), dioctylphthalate (DOP) etc. [21–23]. The data on compatibility also ensures a proper choice of materials for explosive, propellant and pyrotechnic formulations and for hardware assemblies. The interactions among the ingredients of explosive or propellant formulations lead to reduction in chemical stability of explosive or propellant formulations or enhance their sensitivity to ignition by heat, friction, mechanical shock or electrostatic discharge or lead to the failure in material itself following exposure to explosives or propellants.

Stability is the ability of an explosive to be stored without any deterioration and it is affected by the following factors.

1) **Temperature of storage:** It has been established by a number of investigators notably Will [24], Robertson [25], Farmer [26–28] and Hinshelwood [29] that all explosives undergo a thermal decomposition at temperatures far below those at which spontaneous explosion occurs. Therefore, decomposition reactions are of considerable importance in determining stability of explosives and it can be determined by measuring their rate of decomposition at elevated temperatures.

   All military explosives are considered to possess stability of a high order at temperatures ≈–40 °C to +60 °C but each has a higher temperature at which decomposition rate becomes rapidly accelerated and stability is reduced. As a rule of thumb, most explosives become dangerously unstable at temperatures above +70 °C.

2) **Chemical constitution:** The fact that some common chemical compounds which contain groups like nitro ($-NO_2$), nitrate ($-ONO_2$) and azide ($-N_3$) etc. undergo explosion when heated means that these are intrinsically in a condition of internal strain and on heating, this strain increases leading to a sudden disruption of molecules and consequent explosion. In some explosives, this condition of molecular instability is so high that decomposition takes place at ordinary temperatures.

3) **Exposure to sunlight:** Many explosives which contain nitrogen groups (primary explosives such as LA, MF etc.) decompose rapidly on exposure to the ultraviolet (UV) rays of the sun, and thus affect their stability.

4) **Electrostatic discharge:** Static or electrostatic discharge may be sufficient to initiate detonation in a number of explosives under some circumstances. As a result, the handling of explosives and pyrotechnics, most of the time, is unsafe and requires electrical grounding of working tables and operators.

Most of the high explosives used for military applications such as TNT (nitroaromatic), RDX and HMX (nitramines) and PETN (nitrate ester) are solids. Such explosives generally possess excellent thermal stability at temperatures below their melting points, but show a marked decrease in stability in the molten state. Acids, alkalis, organic bases and strong oxidizing or reducing agents are generally incompatible with high explosives. As a rule, it is not advisable to allow high explosives to come into contact with substances of an alkaline nature.

The vacuum stability test (VST) is considered the most acceptable test for measuring stability and compatibility of explosives, worldwide. This is an empirical test in which rate of gas evolution is measured under isothermal conditions and a limit of 01 cm^3 of gas per gram of an explosive is set for explosives heated at 120 °C (150 °C for RDX) for 40 h (25 h for PETN). A similar test but at somewhat lower temperatures, is used to assess compatibility of an explosive with other explosives or with non-explosive materials such as binders (polymers), plasticizers etc.

Primary explosives are very sensitive to heat, impact, friction, spark etc. and care is taken at all stages of their manufacture, filling and storage to ensure that the sensitivity is not further increased by contamination or choice of ingredients or structural materials. Most of the commonly used primary or initiatory explosives possess adequate thermal stability for general purposes. However, some degradation is expected to occur if these explosives are exposed to moisture. Sealing with a compatible varnish or sealant may provide sufficient protection against such attacks.

Most pyrotechnics consist of intimate mixtures of metallic fuels such as magnesium (Mg), aluminum (Al) or zinc (Zn) etc and oxidizers: potassium nitrate (KNO_3), sodium nitrate ($NaNO_3$), potassium/sodium chlorate/perchlorate etc. and some other ingredients for modifying their performance or improving quality of filling or stability. The individual ingredients of pyrotechnics are generally stable but storage problems arise due to interaction of the final products with moisture or reactive vapors from plastics, rubbers etc. Moisture is particularly troublesome when free metals are used in pyrotechnic compositions. Coating metals with a suitable oil or resin provides some degree of protection against moisture. Compatibility test methods depend upon the nature of the pyrotechnics and their intended application. Visual observations may be supported in conjunction with thermogravimetric analysis (TGA) of mixture and chemical analysis of residual explosive; evolution of gases is conveniently measured by vacuum stability tests.

Gun and rocket propellants are based on nitrocellulose (NC–SB), NC with NG as second principal ingredient (DB) and nitroguanidine (picrite) in addition to NC and NG (TB) propellants. Propellant formulations also contain stabilizer, plasticizer, coolant and ballistic modifier, in addition to their principal ingredients.

In the case of SB, DB and TB propellants, slow but autocatalytic decomposition of NC and NG takes place even at ambient temperatures. This is retarded by the addition of a stabilizer to these propellants and thus the compatibility and the stability or life of these propellants increases. The 'silvered vessel test' and 'stabilizer consumption rate' are the methods which are generally used to predict safe chemical life of propellants in Europe, USA, India and other countries. The migration of explosive plasticizer (NG) and non-explosive plasticizers (TA, DEP) from propellants to inhibitors or vice-versa also affect the ballistics, mechanical properties and life of inhibited propellants.

Composite propellants consist of an oxidizer (AP/AN/ADN), a metallic fuel such as Al, Mg etc and a binder, usually a polymer which also serves as a fuel. Vacuum stability tests (VSTs) suggest that composite propellants are intrinsically more stable than SB, DB and TB propellants. However, use of more exotic ingredients such as oxidizers (ADN and hydrazinium nitroformate, HNF), binders [poly([NiMMO)] and poly([GlyN)] are likely to introduce severe compatibility-related problems [30, 31]. Some recent research in this direction indicates that stability of such propellants is largely determined by the chemical and mechanical properties of propellants. However, early evidence of deterioration generally comes from a change in their mechanical properties rather than from chemical investigations [32].

1.4.2
Oxygen Balance (OB)

The concentration of oxygen within an explosive or oxidizer is represented by a term known as 'oxygen balance' (OB represented by Ω) which is an important parameter for identifying their potential as an explosive or oxidizer. Oxygen balance may be defined as the amount of oxygen remaining after the oxidation of hydrogen, carbon and metals (like Mg, Al etc.) to produce H_2O, CO_2, MgO, Al_2O_3 etc. If excess of oxygen remains after the oxidation reaction, explosive or oxidizer is said to have a 'positive' OB. On the other hand, if the oxygen is completely consumed and excess fuel remains, explosive or oxidizer is said to have a 'negative' OB. Thus OB values can be positive or negative. However, if an explosive molecule contains just enough oxygen to convert all its carbon (C) to carbon dioxide (CO_2), all its hydrogen to water (H_2O) and all its metal to metal oxide with no excess, the explosive is said to have a zero OB, but explosives are rarely perfectly balanced. In other words, OB is an expression that is used to indicate the degree to which an explosive can be oxidized.

The OB is calculated from the empirical formula of an explosive as the percentage of oxygen required for complete oxidation of $C \rightarrow CO_2$ and $H \rightarrow H_2O$ by the following expression (Equation 1.3) for an explosive with the general formula $C_aH_bN_cO_d$ and molecular mass M. The unit of OB is %.

$$\text{OB}, \% = \frac{(\text{d} - 2\text{a} - \text{b}/2)}{\text{Molecular mass of explosive } (M)} \cdot 1600 \tag{1.3}$$

If metal is also present in the explosive, the above equation is slightly modified as shown in Equation 1.4 in order to calculate OB.

$$\text{OB, \%} = \frac{(\mathrm{d} - 2\mathrm{a} - \mathrm{b}/2 - n)}{\text{Molecular mass of explosive } (M)} . 1600 \tag{1.4}$$

where n = number of atoms of metal which is converted to metallic oxide [33, 34].

Since TNT is heavily oxygen-deficient, some carbon is left without any oxidation and that is why, TNT gives a black sooty smoke on detonation. The knowledge of oxygen balance is useful in the processing of mixtures of explosives. The family of explosives called Amatols are mixtures of ammonium nitrate and TNT. As given in the literature, ammonium nitrate has an oxygen balance of +20% while TNT has an OB of –74%. Therefore it appears that the mixture yielding an oxygen balance of zero would also result in the best explosive properties. In actual practice, a mixture of 80% ammonium nitrate and 20% TNT (by weight) yields an oxygen balance of +1% which gives best properties of all mixtures, and an increase in strength of 30% over TNT.

The OB also provides information on the types of gases liberated. If the OB is large and negative, then oxygen is not enough for the formation of carbon dioxide and consequently, toxic gases such as carbon monoxide are liberated. This is very important for commercial explosives, as liberation of the minimum amount of toxic gases is desirable. The OB of some primary, secondary and tertiary explosives is calculated using Equation 1.4 and these are given in Table 1.2.

Organic high explosives are mainly hydrocarbon structures to which substituent groups containing loosely bound oxygen are attached. An initial stage in the detonation reaction is the disruption of the explosive molecule. The oxygen which is linked wholly to nitrogen is now available for the complete reaction with fuel atoms from which it was separated by nitrogen. The energy released during explosion or detonation is derived mainly from the oxidation of the carbon and hydrogen and this energy is related to the percentage oxygen excess or deficiency per mole. In contrast, the oxygen of oxo and hydroxyl groups cannot lead to a net increase of energy on oxidation because the energies of disruption and recombination are equivalent. On the other hand, the oxygen in the form of -C–O–N is considered to have an intermediate effect since it combines with both the possibilities. It means that oxygen atoms in an explosive molecule vary in their energy potential according to their bonding in the substituent groups. There are some explosives, however, in which the exothermic reaction is not oxidation. For example, cyanuric triazide is an organic explosive which contains no oxygen but on disruption of the molecule, large energy is released due to the large negative 'heat of formation' ($-1110\,\mathrm{cal\,g^{-1}}$). OB is also related to some important properties such as brisance, power, velocity of detonation [35]and sensitivity of explosives [36, 37]. When it is used to predict brisance, power and sensitivity of explosives, it is expected that an explosive with OB value close to zero will be more brisant, powerful and sensitive. However, there are many exceptions to this rule.

Table 1.2 Oxygen balance of some primary, secondary and tertiary explosives.

Name	Empirical formula	Oxygen balance (%)
Primary explosives		
Diazodinitrophenol (DDNP/Dinol)	$C_6H_2(NO_2)_2O{-}N{=}N{-}$	–61.00
Lead trinitroresorcinate monohydrate (Lead styphnate monohydrate)	$C_6H(NO_2)_3O_2Pb.H_2O$	–22.00
Mercury fulminate	$Hg(ONC)_2$	–11.20
Lead azide	$Pb(N_3)_2$	–
Basic lead azide	$3Pb(N_3)_2.2PbO$	–02.85
Secondary explosives		
Tetranitro-dibenzo-1,3a,4,4a-tetraazapentalene (TACOT)	$(C_6H_2)_2(NO_2)_4N_4$	–74.20
2,4,6-Trinitrotoluene (TNT)	$C_6H_2(NO_2)_3CH_3$	–74.00
2,2′,4,4′,6,6′-Hexanitrostilbene (HNS)	$(C_6H_2)_2(CH)_2(N0_2)_6$	–68.00
Triethylene glycol dinitrate (TEGDN)	$(CH_2)_6(ONO_2)_2O_2$	–66.70
1,3,5-Trinitrobenzene (TNB)	$C_6H_3(NO_2)_3$	–56.30
1,3,5-Triamino-2,4,6-trinitrobenzene (TATB)	$C_6\ (NH_2)_3(NO_2)_3$	–56.00
1,3-Diamino-2,4,6-trinitrobenzene (DATB)	$C_6H(NH_2)_2(NO_2)_3$	–55.80
2,4,6-Trinitrophenyl methyl nitramine (CE or Tetryl)	$C_6H_2(NO_2)_3NNO_2CH_3$	–47.39
2,4,6-Trinitrophenol (picric acid)	$C_6H_2(NO)_3OH$	–45.40
Diethylene glycol dinitrate (DEGDN)	$(CH_2)_4(ONO_2)_2O$	–41.00
Nitroguanidine or Picrite (NQ)	$HN{=}CNH_2NHNO_2$	–31.00
Cyclotetramethylene tetranitramine (HMX)	$(CH_2)_4(NNO_2)_4$	–21.68
Cyclotrimethylene trinitramine (RDX)	$(CH_2)_3(NNO_2)_3$	–21.60
Hexanitrohexaazaisowurtzitane (HNIW or CL-20)	$(CH)_6(NNO_2)_6$	–10.95
Pentaerythritol tetranitrate (PETN)	$C(CH_2)_4(ONO_2)_4$	–10.30
Ethylene glycol dinitrate (EGDN) or Nitroglycol	$(CH_2)_2(ONO_2)_2$	00.00
Glycerol trinitrate/Nitroglycerine (NG)	$C_3H_5(ONO_2)_3$	+03.50
Tertiary explosives		
Ammonium dinitramide (ADN)	$NH_4N(NO_2)_2$	+25.80
Hydrazinium nitroformate (HNF)	$N_2H_5C(NO_2)_3$	+13.00
Ammonium nitrate (AN)	NH_4NO_3	+20.00
Ammonium perchlorate (AP)	NH_4ClO_4	+34.04

1.4.3
Sensitivity and Sensitiveness

These two terms: ‘sensitivity’ and ‘sensitiveness’ are referred in the context of explosives, propellants and pyrotechnics and relate to two rather similar properties of explosives that is, ‘ease of initiation’ and ‘propagating capability’. In some circles, it is customary to use ‘sensitivity’ to mean ‘ease of initiation’ whereas 'sensitiveness' to mean 'propagating capability'. In others, the converse is believed to be true and in yet others, these terms are used synonymously. There are mainly five types of sensitivity [38].

1.4.3.1 Sensitivity to Impact

This represents the ease with which an explosive can be set off by a blow impact and is expressed in terms of the distance through which a standard weight is allowed to drop to cause an explosive to explode.

1.4.3.2 Sensitivity to Friction

This represents the ease with which an explosive can be set off by a blow friction and is expressed in terms of what occurs when a pendulum of known weight scrapes across an explosive (ignites or explodes or snaps or crackles). Sensitivity to friction is less well-defined than the sensitivity to impact and is expressed only by figures compared with a standard. Some explosives can be arranged as follows in terms of decreasing sensitivity.

- initiating explosives (azides not included);
- *O*-nitro compounds;
- *N*-nitro compounds and metal azides;
- *C*-nitro compounds.

1.4.3.3 Sensitivity to Shock

This represents the ease with which an explosive can be set off by a blow shock from another explosive charge. This is also termed 'gap sensitivity' or 'initiability' which is less defined than the impact sensitivity and cannot be expressed in absolute units. The sensitivity of high explosives (HE) to initiation is usually determined

- by the amount of initiating explosive in the detonator (the method which is also used to determine the 'initiating strength' of primary explosives);
- by transmitting the detonation from one charge to another through air or any other medium (water or sheet of a metal or polymer of different thickness);
- by determining the critical diameter, that is, minimum diameter which is able to transmit the detonation.

1.4.3.4 Sensitivity to Spark

This represents the ease with which an explosive can be set off by an electrostatic spark.

1.4.3.5 Sensitivity to Heat

This represents the ease with which an explosive can be set off by heat.

Sensitivity to heat is expressed in terms of the temperature at which ignition, explosion or flashing of an explosive occurs. The application of heat is the simplest way of initiation of explosives and leads to explosion when heat is liberated by a reaction at a greater rate than heat is lost [39]. This has been discussed in detail under chemical stability. However, theoretically speaking, all explosives decompose very slowly with the evolution of heat at ordinary temperatures and also all explosives increase in sensitiveness with rise in temperature. The energy which is supplied to raise the rate of decomposition to that of explosion is a measure of its sensitiveness. Also the quantity of heat liberated by the explosive on decomposition plays an important role in raising the rate of decomposition leading to explosion. It is found that in similarly constituted substances, the higher the heat of explosion, the less is the quantity of energy required. In other words, it may be dealt in the following manner: suppose for an explosive, the time required for the build-up of an explosion is 't' at absolute room temperature (T). In light of the fact that as the temperature increases, the time required for build-up of an explosion decreases and therefore, the time will vary with temperature as exemplified below:

Temperature	Time Required for explosion (termed explosion delay, D_E)
Absolute room temp (T)	Time (t)
T_1	t_1
T_2	t_2
T_3	t_3
T_4	t_4

where $T < T_1 < T_2 < T_3 < T_4 \ldots\ldots\ldots\ldots$
and $t > t_1 > t_2 > t_3 > t_4 \ldots\ldots\ldots\ldots\ldots$

The curve obtained by plotting log D_E against ($1/T$) is almost rectilinear ($y = mx + c$) and represents the relationship (Equation 1.5):

$$\begin{aligned} D_E &= A . e^{E/RT} \\ \text{or } \log D_E &= (E/4.57).(1/T) + B \end{aligned} \tag{1.5}$$

where D_E = explosion delay,
E = activation energy,
T = absolute temperature of the bath
B = $\log_{10} A$ (a constant).

From the slope of this curve (m), the value of activation energy (E) is calculated [40–45] that is, (Equation 1.6):

$$m = E/4.57 \text{ or } E = m \times 4.57 \tag{1.6}$$

Explosives must be handled with care because an impact, friction, shock, spark or application of heat to an explosive may bring about explosion. The information on sensitivity to these stimuli is considered very valuable as it gives assurance about safety in manufacture, handling, transportation and storage. Also, sensitivity is an important consideration in selecting an explosive for a particular application. For example, explosive in an armor-piercing projectile must be relatively insensitive, otherwise the shock of impact would cause it to detonate before it penetrates to the desirable depth. The sensitiveness of explosives to mechanical shock is undoubtedly closely related to their chemical constitution but the relationships are frequently masked by differences in physical characteristics which greatly modify the pressure developed by a blow of certain intensity.

Urbanski expressed the view way back in 1933 that the sensitivity of solid explosives to impact is a complex function of a few factors, and most important among them are: sensitivity to high temperature and sensitivity to friction [46]. Subsequently, Bowden and Yoffe developed a well-known concept of 'hot spots' and the initiation of explosion from 'hot spots' created by thermal factors, crystal hardness and shapes [47]. According to Bowden and Yoffe, when a solid or liquid explosive is subjected to impact or friction, the explosion which may result is generally thermal in origin. That is to say the mechanical energy is first degraded to heat and concentrated in a small localized region to form a 'hot spot'. The size of the 'hot spot' is of the order of 10^{-3} to 10^{-5} cm in diameter. Thermal decomposition takes place at the 'hot spot', and because of the exothermic nature of the decomposition, the rate of decomposition rapidly increases and a 'thermal explosion' may result. Suitable 'hot spots' may be formed in four different ways [48, 49] as described briefly in Chapter 3.

The impact sensitivity of some well-known primary, secondary and tertiary explosives is given in the Table 1.3.

Small bubbles of air included in liquid explosives (such as NG) also increase sensitivity to impact through the adiabatic compression of air and a rapid increase in temperature [50]. Kamlet also agrees with the thermal character of sensitivity to impact and friction and proposed an ingenious method to calculate the sensitivity of explosives to impact [36, 37]. Kamlet *et al.* also proposed a linear relationship between logarithmic 50% impact heights and oxidant balance (OB_{100}) for similar explosives. The OB_{100} is defined as the number of equivalents of oxidant per 100 grams of explosive above the amount required to oxidize hydrogen to water and all carbon to carbon monoxide. For the purpose of calculation of OB_{100}, an atom of oxygen represents two equivalents of oxidant, an atom of hydrogen represents one equivalent of reductant and an atom of carbon represents two equivalents of reductant. As carboxyl groups are considered to be 'dead weight', two equivalents of oxidant are subtracted for each such group in the molecule. For a C–H–N–O type explosive, OB_{100} is calculated by Equation 1.7:

$$OB_{100} = 100(2n_o - n_H - 2n_C - 2n_{COO})/\text{Mol. Mass} \tag{1.7}$$

where n_O, n_H and n_C represent the number of atoms of the respective elements in the molecule and n_{COO} is the number of carboxyl groups. For explosives balanced to the CO-level of oxygen balance, OB_{100}=O; at the CO_2-level of oxygen balance, OB_{100} = ca +2.5. Based on their exhaustive study of a number of polynitroaliphatic and aromatic explosives, they concluded that:

- Polynitroaliphatic explosives containing at least one *N*-nitro linkage are more sensitive as a class than nitroaliphatic explosives containing only C-nitro linkages.

Table 1.3 Impact sensitivity of some primary, secondary and tertiary explosives.

Name	Empirical formula	Molecular mass	$h_{50\%}$	
			Cm	Nm
Primary explosives				
Lead azide	$Pb(N_3)_2$	291.30	–	2.5–4.0
Mercury fulminate	$Hg(ONC)_2$	284.60	–	2.5–5.0
Lead trinitroresorcinate monohydrate (Lead styphnate monohydrate)	$C_6H(NO_2)_3O_2Pb.H_2O$	468.30	–	1.0–2.0
Diazodinitrophenol (DDNP/Dinol)	$C_6H_2(NO_2)_2O{-}N{=}N{-}$	210.12	–	1.5
Secondary explosives				
2,4,6-Trinitrotoluene (TNT)	$C_6H_2(NO_2)_3CH_3$	227.15	160	15.0
2,4,6-Trinitrophenol (picric acid)	$C_6H_2(NO)_3OH$	229.12	87	7.4
1,3,5-Trinitrobenzene (TNB)	$C_6H_3(NO_2)_3$	213.10	100	7.4
Glycerol trinitrate/Nitroglycerine (NG)	$C_3H_5(ONO_2)_3$	227.11	1	0.2
Ethylene glycol dinitrate (EGDN) or Nitroglycol	$(CH_2)_2(ONO_2)_2$	152.00	0.2	0.2
Diethylene glycol dinitrate (DEGDN)	$(CH_2)_4(ONO_2)_2O$	196.10	–	0.1
Triethylene glycol dinitrate (TEGDN)	$(CH_2)_6(ONO_2)_2O_2$	240.10	–	12.7
Pentaerythritol tetranitrate (PETN)	$C(CH_2)_4(ONO_2)_4$	316.16	20	2–3
2,4,6-Trinitrophenyl methyl nitramine (CE or Tetryl)	$C_6H_2(NO_2)_3NNO_2CH_3$	287.17	49	2–3
Nitroguanidine or Picrite (NQ)	$C{=}NHNH_2NHNO_2$	104.08	>320	>49.0
Cyclotrimethylene trinitramine (RDX)	$(CH_2)_3(NNO_2)_3$	222.12	28	7.4
Cyclotetramethylene tetranitramine (HMX)	$(CH_2)_4(NNO_2)_4$	296.19	33	7.5
Hexanitrohexaazaisowurtzitane (HNIW or CL-20)	$(CH)_6(NNO_2)_6$	438.24	28	4.0
1,3-Diamino-2,4,6-trinitrobenzene (DATB)	$C_6H(NH_2)_2(NO_2)_3$	243.00	320	–
1,3,5-Triamino-2,4,6-trinitrobenzene (TATB)	$C_6(NH_2)_3(NO_2)_3$	258.17	>320	50.0
2,2′,4,4′,6,6′-Hexanitrostilbene (HNS)	$(C_6H_2)_2(CH)_2(NO_2)_6$	450.00	54	5.0
Tetranitro-dibenzo-1,3a,4,4a-tetraaza-pentalene (TACOT)	$(C_6H_2)_2(NO_2)_4N_4$	388.22	102	69.0
Tertiary explosives				
Ammonium nitrate (AN)	NH_4NO_3	80.04	149	50.0
Ammonium perchlorate (AP)	NH_4ClO_4	117.50	93	15.0–25.0
Ammonium dinitramide (ADN)	$NH_4N(NO_2)_2$	124.07	8–12	3.0–5.0
Hydrazinium nitroformate (HNF)	$N_2H_5C(NO_2)_3$	183.19	25	2.0–5.0

- Polynitroaromatic explosives containing a -C–H linkage alpha to the aromatic ring are more sensitive as a class than explosives without such a linkage and results may be fitted into a linear relationship log ($h_{50\%}$) = 1.33 – 0.17 (OB_{100}).
- There is a general trend in which logarithm of 50% drop height (log $h_{50\%}$) decreases with increasing oxidant balance (OB_{100}).
- Diazophenols and aromatic azides are much more sensitive to impact than polynitroaromatics. A similar trend is observed for polynitroaromatics containing nitramine groups. The initial reaction on impact of this class is believed to be cleavage of the $-N–NO_2$ bond.
- The data for those explosives which do not contain an α C–H bond may be fitted into a linear relationship (Equation 1.8):

$$\log(h_{50\%}) = 1.72 - 0.21(OB_{100}) \tag{1.8}$$

- Benzofuroxans correlate well with polynitroaromatics and amine groups appear to show link desensitizing effect over that indicated by the reduction in OB.

In summary, the impact sensitivity of polynitroaromatics ranges from about 8 cm to over 230 cm, with a general tendency to greater sensitivity (smaller drop heights) with increasing OB. When the class of explosives is restricted to those containing NO_2, NH_2 and furoxan functional groups, correlation between impact sensitivity and OB is excellent. However, when other functional groups such as azido, diazonium, methyl, and methylnitramino are included, this correlation is not so good. Amino groups act as desensitizers particularly when interposed between nitro groups. Such findings are supported by the rates of thermal decomposition processes taking place in the temperature regimes generated under the impact of hammer [51, 52]. Values for impact sensitivity and OB_{100} of some typical nitroaromatic and nitramine explosives are given in Table 1.4.

A very important addition to the knowledge of the sensitivity of explosives to impact has been made by Delpuech and Cherville [53–55]. As a result of their exhaustive study, they concluded that the basic criterion of sensitivity of explosives lies in the distribution of electrons in their ground state and the comparison with that in the excited state. This has introduced a new dimension to the sensitivity of explosives and has been discussed in detail by T. Urbanski in his book [56].

1.4.4
Heat of Formation

The ‘heat of formation’ of explosives is of fundamental importance in affording data for the study of their chemical characteristics and evaluation of their explosive properties [57].

When a chemical compound is formed from its constituents, the reaction may either absorb or give off heat, which is called ‘heat of formation’ and is expressed

Table 1.4 Impact sensitivity and oxidant balance (OB_{100}) of some explosives.

Explosive	Molecular formula	Mol. mass	OB_{100}	$h_{50\%}$, Cm
Explosives without α C-H Linkage				
1,3,5-Trinitro benzene (TNB)	$C_6H_3N_3O_6$	213	−1.46	100
Picric acid	$C_6H_3N_3O_7$	229	−0.44	87
Styphnic acid	$C_6H_3N_3O_8$	245	+0.41	43
2,3,4,6-Tetranitro aniline (TNA)	$C_6H_3N_5O_8$	273	+0.37	41
2,3,4,5,6-Pentanitro aniline	$C_6H_2N_6O_{10}$	318	+1.88	15
2,4,6-Trinitrobenzoic acid	$C_7H_3N_3O_8$	257	−1.12	109
Picramide	$C_6H_4N_4O_6$	228	−1.75	177
1,3-Diamino-2,4,6-trinitro benzene (DATB)	$C_6H_5N_5O_6$	243	−2.06	320
Explosives with α C-H Linkage				
TNT	$C_7H_5N_3O_6$	227	−3.08	160
2,4,6-Trinitrobenzaldehyde	$C_7H_3N_7O_7$	241	−1.24	36
3,5-Dimethyl-2,4,6-trinitro phenol	$C_8H_7N_3O_7$	257	−3.50	77
Nitramines				
RDX	$C_3H_6N_6O_6$	222	0	24
HMX	$C_4H_8N_8O_8$	296	0	26
Tetryl	$C_7H_5N_5O_8$	287	−1.04	32
Ethylenedinitramine (EDNA)	$C_2H_6N_6O_6$	210	−1.33	34
N-Methyl EDNA	$C_3H_8N_4O_4$	164	−3.65	114

in units of kilocalories per gram molecule. The value of the ‘heat of formation’ can be negative or positive. The negative value indicates absorption of heat during the formation of compound from its elements and such a reaction is called an ‘endothermic’ reaction whereas a positive value indicates liberation of heat during the formation of compound meaning the reaction is ‘exothermic’. For explosives, the reactions are always exothermic. In an exothermic reaction, the energy evolved may appear in many forms, but for practical purposes, it is usually in the form of heat. Since the ‘heat of formation’ of an explosive is the net difference between ‘heat content’ of the explosive and that of its elements (taken as zero by convention), it means that the ‘heat content’ of an explosive is equal to its ‘heat of formation’. The net amount of heat liberated during an explosion is the sum of ‘heats of formation’ of the products of explosion, minus the ‘heat of formation’ of the original explosive.

The net heat difference between the ‘heats of formation’ of the reactants and products in a chemical reaction is termed the ‘heat of reaction’. For oxidation, this ‘heat of reaction’ may be termed ‘heat of combustion’. The energy liberated when explosives deflagrate is called the ‘heat of deflagration’ whereas the energy liberated on detonation of explosives is called the ‘heat of detonation’ in kJ mol^{-1} or the ‘heat of explosion’ in kJ kg^{-1}. In primary explosives, which are used as initiators, a very low or negative ‘heat of formation’ reflects their great internal strain and some well-known examples of such explosives are MF, LA etc.

The ‘heats of formation’ of some primary, secondary and tertiary explosives are given in the Table 1.5.

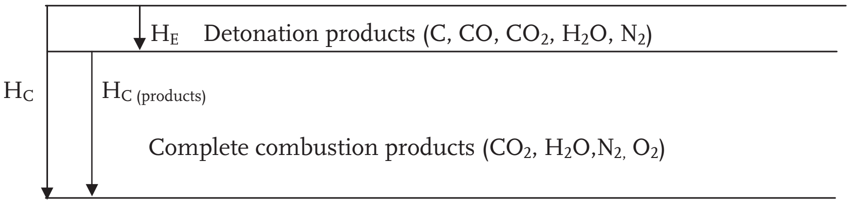
Table 1.5 ‘Heats of formation’ of some primary, secondary and tertiary explosives.

Name	Empirical formula	ΔH_f/kJ kg^{-1}	ΔH_f/kJ mol^{-1}
Lead azide	$Pb(N_3)_2$	+1612	+469
Mercury fulminate	$Hg(ONC)_2$	+1354	+386
Lead trinitroresorcinate monohydrate (Lead styphnate monohydrate)	$C_6H(NO_2)_3O_2Pb.H_2O$	–1747	–855
Diazodinitrophenol (DDNP/Dinol)	$C_6H_2(NO_2)_2O{-}N{=}N{-}$	+989	+207
2,4,6-Trinitrotoluene (TNT)	$C_6H_2(NO_2)_3CH_3$	–115	–26
2,4,6-Trinitrophenol (picric acid)	$C_6H_2(NO)_3OH$	–978	–224
1,3,5-Trinitrobenzene (TNB)	$C_6H_3(NO_2)_3$	–135	–28.7
Glycerol trinitrate/Nitroglycerine (NG)	$C_3H_5(ONO_2)_3$	–1674	–380
Ethylene glycol dinitrate (EGDN) or Nitroglycol	$(CH_2)_2(ONO_2)_2$	–1704	–259
Diethylene glycol dinitrate (DEGDN)	$(CH_2)_4(ONO_2)_2O$	–2120	–415.7
Triethylene glycol dinitrate (TEGDN)	$(CH_2)_6(ONO_2)_2O_2$	–2506	–601.7
Pentaerythritol tetranitrate (PETN)	$C(CH_2)_4(ONO_2)_4$	–1703	–538
2,4,6-Trinitrophenyl methyl nitramine (CE or Tetryl)	$C_6H_2(NO_2)_3NNO_2CH_3$	+118	+34
Nitroguanidine or Picrite (NQ)	$C{=}NHNH_2NHNO_2$	–913	–95
Cyclotrimethylene trinitramine (RDX)	$(CH_2)_3(NNO_2)_3$	+279	+62
Cyclotetramethylene tetranitramine (HMX)	$(CH_2)_4(NNO_2)_4$	+253	+75
Hexanitrohexaazaisowurtzitane (HNIW or CL- 20)	$(CH)_6(NNO_2)_6$	+1006	+460
1,3,5-Triamino-2,4,6-trinitrobenzene (TATB)	$C_6(NH_2)_3(NO_2)_3$	–597	–154
2,2′,4,4′,6,6′-Hexanitrostilbene (HNS)	$(C_6H_2)_2(CH)_2(NO_2)_6$	+128	+58
Tetranitro-dibenzo-1,3a,4,4a-tetraaza-pentalene (TACOT)	$(C_6H_2)_2(NO_2)_4N_4$	+4103	+1592.8
Ammonium nitrate (AN)	NH_4NO_3	–4428	–355
Ammonium perchlorate (AP)	NH_4ClO_4	–2412	–283
Ammonium dinitramide (ADN)	$NH_4N(NO_2)_2$	–1087	–148
Hydrazinium nitroformate (HNF)	$N_2H_5C(NO_2)_3$	–393	–72

1.4.5
Heat of Explosion and Gaseous Products

When an explosive is initiated to rapid burning and detonation, energy is released in the form of heat mainly due to the oxidation reactions. The heat so released under adiabatic conditions is called the 'heat of explosion', denoted by the letter Q which is a very important characteristic of an explosive and provides information about its work capacity. The secondary high explosives and propellants possess high values of Q. For propellants burning in the gun chambers and secondary explosives in detonating devices, the 'heat of explosion' is conventionally expressed in terms of constant volume conditions (Q_v). On the other hand, it is customary to employ constant pressure conditions for rocket propellants burning in the combustion chamber of a rocket motor under conditions of free expansion to the atmosphere and accordingly 'heat of explosion' is expressed by Q_P. The calculated values of Q for some primary, secondary and tertiary explosives are given in the Table 1.6.

In other words, 'heat of explosion' is simply the difference between 'heat of formation' of the products of explosion and 'heat of formation' of the explosive itself. The 'heat of formation' of chemical explosives may be calculated from the knowledge of the individual bond energies between the atoms of an explosive molecule. At the same time, the values of 'heat of formation' of gases such as carbon dioxide, carbon monoxide and water are available in the literature [58, 59]. Thus their knowledge enables calculation of 'heat of explosion'. The heat of explosion may also be very closely approximated by using the equation $H_E = H_C - H_{C\ (\text{products})}$ after determining 'heat of combustion' (H_C) by standard calorimetric methods [60–63] and H_C (products) values available in the literature. This is evident from the changes in energy while passing from one level to another as shown below:



The 'heat of explosion' has also been successfully evaluated by the use of a suitable bomb calorimeter [64].

The oxidation of carbon and hydrogen takes place in the light of available oxygen. That is to say 'heat of explosion' varies directly with OB and reaches a maximum value at zero OB. When there is exactly enough oxygen in the explosive to completely oxidize carbon and hydrogen to carbon dioxide and water respectively (i.e., OB = 0), then 'heat of explosion' is optimal or maximum [65]. Any deviation from the zero OB will affect the 'heat of explosion'. It is also known that H_E is directly related to the power of an explosive [66, 67].

Table 1.6 Calculated 'heats of explosion' for some primary, secondary and tertiary explosives (considering water as a gas).

Name	Empirical formula	ΔH/J g^{-1}	ΔH/cal g^{-1}
Primary explosives			
Lead azide	$Pb(N_3)_2$	1610	385
Mercury fulminate	$Hg(ONC)_2$	1735	415
Lead trinitro resorcinate monohydrate (Lead styphnate monohydrate)	$C_6H(NO_2)_3O_2Pb.H_2O$	1453	347
Diazodinitrophenol (DDNP/Dinol)	$C_6H_2(NO_2)_2O{-}N{=}N{-}$	3646	871
Secondary explosives			
2,4,6-Trinitrotoluene (TNT)	$C_6H_2(NO_2)_3CH_3$	3720	925
2,4,6-Trinitrophenol (picric acid)	$C_6H_2(NO)_3OH$	3350	801
1,3,5-Trinitrobenzene (TNB)	$C_6H_3(NO_2)_3$	3876	926
Glycerol trinitrate/Nitroglycerine (NG)	$C_3H_5(ONO_2)_3$	6214	1485
Ethylene glycol dinitrate (EGDN) or Nitroglycol	$(CH_2)_2(ONO_2)_2$	6730	1610
Diethylene glycol dinitrate (DEGDN)	$(CH_2)_4(ONO_2)_2O$	4141	990
Triethylene glycol dinitrate (TEGDN)	$(CH_2)_6(ONO_2)_2O_2$	3317	793
Pentaerythritol tetranitrate (PETN)	$C\ (CH_2)_4(ONO_2)_4$	5940	1365
2,4,6-Trinitrophenyl methyl nitramine (CE or Tetryl)	$C_6H_2(NO_2)_3NNO_2CH_3$	4166	996
Nitroguanidine or Picrite (NQ)	$C{=}NHNH_2NHNO_2$	2730	653
Cyclotrimethylene trinitramine (RDX)	$(CH_2)_3(NNO_2)_3$	5297	1266
Cyclotetramethylene tetranitramine (HMX)	$(CH_2)_4(NNO_2)_4$	5249	1255
Hexanitrohexaazaisowurtzitane (HNIW or CL-20)	$(CH)_6(NNO_2)_6$	6084	1554
1,3-Diamino-2,4,6-trinitrobenzene (DATB)	$C_6H(NH_2)_2(NO_2)_3$	3805	910
1,3,5-Triamino-2,4,6-trinitrobenzene (TATB)	$C_6(NH_2)_3(NO_2)_3$	3062	732
2,2′,4,4′,6,6′-Hexanitrostilbene (HNS)	$(C_6H_2)_2(CH)_2(NO_2)_6$	4008	958
Tetranitro-dibenzo-1,3a,4,4a-tetraaza-pentalene (TACOT)	$(C_6H_2)_2(NO_2)_4N_4$	4015	960
Tertiary explosives			
Ammonium nitrate (AN)	NH_4NO_3	1441	344
Ammonium perchlorate (AP)	NH_4ClO_4	1972	471
Ammonium dinitramide (ADN)	$NH_4N(NO_2)_2$	2668	638

To calculate 'heat of explosion' and other explosive performance parameters, a knowledge of the composition of the gaseous products of explosion is considered essential. This may be calculated from equilibrium constants of the water gas and other reactions which is a tedious process. Also, the volume of gaseous products produced during an explosion provides information on the amount of work done by an explosive. To measure the volume of gases produced during explosion, standard conditions are established as the volume of gas varies according to the temperature. The standard conditions also enable comparison among the gaseous products of explosion of various explosives. The standard temperature and standard pressure are 0 °C/273 K and 1 atm respectively. These conditions are known as 'standard temperature and pressure' (STP). Under these standard conditions, one mole of any gas occupies 22.4 liters which is known as the molar gas volume [10].

Avogadro's Law states that equal volumes of all gases under the conditions of STP contain the same number of molecules. It implies that the molar volume of one gas is equal to the molar volume of any other gas, that is, the molar volume of any gas at 0 °C and 1 atm pressure is very close to 22.4 liters. This may be illustrated by the decomposition of NG.

The decomposition of NG may be shown as (Equation 1.9):

$$C_3H_5\,(NO_3)_3 \rightarrow 3CO_2 + 2.5\,H_2O + 1.5\,N_2 + 0.25\,O_2 \tag{1.9}$$

In other words, one mole of NG produces 7.25 molar volumes of gas (since a molar volume is the volume of one mole of gas). These molar volumes at 0 °C and 1 atm form an actual volume of 7.25 × 22.4 = 162.4 liters of gas (provided the products H_2O and CO_2 are in gaseous form). Thus, volume of the products of explosion can be predicted for any quantity of explosive. Further, by employing Charles' Law for perfect gases, the volume of the products of explosion may be calculated for any given temperature. Therefore,

$$\begin{aligned}\text{Molar volume of an ideal gas at } 15\,^\circ\text{C}\,(V_{15}) &= 22.4 \times 288/273.15\\ &= 23.62\ \text{liters}\end{aligned}$$

Thus, the volume of gas produced by the decomposition of one mole of NG becomes

$$\begin{aligned}V &= (23.62\ \text{liters per mole}) \times 7.25\\ &= 171.25\ \text{liters per mole}\end{aligned}$$

Similarly, volume of gases on detonation of RDX may be calculated based on Equation 1.10:

$$C_3H_6O_6N_6\ (\text{RDX}) \rightarrow 3\text{Co} + 3N_2 + 3H_2O \tag{1.10}$$

$$\text{that is, 1 mole of RDX} \rightarrow 9 \text{ moles of gases V}$$

$$\text{or}\quad 222\,\text{g of RDX} \rightarrow 9 \times 22\,400\,\text{cm}^3 \text{ of gases}$$

$$\text{or}\quad 1\,\text{g of RDX gives } 908.11\,\text{cm}^3 \text{ of gases}$$

$$\text{Therefore}\quad V = 908.11\,\text{cm}^3\,\text{g}^{-1}$$

The performance of an explosive is mainly determined in terms of velocity of detonation (VOD), detonation pressure (P_{CJ}) and power or strength. Sometimes, users of explosives are also interested to have an idea of brisance which is essentially shattering power of an explosive. The literature suggests that the detonation pressure, velocity of detonation, brisance and power or strength of an explosive are strong functions of the density of explosive and hence, all these parameters are interrelated. Thus by increasing the density of explosives, all these parameters can be increased resulting in more energetic explosives.

1.4.6
Velocity of Detonation (VOD)

Detonation is a process in which the explosive undergoes chemical reactions at a considerably high speed and produces a shock wave also called a detonation wave. High temperature and pressure gradients are generated in the wave front so that the chemical reaction is initiated instantaneously. The detonation wave propagates through the explosive, supported and reinforced by the chemical reactions. In general, except in the early stages of detonation, detonation waves travel through a column of an explosive at a constant speed, a fact which simplifies the mathematical solution of the 'hydrodynamic theory'. The velocity with which detonation waves travel in an explosive is called velocity of detonation (VOD) or in other words, detonation velocity may be defined as the rate, speed or velocity of propagation of detonation waves in an explosive [68]. If density of the explosive is at its maximum value and also if the explosive is charged into columns which are considerably wider than the critical diameter, the VOD is a characteristic of each individual explosive and is not influenced by external factors. It increases with increase in density of packing of explosive in the column. The detonation velocities of confined and unconfined explosives have different values and are known as upper and lower detonation velocities respectively.

The VOD of an organic explosive is also a function of the energy produced by its decomposition and therefore, a relationship has been derived between detonation properties of an explosive and its chemical constitution. Similarly to Bernard [69, 70], Rothstein and Peterson [71] also postulated for a gamut of an ideal C, H, N, O type explosive, a simple empirical linear relationship (Equation 1.11) between VOD at theoretical maximum density (TMD) and a factor, F, which solely depends upon chemical constitution and structure.

$$F = 0.55D + 0.26 \tag{1.11}$$

or

$$D = (F - 0.26)/0.55$$

where D = Velocity of detonation
F = Factor which is calculated by Equation 1.12:

$$F=\frac{100}{\mathrm{MW}}\cdot\left[n(\mathrm{O})+n(\mathrm{N})-\left(\frac{n(\mathrm{H})}{2n(\mathrm{O})}\right)+\left(\frac{A}{3}\right)-\left(\frac{n(\mathrm{B})}{1.75}\right)-\left(\frac{n(\mathrm{C})}{2.5}\right)-\left(\frac{n(\mathrm{D})}{4}\right)-\left(\frac{n(\mathrm{E})}{5}\right)\right]-G \tag{1.12}$$

where

G = 0.4 for liquid explosives and G = 0 for solid explosives
A = 1.0 for aromatic explosive, otherwise 0
MW = Molecular weight
n(O) = number of oxygen atoms,
n(N) = number of nitrogen atoms,
n(H) = number of hydrogen atoms,
n(B) = number of oxygen atoms in excess of those already available to form CO_2 and H_2O,
n(C) = number of oxygen atoms double bonded to carbon as in C=O,
n(D) = number of oxygen atoms singly bonded directly to carbon in C–O–R linkage where R = H, NH_4 or C.
n(E) = number of nitrate groups either as nitrate-esters or nitrate salts.

The principal feature of this relationship is that F values are derived solely from molecular formulae and chemical structures and require no prior knowledge of any physical, chemical or thermochemical properties other than the physical state of the explosive that is, explosive is a solid or a liquid [72]. Another parameter related to the molecular formulae of explosives is OB which has been used in some predictive schemes related to detonation velocity similar to the prediction of brisance, power and sensitivity of explosives [35, 73, 74]. Since OB is connected with both, energy available and potential end products, it is expected that detonation velocity is a function of OB. As a result of an exhaustive study, Martin *et al.* established a general relation that VOD increases as OB approaches to zero. The values of VOD calculated with the use of these equations for some explosives are given in the literature [75] and deviations between the calculated and experimental values are in the range of 0.46–4.0%.

1.4.7
Detonation Pressure (DP or P_{CJ})

The peak dynamic pressure in the shock front is called DP of an explosive. It has been established that a linear regression plot of experimental detonation pressures (DP) or Chapman–Jouguet Pressure (P_{CJ}) versus detonation velocities D for selected explosives fits the relationship in Equation 1.13:

$$P_{CJ}=93.3D-456 \tag{1.13}$$

The value of D can be calculated from Equation 1.11 that is, $D = (F–0.26)/0.55$ and therefore, P_{CJ} can be calculated from Equation 1.13. This equation was tested for a number of explosives by determining P_{CJ} experimentally, and calculating it on the basis of this equation. Therefore, this method offers a simple and quick method for estimating detonation pressure (P_{CJ}) at TMDs when a high degree of accuracy is not essential.

Cook also proposed an empirical method for calculating P_{CJ} and for practical purposes, it was calculated by using Equation 1.14 [76]:

$$P_{CJ} = 1/4 . \rho D^2 \tag{1.14}$$

where ρ = Charge density in $g\,cm^{-3}$
D = velocity of detonation in ms^{-1}.

It is reported that the explosion pressures are of a much lower order of magnitude than detonation pressures. It appears that the calculation of some important detonation parameters is still in progress and further improvements with respect to 'enthalpy of detonation' and 'kinetic theory of detonation' are taking place. An account of such problems and their treatment is given in the literature by several investigators [77–82].

1.4.8
Explosive Power or Strength

The power or strength of an explosive is a measure of its ability to do useful work. This is also termed the potential of an explosive and is the total quantity of heat given off by an explosive at constant volume. The volume of gas (V) and heat of explosion (Q) can be calculated independently. The explosive power of an explosive is then obtained on multiplying Q with V that is, (Equation 1.15):

$$\text{Explosive Power} = Q . V \tag{1.15}$$

In order to calculate the power index of an explosive, its explosive power (as calculated above), is compared with the explosive power of a standard explosive (usually picric acid) that is, (Equation 1.16):

$$\text{Power Index, \%} = \frac{Q . V}{Q\ (\text{Picric acid}) . V\ (\text{Picric acid})} \cdot 100 \tag{1.16}$$

where Q (Picric acid) = $3250\,kJ\,g^{-1}$
V (Picric acid) = $0.831\,dm^3$

Values of power index for some primary and secondary explosives are given in the Table 1.7 which shows that the values for power index of secondary explosives are more than the values for primary explosives.

1.4.9
Brisance

The word 'brisance' has been derived from a French term meaning 'to break' and is distinguished from the total work capacity of explosives. It is essentially the shattering power of an explosive and the rapidity with which the explosive reaches

Table 1.7 Power index values of some primary and secondary explosives (standard – picric acid).

Name	Empirical formula	Power index (%)
Primary explosives		
Lead azide	$Pb(N_3)_2$	13.0
Mercury fulminate	$Hg(ONC)_2$	14.0
Lead trinitroresorcinate monohydrate (Lead styphnate monohydrate)	$C_6H(NO_2)_3O_2Pb.H_2O$	21.0
Secondary explosives		
2,4,6-Trinitrotoluene (TNT)	$C_6H_2(NO_2)_3CH_3$	118.0
2,4,6-Trinitrophenol (picric acid)	$C_6H_2(NO_2)_3OH$	100.0
Glycerol trinitrate (NG)	$C_3H_5(ONO_2)_3$	170.0
Ethylene glycol dinitrate (EGDN) or Nitroglycol	$(CH_2)_2(ONO_2)_2$	182.0
Pentaerythritol tetranitrate (PETN)	$C(CH_2)_4(ONO_2)_4$	167.0
Trinitrophenyl methyl nitramine (CE or Tetryl)	$C_6H_2(NO_2)_3NNO_2CH_3$	132.0
Nitroguanidine or Picrite (NQ)	$C{=}NHNH_2NHNO_2$	99.0
Cyclotrimethylene trinitramine (RDX)	$(CH_2)_3(NNO_2)_3$	169.0
Cyclotetramethylene tetranitramine (HMX)	$(CH_2)_4(NNO_2)_4$	169.0
1,3-Diamino-2,4,6-trinitrobenzene (DATB)	$C_6H(NH_2)_2(NO_2)_3$	132.0
1,3,5-Triamino-2,4,6-trinitrobenzene (TATB)	$C_6\ (NH_2)_3(NO_2)_3$	101.0
2,2′,4,4′,6,6′-Hexanitrostilbene (HNS)	$(C_6H_2)_2(CH)_2(NO_2)_6$	109.0

its peak pressure is a measure of its brisance. Attempts have been made to devise an apparatus to measure it without any marked success. Brisance is approximately related to detonation pressure (P_{CJ}) in a linear manner. Further, detonation pressure is related to density (ρ) and velocity of detonation (D) of an explosive. Therefore, brisance is a function of $\rho \cdot D^2$ that is, (Equation 1.17):

$$\text{Brisance}\ \alpha\ (\rho \cdot D^2) \tag{1.17}$$

where ρ = density of explosive and
D = velocity of detonation of explosive

It has been established that the product ($\rho \cdot D^2$) is an adequate substitute for brisance for all practical purposes. Brisance is of practical importance in determining the effectiveness of an explosive in fragmenting shells, bomb casings and grenades etc. Brisance values are primarily employed in France and Russia.

1.5
Additional Requirements for Military Explosives

Not all explosives are suitable for military applications. For example, dynamite has been used for many years in the industrial and construction fields but is not suitable for military applications. The common explosives such as TNT, NG, NC, RDX, HMX etc., on the other hand, are ideally suited as military explosives, particularly for ammunition.

The requirements of a military explosive are very stringent and very few explosives meet all the characteristics necessary to make them acceptable for military applications. In order to determine suitability of an explosive for military applications, explosives are first investigated for properties described in the previous section followed by their study from the point of view of volatility, toxicity, hygroscopicity and density which are considered of paramount importance because of field conditions and optimal performance requirement.

1.5.1
Volatility

Volatility or readiness with which a substance vaporizes, is an undesirable characteristic for military explosives. Explosives must be no more than slightly volatile at the temperature at which they are loaded or at the highest storage temperature. Excessive volatility often results in the development of pressure within the rounds of ammunition and separation of mixtures into their constituents. Volatility also affects chemical composition of the explosive resulting in the marked reduction in stability leading to an increase in the danger of handling.

1.5.2
Toxicity

Explosives have an abundance of toxicological hazards, the extent of which is being increasingly identified. Due to their chemical structure, most explosives are toxic to some extent. Since the effect of toxicity may vary from a mild headache to serious damage of internal organs, toxicity in military explosives should be contained to a minimum level. Any explosive of high toxicity is unacceptable for military use.

1.5.3
Hygroscopicity

Hygroscopicity is used as a measure of a material's moisture-absorbing tendency. Moisture affects explosives adversely by acting as an inert material that absorbs heat when vaporized and also by acting as a solvent medium that can cause undesirable chemical reactions. The introduction of moisture into an explosive is highly undesirable since it reduces its sensitivity, strength and velocity of detonation. When the moisture evaporates during detonation, cooling occurs which reduces the temperature of reaction. Stability is also affected by the presence of moisture since moisture promotes decomposition of explosive and in addition, causes corrosion of the explosive's metal container. For all of these reasons, hygroscopicity must be negligible in military explosives.

1.5.4
Density

Density of loading refers to the mass of an explosive per unit volume. Several methods of loading: pellet loading, cast loading, or press loading are available and which method is to be used is determined by the characteristics of an explosive. Depending upon the method employed, an average density of the loaded charge can be obtained in the range of 80–95% of the TMD of the explosive. At the same time, high loading density can reduce sensitivity by making the mass more resistant to internal friction. If density is increased to the extent that individual crystals are crushed, the explosive becomes more sensitive. The increased loading density permits the use of more explosive, thereby increasing performance of the warhead, grenade, bomb, shell etc.

In addition, there are some important desirable characteristics which are also considered before their use for military applications.

1.5.5
Life

The armed forces desire a minimum life of 12–15 years for a warhead or ammunition and accordingly, an explosive should also have a minimum life of 12–15 years. It is a bonus if an explosive has a life of more than 15 years. In countries like India where there is a wide variation in temperature in different parts of the country, an explosive is also expected to give desirable performance over a wide range of temperatures, generally –40 °C to +60 °C.

1.5.6
Availability, Cost and Demilitarization or Recycling

The cost of explosives was never given a thought for their use for military applications in the past. However, due to globalization in the recent past, this aspect is now considered. In view of the enormous quantity demands during warfare, explosives must be produced from cheap raw materials that are non-strategic and available in abundance. Further, manufacturing operations must be reasonably simple, cheap and safe. Also, in order to bring down the cost further, the concept of recycling or demilitarization at the end of useful life has also been introduced in recent years. This also brings down the cost in the long run. For example, explosives and propellants used to contain irreversibly crosslinked polymers to bind high energy ingredients together. The crosslinked polymers cannot be removed from explosive and propellant formulations at the end of their useful life. One alternative to this problem is to replace irreversibly crosslinked polymers by thermoplastic elastomers (TPEs) which are linked physically not chemically. At operational temperatures, TPEs are solids and behave much similar to the polymers which are used at present. On the other hand, they melt at high temperatures. Once melted, the ingredients which are bound together in the TPEs, can be separated, recovered and saved for future use. At the same time, TPEs can be repeatedly melted and used to manufacture new products [83].

1.5.7
Eco-friendliness

Injection of wastes into the atmosphere from production and consumption activities results in pollution of the environment. In India, as elsewhere in the world especially Asia, uncontrolled growth of industries and population and consequent environmental deterioration are fast assuming menacing proportions and most of the cities of the world and a majority of the population are afflicted with this problem.

For the first time, the attention of the world was drawn toward environment in early 1970s and on June 05–16, 1972, under the auspices of the UNO, a conference (commonly known as Stockholm Conference on Environment and Development, 1972) was held at Stockholm on the subject. It was during this conference that the governmental agencies, voluntary organizations and people came to realize that protection of the environment is of utmost significance for the survival of human beings and requires concerted efforts at all levels: local, regional, national and global. In India also, an 'Environment (Protection) Act' was enacted by the Parliament in 1986 to provide protection and improvement of environment and prevention of hazards to human beings, other living creatures, plants and property. This act empowers the central government to take all such measures as it deems necessary to protect and improve the quality of the environment and in preventing, controlling and abating environmental pollution. It is in this context that the HEMs community also realized the importance of environment-friendly HEMs and hence efforts were directed in this direction. This also created a need for military to use 'green' munitions that not only minimize adverse effects on human health and environment but also can be more cost-effectively demilitarized at the end of their life cycles [84].

All explosive, propellant, and pyrotechnic formulations consists of a mixture of several ingredients: a metallic fuel (to enhance energy output), a polymeric binder (to impart mechanical integrity and also to act as a fuel), a plasticizer (to facilitate processing), a curing agent (to cure the binder) and other additives (to impart special features). Composite propellants are extensively used for rockets, missiles and space shuttles and most of the current operational composite propellants make use of ammonium perchlorate (AP) as an oxidizer. Sometimes pyrotechnic formulations also use potassium chlorate/perchlorate as an oxidizer. For example, the space shuttle boosters have two loads each of 503 tonnes of AP/Al composite propellant containing ≈ 70% AP (by weight). During the burning of these large boosters, an enormous amount of exhaust gases containing hydrochloric acid and other chlorine-containing compounds which are highly toxic and corrosive in nature are produced. It is estimated that 503 tonnes of propellant liberates ≈ 100 tonnes of HCl and other chlorine containing compounds during its burning thereby polluting the atmosphere and hence causing 'ozone depletion' in the stratosphere. The large amount of HCl emission also causes 'acid rain'. These aspects have become a matter of serious concern for environmentalists in view of stringent environmental laws all over the world and improved public awareness. Hence, there is a need for development of alternate materials which are both environmentally-friendly as well as more energetic to meet the requirements of existing and future military and space missions [85–89].

Lately, concerted efforts have been made to produce eco-friendly propellants with reduced component of such pollutants or altogether free from them. It is due to the sustained efforts of several groups working all over the globe that ammonium perchlorate (AP) is on the verge of replacement by ammonium dinitramide (ADN) and hydrazinium nitroformate (HNF) [90–99]. A major advantage of developing chlorine-free propellants is that they eliminate both primary smoke of metal oxide and secondary smoke of aerosol formed by the condensation of atmospheric water vapor and exhaust plume. This is also important as it mitigates the risk of detection of the launch site due to the absence of a visible signature plume. The rockets employing such propellants would be favored in military applications or in large boosters to check the hazard of 'acid rains' even at the cost of tolerable performance penalty. The rocket propellants with reduced smoke and acceptable burning characteristics, are obviously favored for use in high acceleration tactical missiles. They can also provide an improved camouflage and superior guidance and control due to the higher transmission of their rocket plume compared with metalized composite propellants incorporating AP. Chlorine-free solid propellants also find wide applications in gas generators for turbo pumps of liquid propulsion systems. Combustion products devoid of corrosive constituents, low flame temperature and solid particle content in combustion gases, make them a favorable option. Yet another promising application of eco-friendly propellants is their use in pyrotechnic igniters for liquid rocket engines. The Vulcain liquid rocket engine of the Ariane-5 employs one such igniter. High energy eco-friendly propellant formulations are also being developed for underwater propulsion applications, air-bag industry and automotive safety devices.

1.6
Applications of Explosives

Today, the variety and number of explosives for various applications have become innumerable and this section describes the overwhelming role played by explosives in the progress and prosperity of humanity. A critical assessment of this comprehensive coverage of applications of explosives indicates that the benefits which accrue on account of the use of explosives outweigh their misuse in military pursuits. Two very important quotations regarding the use of explosives are relevant in this context.

> The explosives technologist, who has usually seen and perhaps even experienced the effects of explosives, is the last to want war or to want his

> products to be used for warlike purposes. It is no accident that Nobel, who founded the modern explosives industry, also founded the Peace Prize associated with his name.
>
> Dr. S. Fordham, *High Explosives and Propellants*, Pergamon Press, 1966.

> More explosives have been used in peace than in war. Modern civilization and modern progress would be impossible without explosives.
>
> Prof. T. Urbanski, *Chemistry and Technology of Explosives*, Vol. 1 Pergamon Press, 1964.

However, it is difficult to distinguish between military and peaceful applications of military weapons. Here are a few examples which illustrate that it is extremely difficult to classify them under military or civil applications.

- Gas burning from a newly drilled oil pit in Karlin in Northern Poland in 1981 was successfully extinguished with howitzer shells.
- The danger of an avalanche of snow can be prevented by firing special guns with shells filled with high explosives.
- Firing rockets with explosives loaded with silver iodide is in use for promoting rain. Silver iodide dispersed in higher layers of atmosphere by anti-aircraft rounds is in use in the USSR.

  'TWA Ambassador' p. 37, May 1981 and Prof. T. Urbanski, *Chemistry and Technology of Explosives*, Vol. 4, Pergamon Press, 1984.
- Anti-hail rockets and anti-frost smoke have been reported for the protection of orchard crops to avoid the effects of disastrous weather conditions.

  Dr. C.E. Gregory, *Explosives for Engineers*, Trans Tech Publications, 1993, p. 261.

Explosives are now widely employed for: (i) military applications; (ii) commercial applications; (iii) space applications; (iv) nuclear applications and (v) miscellaneous applications. Military and commercial applications of explosives have been discussed in detail by Dr. Fordham [100] and only salient features are given here.

1.6.1
Military Applications

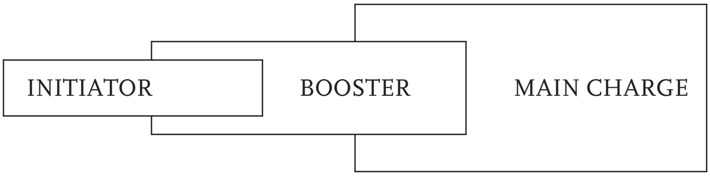
Military requirements for high explosives impose conditions entirely different from most commercial applications as commercial high explosives do not possess the necessary brisance or shattering action. Also explosives suitable for commercial use are generally wholly incapable for most military needs because many of them, particularly the dynamites are too sensitive to impact and shock and present many hazards for modern warfare. For military purposes, high explosives are used as filling materials for warheads of rockets and missiles, bombs and shells etc. The basic requirements of such explosives are maximum power per unit volume, high velocity of detonation, high thermal stability under adverse storage conditions and insensitivity to shock, friction and impact.

It is convenient to broadly classify the use of high explosive fillings as under:

1) The explosive is designed to rupture its container into fragments which are projected as shrapnel against enemy personnel.
2) The explosive is used to produce a blast effect against enemy buildings and equipment.
3) The explosive is used to penetrate targets such as armored vehicles.

For the first purpose, relatively small amounts of explosives are used and the nature of the explosive is of secondary importance. However, larger proportions are necessary for the other purposes. Further, it is desirable to use most powerful explosive in order to get the maximum effect.

High explosives (HEs) are used as fillings for shells, bombs, grenades, warheads, torpedoes, shaped charges etc. The HE fillings which are the source for damage are relatively insensitive and the shock energy required to set off these HE fillings is obtained by the use of explosive train consisting of initiator (initiating system) and a booster. A schematic diagram of an explosive train is given below.



In other words, the initiator, also called primary explosive, is initiated by a small energy input and its explosive output initiates the booster, which in turn, initiates the main charge that is, HE filling. The booster is sufficiently insensitive yet capable of initiation by the initiator. Booster explosives are limited in number (Tetryl and PETN) and their explosive properties are in between initiators and main charges.

1.6.1.1 **Shells**

A shell is a hollow projectile filled with high explosive and is fired from an ordnance other than muzzle loading. A shell has a dual function (i) producing fragments as an anti-personnel weapon and (ii) producing blast against enemy installations. The explosive charge is invariably of high density and high power for the purpose of producing blast against enemy installations. The suitable fillings are TNT, Amatol, or desensitized RDX/TNT mixtures which are usually filled into the shell by casting. Shells for penetrating armor have heavier steel bodies with the nose made of specially hardened metal. The explosive is exceptionally resistant to detonation by impact so that the shell penetrates the armor before the explosive is initiated or detonated by the fuse. The armor-piercing projectiles for anti-tank use contain no explosive but have high-density cores made of tungsten alloy.

1.6.1.2 **Bombs**

Bombs are usually referred to as containers filled with explosives or chemicals and other nuclear, biological, and chemical (NBC) warfare agents along with an explosive train and are designed for release from aircrafts. Bombs carried by aircraft are made of lighter construction than shells. Bombs intended to produce a blast effect against buildings have a lighter casing and are usually filled with an explosive containing aluminum to increase the blast effect. On the other hand, anti-personnel bombs have a relatively heavy casing and are filled with an explosive such as Amatol which is strong enough to break the casing into fragments on impact. Similarly, armor-piercing bombs for use against warships have heavy bodies with smaller high explosive charge and resemble armor-piercing shells in their type of construction. Bombs intended to set fire to buildings, petrol, oil, and lubricant (POL) (now fuel, oil, and lubricant [FOL]) depots etc. are filled with gelled petrol and the Napalm bomb is a typical example of such bombs.

1.6.1.3 **Grenades**

The term ‘grenade’ embraces hand-thrown and rifle-projected anti-personnel grenades. These are self-contained fragmenting, blast, smoke or gas munitions. The hand grenade is considered as the modern equivalent of a stone thrown by hand. The steel body is thinned along crossing lines so that it is broken into fragments of pre-determined size to provide the shrapnel. Sometimes small metal objects such as nuts and bolts, are also used in these explosive fillings. Grenades projected from rifles have a longer range but their construction is essentially the same. The most common smoke grenades are canister-type and are used as ground-to-ground or ground-to-air signaling device, target or landing zone marking device and screening device for unit movements. The riot control grenades which are used to create barriers of tear gas in order to prevent movement of large groups of people are also available and are used to maintain law and order.

General purpose anti-personnel grenades are also used by military in both offensive and defensive roles in the hand-mode or launching (from the rifle) mode. The Defence Research and Development Organization, India (DRDO) has recently developed a state-of-the-art multimode grenade named ‘Shivalik’ which has greatly enhanced the fire power of the infantry soldiers.

1.6.1.4 **Torpedoes**

The explosive charge in a torpedo is carried in the nose, and the rear compartments contain fuel and motor together with the control equipment [101]. As the torpedo is required to penetrate the ship to give the best effects, the nose is of heavy steel construction and the fuse operates with a delay. The high explosive charge must therefore be of maximum density and power that is, the explosive formulation must consist of aluminum powder also. A high density, high power and high velocity of detonation filling is therefore used in torpedoes. The Torpex which consists of a mixture of RDX, TNT and aluminum powder is generally used.

1.6.1.5 **Shaped Charges**

The increased level of protection to military personnel, as a result of development of armor-plated vehicles, has led to a rapid growth of weapons which use shaped charges of explosive. The penetrating power of a shaped charge is proportional to the cube of its diameter and also proportional to the detonation pressure of the explosive used. The suitable fillings for shaped charges are cast pentolite or RDX/TNT or HMX/TNT. Shaped charges and linear shaped charges of different calibers are capable of perforating/cutting various types of targets like reinforced cement concrete (RCC) structures, bunkers, mild steel sheets, plates, blocks and bridges etc. whereas large caliber shaped charges can demolish unexploded ordnance (UXO)/unexploded bombs (UXBs) buried in the soil up to a depth of six meters. Shaped charges are frequently used in the warheads for anti-tank missiles (guided and unguided). These are also used to initiate nuclear weapons.

1.6.1.6 **Warheads**

A warhead is a high explosive mass enclosed in a suitable casing assembled with a fuse which consists of an initiation mechanism. The warhead is located in the rocket or missile which is used to deliver it to the target and subsequently, the target is damaged on the initiation or detonation of the warhead. Warheads are specifically designed for different roles and accordingly, are used for providing different target effects. Warheads are classified as follows:

- Shaped charge warhead (with Octol 85/15 and 70/30 and formulation HMX/Wax 95/5) – used for anti-tank or anti-armor applications.
- Fragment type warhead (with Octol 70/30 formulation) – used for anti-aircraft and anti-personnel applications.
- Blast type warhead (with Dentex and aluminized explosive formulations) – used for damaging soft and semi-hard targets.
- Blast-cum-earth shock type warhead (with Torpex and HBX formulations which are shock-insensitive) – used for damaging runways and heavily built-up bunkers.
- Incendiary type warhead (with gelled formulations like Napalm and solid formulations based on pyrophoric metals) – used against fuel and ammunition dumps etc.

RDX- or HMX-based formulations are generally used in anti-tank bomblets and minelets using casting and pressing techniques. Warheads are based on conventional high explosives for most of the tactical missiles; nuclear warheads are deployed only in strategic and certain tactical missiles by the nuclear club nations, namely USA, ex-USSR, UK, France, China and India.

The ordnance commonly used by the military also includes small arms ammunition, large caliber guns (tank guns), projectiles, rockets and missiles. A propellant (low explosive which undergoes rapid and controlled combustion without detonation resulting in a large volume of hot gases) is used to propel a projectile, be it bullet, grenade, shell, rocket, missile, or in gas generators to drive turbine torpedoes. SB, DB and TB propellants are used for guns or tank guns whereas composite propellants are extensively used for rockets and missiles. Some examples are given below.

- **DB propellants –** Konkurs and HOT missiles (Russian), Milan missile (French), X-29 and 122 mm rockets (Russian).
- **Composite propellants –** Pechora and RZ-61 missiles (Russian), Trishul (booster and sustainer) and AGNI (1st stage) missiles (Indian), magic missile (French) and multi-barrel rocket system (MBRS – Pinaka Rocket [Indian]) etc. India has achieved a significant breakthrough in free flight artillery rocket system technologies with the indigenous development and introduction of Pinaka rocket which is capable of firing a salvo of 12 rockets in less than 40 seconds to a range of 40 km providing a cutting edge technology to the Indian Army. High energy composite propellant is used in Pinaka rockets.
- **Fuel-rich propellants –** Sustainers of Kvadrat (Russian) and Akash (Indian) missiles.

Pyrotechnics are specially formulated to produce a large volume of gases and a lot of energy. The special effects due to pyrotechnics are classified as

Special Effect	**Example**
Smoke	Screening, signaling
Light	Tracking, signaling, decoys, illumination
Heat	Igniters, incendiaries
Sound	Distractions, signaling

Pyrocartridges (also known as electrical initiators) are used to initiate the explosive train for specific applications in rockets and missiles. The pyrocartridges contain broadly the following ingredients or explosives.

- lead styphnate, lead ferrocyanide, potassium perchlorate and aluminum powder;
- propellant NGB 051;
- APC-217;
- pyrotechnic compositions: ME-422, ME-436, ME-436(a), ME-446 and ME-446(a) etc.

The end use of pyrocartridges decides the pyrotechnic composition and its charge mass. The pyrocartridges function on receiving electrical energy and produce a flame with hot gases and particles in order to ignite the igniter composition for propellant combustion. The gas pressure produced can also be used for some specific functions such as:

- pushing a piston;
- fracturing or puncturing a diaphragm;

- separation of nuts and bolts;
- operation of pneumatic valves;
- cutting of various types of cables of sonar systems or parachutes;
- ejection systems of parachute canopy of aircrafts and seats of pilots and opening of aircraft canopy;
- locking and unlocking systems;
- operation of fire extinguishers.

Tanks are most important weapon systems for land battles and their performance is decided in terms of fire power, mobility and protection. In order to provide protection to tanks in the battlefield, add-on explosive reactive armor (ERA) has been developed in several countries including India. ERA consists of an explosive layer sandwiched between two plates which are enclosed in metallic containers and fitted on tanks. Such ERAs are reported to provide protection to tanks against HEAT and HESH warheads, hand held anti-tank (A/T) weapons and to some extent against 'tandem' warheads.

Combustible cartridge cases (CCCs) based on nitrocellulose (NC), cellulose, nitroguanidine etc. have been developed in India and are reported to be useful for 105 mm APDS and HESH tank gun ammunition, 120 mm FSAPDS and HESH tank gun ammunition and 125 mm FSAPDS tank gun ammunition. India has also developed advanced CCCs based on resins likely to be useful for 155 mm howitzer (artillery gun) ammunition in addition to the above-mentioned ammunition.

1.6.2
Commercial Applications

The requirement of explosives for mining and civil applications are increasing every year and the annual growth rate is around 8–9%. The majority applications of blasting explosives are in mining and quarrying (coal and ores: gypsum, anhydrite, non-ferrous metal ores, iron ore and to a small extent, rock salt etc). The gold mines in South Africa, metal mines in USA, Canada and Sweden all use considerable amounts of commercial or civil explosives. Other important applications of explosives are for many civil engineering works such as road building, tunnel driving, land reclamation, canal construction, changing the course of rivers and even for extinguishing fires (i.e., conflagrations of oil wells). In recent years, large quantities of explosives have also been employed in seismographic prospecting for new oil fields.

For all these applications, the general procedure is to drill a hole into the solid rock or coal, insert cartridge of explosive with a detonator followed by firing of explosive to fracture and bring down the rock or coal bed.

1.6.2.1 Coal Mining

Coal mining is usually done by a method which is known as the 'long wall system', the details of which are already available in the literature [100]. The most important thing to remember during coal mining is that methane gas may be liberated not only in the coal itself but also in the nearby stone. It is therefore, mandatory to use 'permitted explosives', both in and near a seam of coal. Further, before any shot is fired in a coal mine, tests are carried out for the presence of methane gas in the air by means of a safety lamp (also known as the Davy lamp). Tests are generally done near the roof where methane gas, being lighter than air, is likely to accumulate. The neighborhood in the mine is sprinkled with large quantities of limestone dust which suppresses these explosions as a precaution against coal dust explosions.

Around 60% of the commercial explosives produced in India are used by the mining industry. Permitted and conventional explosives are extensively used for gassy and open pit mines. In the majority of coal mines, particularly those located in the Indian State of Bihar, there is a continuous evolution of methane gas which forms an explosive mixture with air. By suitably reducing the flame temperature (T_f) and duration of explosion, the ignition of explosive mixture (methane + air) is considerably reduced.

One of the major problems faced by the Indian coal mining industry is the extraction of coal from mines which are on fire during summer (+40 °C to + 48 °C ambient temperature). To meet this requirement, thermally stable compositions have been developed and evaluated. Development of site mixed slurry (SMS) explosives with suitable pump trucks has considerably increased their application in open pit mining of large diameter and deep bore holes. More than 100 holes are routinely fired in a single blast for best performance by sequential firing. To obtain higher water resistance particularly for boreholes having watery discharge, 'emulsion explosives' have been developed. These are more water-resistant in view of the oxidizer solution being covered by a continuous film of fuel. Better detonating properties are another unique feature of 'emulsion explosives' and is attributed to the presence of droplets of super saturated oxidizer phase leading to better intimacy of oxidizer and fuel resulting in a short reaction time.

1.6.2.2 **Tunneling**

Tunneling is a process common to all mining operations and frequently used in hydroelectric and civil engineering work. The principle employed is to drive a number of boreholes into the rock (drilling), load them with explosive (charging) and fire the explosive (firing the round). The broken rock is cleared away and the length of the tunnel increases by approximately the depth of drilled boreholes. The most common explosive which is used for this operation is ammonium nitrate gelatin such as polar ammon gelignite. Nowadays ANFO is also used. When ANFO is used, the primer is usually inserted last to allow time for dispersal of any static electrical charge caused by the loading of the hole.

1.6.2.3 **Quarrying**

Building stone (dimension stone) is usually cut from the quarry face by means of a wire saw. Explosives are used only for clearing overburden or to remove obstacles. The process of quarrying is analogous to obtaining coal from opencast sites where the coal is at or near the surface of the ground. Under wet conditions, a gelatinous explosive is used whereas ANFO is considered suitable under dry conditions. The holes are charged either by lowering cartridges downwards or by pouring in free-flowing explosive such as ANFO. The charges are fired with electric detonators but the common method is to use detonating fuse which is capable of initiating gelatin explosives such as opencast gelignite without the use of a detonator. It is also a convenient method for connecting boreholes together.

1.6.2.4 Other Mining

Apart from coal mining, mining is carried out for gold, anhydrite and gypsum, iron ore, non-ferrous ores and rock salt etc. Copper ores are usually compact and mechanically strong and are broken-up by blasting before they can be removed. The taconite iron ore deposits now being worked in the Lake Superior region, USA, are also extremely tough. The development of inexpensive but powerful ANFO explosives has made their exploration possible.

1.6.3
Military Explosives and Devices for Commercial Applications

In addition to civil and commercial explosives for commercial applications, there are some military explosives and devices which are also being used for commercial applications. The possibilities of using such military explosives for commercial use are described in the following paragraphs.

1.6.3.1 Detonators

Different types of initiatory explosives essentially developed for military applications have also been used for commercial detonators and cap compositions. Service lead azide (SLA) has been extensively used as an initiatory explosive for detonators. However, it has the limitation that hydrazoic acid forms on ageing and ultimately forms sensitive copper azide with copper tube-based detonators (responsible for many unfortunate accidents all over the globe); therefore SLA has been replaced by a new and safe initiatory explosive known as basic lead azide (BLA). BLA has better hydrolytic and thermal stability, better flash pick- up, better free flowing property due to round crystals and higher bulk density. A large number of igniferous detonators for various applications are being manufactured by Indian ordnance factories using BLA as a main ingredient.

1.6.3.2 Pilot Seat Ejection System

The ever increasing speeds of combat aircrafts (mainly the fighters) create difficulties when the pilot has to bale out in an emergency. Flexible linear shaped charges (FLSCs) which when detonated cause separation or severance (without producing any shock or vibration) are used for this purpose. On receiving the pressure impulse from the seat ejection cartridge, the in-flight egress system initiates and cuts the canopy within 2 milliseconds. They can be used for canopy severance system, stage separation of spacecrafts and to obtain clean cutting action. FLSCs with explosive loading from 0.8 to 120 $g\,m^{-1}$ (RDX-based) normally in lead cover have been developed and are used for various applications. FLSC developed for canopy severance system for an advanced aircraft can cut a 7 mm thick acrylic sheet. A few FLSCs have been developed for both military and civilian applications. A miniature detonating cord with an explosive loading of 0.8 $g\,m^{-1}$ designed to cut the canopy material and an explosive transfer line that can transfer the explosive impulse from one point to another (without affecting the surroundings) are among the important explosive components for in-flight egress sub-system of canopy severance system.

1.6.3.3 High Altitude Fuel

Conventional fuels such as firewood, coal etc. are not suitable at high altitudes because of difficulty in ignition, low heat output due to lower oxygen content and low ambient temperature. Gel-based fuels were not found very attractive because of their high degree of inflammability and toxic combustion products.

A solid fuel containing a mixture of wood flour and DB propellant as a binder can provide adequate heat energy to warm food and to prepare tea or coffee. These fuels are highly cost-effective as the ingredients, particularly the DB propellants, are either from the waste available in plenty from the ordnance factories or life-expired DB propellants available from the armed services. This also reduces the disposal problem of DB propellant waste to a large extent.

Compositions based on small pieces of waste DB propellants gelled with acetone and then mixed with fine sawdust as a major ingredient have been formulated, pelletized and finally coated with wax and evaluated for parameters such as total burn time, flame temperature and ash content. These formulations have also been studied in detail for their ignitability and sustained burning behavior under low atmospheric conditions (an altitude of 3000 m and sub-zero temperatures) and for actual performance of boiling the water in an aluminum vessel on a specially designed foldable stove. Fuel performance has been satisfactory. The toxicity level in terms of carbon monoxide and hydrocarbons was also found within the acceptable limits. In addition, it is safe for storage and transportation. A promising high altitude fuel (HAF) composition containing around 25 parts of DB propellant and 75 parts of 10 BSS size sawdust gave density of 0.80 $g\,cm^{-3}$, flame temperature of 1050 °C and ash content of 3%.

1.6.3.4 Air Re-generating Composition

A chemical mixture, whose active ingredient is potassium super oxide (KO_2) regenerates air inside a confined space by liberating oxygen and absorbing carbon dioxide simultaneously, thereby maintaining the breathable air within restorable limits. This composition has already been developed for the Indian Navy in the form of thin sheets to regenerate air inside a submerged submarine, and in the form of granules for self-contained breathing apparatus by divers during underwater operations etc. It can be used in sealed battle tanks against NBC warfare, for high altitude applications and in primary health centers, toxic gas chemical plant operations, manned spacecrafts, medical oxygen in inaccessible places, underwater habitat or mineral exploration, underground public shelter or control rooms and oxygen for gas cutting in inaccessible environments etc. This composition in the form of granules and sheets is available in Russia and has been developed and manufactured on the pilot plant scale by High Energy Materials Research Laboratory (HEMRL), Pune. Further, the technology has been transferred to a private sector in order to meet both military and commercial requirements.

1.6.3.5 **Metal Cladding and Welding**

One of the most innovative uses of explosives is in the field of explosive cladding and welding which was first introduced by Du Pont (USA) in the early 1960s. It is a technique for joining similar and dissimilar metal plates, tube to tube-plate etc. resulting in high integrity joints. The set-up of cladding and welding is shown in Figure 1.3.

In cladding, an explosively driven metal plate (flyer plate) hits another plate (base plate) kept at a specified distance – greater than half the flyer plate thickness in order to allow this plate to achieve its maximum impact velocity. The extreme temperature and pressure produced with high-energy impact, bonds the plates together through a metallurgical bond. This technique is employed to bond

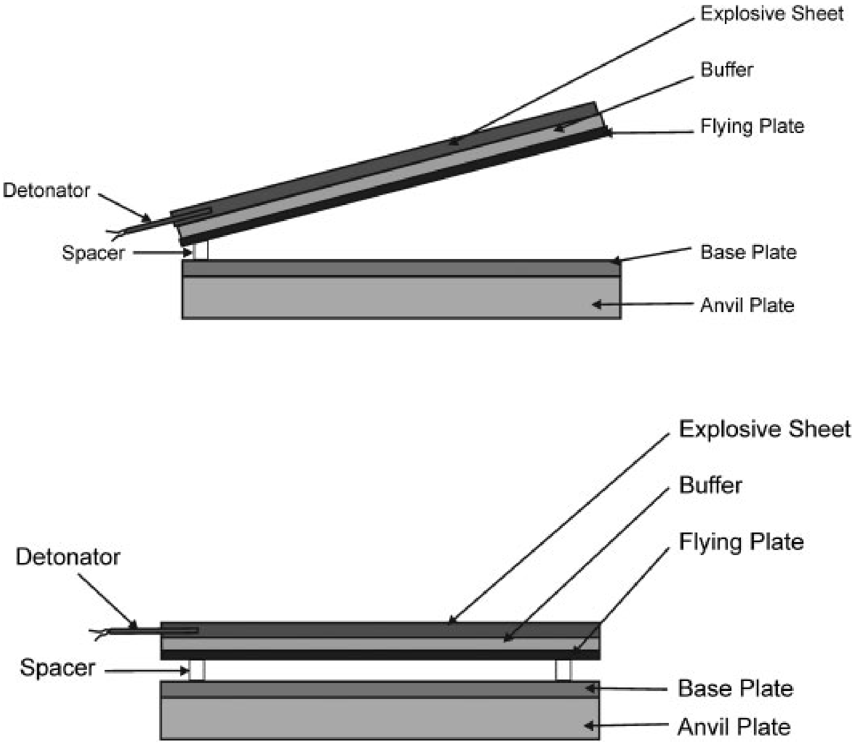


Figure 1.3 Parallel and angular plate welding set-ups.

dissimilar metal plates which are difficult to weld by conventional methods. It is also possible to fabricate heat exchangers by this technique. Explosive welding of 100 tubes to a plate has been successfully used for the manufacture of heat exchangers as well as their repair. This technique increases the service life of heat exchangers and gives much stronger bonds than that obtained in seasoned welding. Commonly used explosives for welding are nitroguanidine, Amatol and dynamite (not containing NG but nitrostarch).

Although stainless steel (SS) remains the most used cladding material, exotic materials such as titanium, zirconium or tantalum are finding increasing applications. Apart from plate-to-plate and tube-to-tube-plate, there are many other applications for explosive welding which are listed below.

- **Chemical retorts for high temperature use:** copper–stainless steel;
- **Containers for water and nuclear waste:** copper–stainless steel and cupro nickel–mild steel;
- **Vessels for treatment of municipal waste water containing chloride ions:** titanium–mild steel;
- **Cooking utensils having good thermal properties**: copper–mild steel and copper–stainless steel;
- **Dual hardness armor plate:** armor–soft steel and armor–aluminum;
- **Hard corrosion resistant edges on tools, earth moving vehicles and factory equipment:** Hastelloy B–mild steel;
- **Bimetallic strip for thermostats:** α-brass–Invar;
- **Electric supply (earthing strip connection):** aluminum–aluminum and copper–aluminum;
- **Transport rail to rail:** copper–steel current carrying joints;
- **Bus-bar connections:** steel–aluminum;
- **Formation of honeycomb structure:** aluminum–aluminum;
- **Heat exchanger:** titanium–mild steel and mild steel–mild steel.

1.6.3.6 Metal Working

Explosives have been extensively used in metal working industry. Operations like explosive forming and explosive sizing have proved to be of high value to aircraft and missile industries. The use of explosive riveting in aircraft construction is well-known [102]. Another interesting application of explosives in metal working is the explosive hardening which results in change of engineering properties such as tensile strength (TS), elongation, yield strength etc. of metals. This is achieved by detonating a thin layer of plastic sheet explosive in contact with the metal surface to be hardened. As reported, the yield strength improves by about 100% whereas TS improves by about 40% using this technique.

1.6.3.7 Explosive Forming

This method is applied advantageously to metal parts of large size or unusual shapes and to the parts from hard-to-work materials which cannot be readily fabricated by conventional methods.

1.6.3.8 Explosive Cutting

This method consists of simply fastening a flat strip of explosive (mixed with some polymeric material as a binder) on the metal to be cut and detonating the explosive. The parting of material that is, cutting results from the interaction of shock waves induced by detonation. The width of the flat explosive strip should be twice the thickness of the metal to be cut in order to get better results. This method is not accurate and can be employed where high cutting accuracy is not required. Flexible linear shaped charges (FLSCs) are usually employed for this purpose.

1.6.4
Space Applications

Rockets constitute a very important system of all kinds of missiles which are used to deliver warheads to the target. Rockets are also used both to launch satellites and to control their motion to some extent, while in orbit. In the first case, the rockets used are large, use a lot of propellant, burn for a long period and produce large thrusts. On the other hand, the second type of rockets are small, burn fuel for a short period and produce small thrust. A satellite is usually carried by a multistage rocket system from the ground. After taking it to a predetermined height and giving it a predetermined velocity in a given direction, the rocket system is shut off and separated from the satellite [103].

At this stage, it is considered necessary to explain the working of a rocket in brief.

1.6.4.1 Solid and Liquid Rockets for Space Applications

The rocket consists of a rocket motor (which also acts as a combustion chamber on ignition of solid propellant) with a nozzle on one end and an ignition device on the other end. (Figure 1.4)

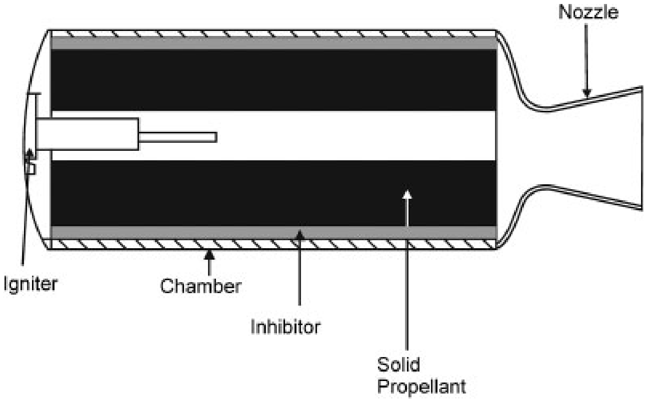


Figure 1.4 Main components of a solid rocket.

The rocket motor houses a propellant which is ignited with the help of an ignition device. As a result of the combustion of propellant, very hot gaseous products are produced. When these hot gaseous products are ejected through a nozzle at a high speed, a thrust is produced in the opposite direction (Newton's third law of motion) and accordingly, the rocket moves. The launching of a satellite uses propellant to provide the required thrust to induce a satellite into a predetermined orbit. The solid fuel booster rocket normally contains several hundred tonnes of propellant which on burning releases copious quantities of carbon dioxide, nitrogen oxides and hydrochloric acid gases and water vapor that help push the satellite into space or orbit. For such propellants, AP is extensively used as an oxidizer because its decomposition products are all gases and therefore, it enhances the rocket's thrust.

The total time taken for the propellant to burn is called burn-out time and the completion of combustion is called burn-out. In large rockets, burn-out time may be as much as 100 to 120 s and pressure in the chamber may be of the order of 30 to 50 times the atmospheric pressure. The temperature inside the chamber may reach 2400 to 4400 K. Thus, materials which withstand high temperature and pressure have to be used in constructing the rocket. At the same time, these materials should be light in weight which brings down the dead weight of the launch vehicle. The nozzle needs to be made of special materials such as carbon-carbon, carbon-phenolic, silica-phenolic composites etc. which withstand high temperature and its shape is crucial to the performance of the rocket. In case of solid rockets, the propellant could be in the rocket all the time until it is ready to be used. However, once the combustion starts, it cannot be controlled or stopped.

In the case of a liquid rocket (Figure 1.5), the propellant has to be injected into the combustion chamber in a controlled manner. Thus two storage tanks are required for storing the fuel and oxidizer. A supply system to introduce the fuel and oxidizer in controlled quantities in the proper sequence is also an additional requirement. The fuel and oxidizer are to be transferred to the storage tanks only

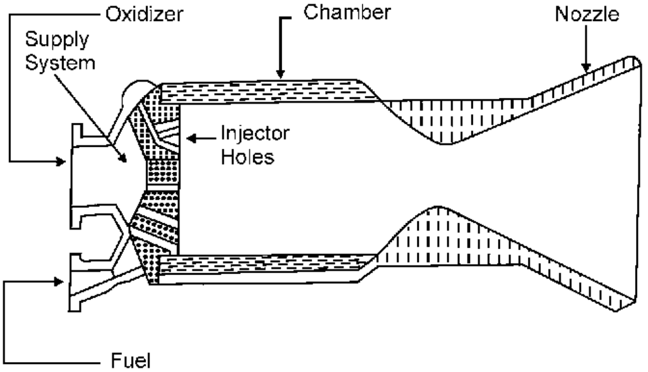


Figure 1.5 Main components of a liquid rocket (without storage tanks for fuel and oxidizer).

when the rocket is to be fired. In this case, the propellant supply system and the nozzle play crucial roles. It is possible to shut off or control combustion in the case of liquid rockets by manipulating the flow system. Solid rockets are however considered to be simpler, more reliable and more cost-effective and that is why solid propulsion has played an important role in the access to space during the second part of the twentieth century.

Whether the rocket is solid or liquid, its motion is governed by the escaping jet of hot gases. At sea level, the gases may escape with a velocity of 1800 to 4500 $m\,s^{-1}$. As the fuel burns, the rocket which is initially at rest, starts moving up, picking up speed with time. The weight of the rocket continuously decreases as the fuel burns and hot gases escape. Thus the velocity increases more rapidly with time. The final velocity depends not only on the burn-out time but also on the final weight of the rocket. The ratio of initial weight to final weight should be as high as possible to attain high velocities. However, because the combustion chamber, nozzle and other parts remain till the end and some fuel also would be left unburned, it is not possible to make this ratio more than 4 or 5, that is, the initial weight of rocket would be about 4–5 times the final weight after burn-out. The final velocity using present day propellants would therefore be such that a single rocket cannot carry a satellite to impart the required velocity. That is why two or three more stages are usually added.

The second stage rocket not only has an initial velocity given to it by the first stage, it has also gained height, thereby needing less increase in velocity to go into the orbit. Before the second stage takes over, the first stage is separated so that the total weight of the system is also reduced. The task of the third stage is even easier.

However, it is found that having more than three or four stages does not make the task of launching a satellite into orbit significantly easier. Having too many stages might also make the system less reliable. Hence, the usual practice is to have not more than a four-stage system for launching satellites. The first stage is usually called the booster stage and the subsequent ones, upper stages.

1.6.4.2 **Various Indian Satellite Launch Vehicles**

Rockets with satellite payloads are used in meteorology, weather forecasting, survey for minerals, satellite communication, mapping etc. Major countries have their own space programs and similarly, India has also its program under which the Indian Space Research Organization (ISRO) has established a strong infrastructure for space research and also to provide space-based services. This program includes:

1) **Indian National Satellite (INSAT):** For telecommunication, television and meteorology.

2) **Indian Remote Sensing (IRS) Satellite:** For resource monitoring and management. IRS Satellite provides a convenient platform for rapid resource survey – minerals, water, agriculture, forest etc. covering large areas and in sufficient detail.

3) **Polar Satellite Launch Vehicle (PSLV):** For launching IRS/Sun-Synchronous Orbit (SSO) Satellites. India launched its first unmanned spacecraft under its mission 'Chandrayaan-1' to explore the moon on October 22, 2008 with the help of upgraded version of PSLV (also called PSLV-XL).

4) **Geo-synchronous Satellite Launch Vehicle (GSLV):** For creating links among remotest and most inaccessible parts of the country. Also, it makes it possible to keep a close watch on our weather, climate and pollution.

India has developed GSLV that can inject 1500–2000 kg Class satellite in geosynchronous transfer orbit (GTO) and efforts are on to develop launch vehicles called GSLV MK III * for 4000–5000 kg Class satellite (* three-stage vehicle with 110 tonnes core liquid propellant stage, strap-on stage with two solid rocket propellant motors each with 200 tonnes propellant and upper stage [cryogenic stage] with a propellant [liquid hydrogen – liquid oxygen] of 25 tonnes) [104–106]. Figure 1.6 depicts various satellite launch vehicles of ISRO.

Table 1.8 describes the general characteristics of various launch vehicles along with their approximate period of development. It also clearly brings out the increase in the variety of propellants used, from solid only in SLV-3 and ASLV to solid and liquid in PSLV and finally, to solid, liquid and cryo in GSLV.

1.6.4.3 Explosives, Propellants (Oxidizers, Binders and Plasticizers) and Pyrotechnics for Satellite Launch Vehicles

The rockets with solid composite propellants consisting of ammonium perchlorate (oxidizer), pulverized aluminum powder, special additives and binder-cum-fuel such as poly(butadiene–acrylic acid–acrylonitrile (PBAN), carboxy-terminated

Figure 1.6 Various satellite launch vehicles of ISRO.

Table 1.8 General characteristics of ISRO's different satellite launch vehicles.

Vehicle	SLV-3	ASLV	PSLV	GSLV
Gross lift-off weight, tonnes	17	39	275	400
Max. dia., m	1.0	1.0	2.8	2.8
Height, m	22.0	23.5	44.0	51.0
No. of stages	4	5	4	3
Propellants	Solid	Solid	Solid and Liquid	Solid, Liquid and Cryo
Guidance	Open-loop inertial	Close-loop inertial	Close-loop inertial	Close-loop inertial
Orbit Injection	Spin Stabilized	Spin Stabilized	3-Axis Stabilized	3-Axis Stabilized
Main Payload, kg	Rohini 40	Sross 150	IRS 1000	INSAT 1500–2000
Primary Mission	Space Science and Technology	Space Science and Technology	Remote Sensing	Communication and Meteorology
Development Period	1972–1983	1982–1994	1982–1995	1991–2002

polybutadiene (CTPB), lactone-terminated polybutadiene (LTPB), hydroxyl-terminated polybutadiene (HTPB) and some liquid propellants (monomethyl hydrazine [MMH] – nitrogen tetroxide [N_2O_4], unsymmetrical dimethyl hydrazine [UDMH]–nitrogen tetroxide [N_2O_4] etc.) have been extensively used for space exploration, meteorological studies, sounding rockets, SLVs, ASLVs, PSLVs and GSLVs with different payloads.

In addition to propellants, pyro devices (based on pyrotechnic formulations) are used for accomplishing various mission-critical events such as rocket motor ignition, stage separation, stage destruction, heat-shield separation, venting out of propellants from the spent stage, opening and closing of valves, opening of solar panels, reorientation of antenna of satellite, command from ground for maneuvering satellite in space etc. The quantities of pyro formulations required for such tasks are meager compared with the quantities of propellants required for booster and upper stages. However, their role is crucial for accomplishing the goals of the mission.

Hexanitrostilbene (HNS) has been reported for use in achieving stage separation in space rockets and also as a component of heat-resistant compositions employed in the Apollo spaceship and for seismic experiments on the moon [107]. Similar to HNS, 3,3′-diamino-2,2′,4,4′,6,6′-hexanitrodiphenyl (DIPAM) has also been reported for such applications [108].

Further, space shuttles, spacecrafts and other new launch vehicles would be used for exploring the moon, Mars, Saturn and other planets and again large quantities of propellants and some pyro devices as well would be required for such missions.

In the last two to three decades, a variety of high energy materials – high performance explosive (CL-20), thermally stable explosives (TATB, PYX, BTDAONAB etc.), melt-castable explosives (TNAZ, Tris-X), insensitive explosives (NTO, DINGU, TNAD, ADNBF etc.), energetic binders (GAP, Poly[NiMMO], Poly[GlyN], NHTPB, PNP etc.), energetic plasticizers (BDNPA/F, Bu-NENA, etc.) and high performance and eco-friendly oxidizers (ADN, HNF etc.) have been reported in the literature and have great potential as possible ingredients in composite propellants and liquid mono and bi propellants for future space applications [15, 109–112].

1.6.5
Nuclear Applications

The information on nuclear weapons is treated as highly classified and as such very little information is available in the open literature. The use of explosives for nuclear weapons is the subject matter of specialized books. However, an attempt has been made to collate this information and include it in this book for the sake of completeness.

1.6.5.1 Types of Nuclear Weapons

Nuclear weapons are broadly divided into two classes: – Fission weapons and fusion weapons depending on the dominant source of the weapon's energy.

1) **Fission weapons or bombs:** They derive their power from nuclear fission when heavy nuclei such as uranium (U) or plutonium (Pu) are bombarded by neutrons and split into lighter elements, more neutrons and energy. The newly generated neutrons then bombard other nuclei which then split and bombard other nuclei and so on. This process continues and leads to a nuclear chain reaction which releases large amount of energy. These are also historically called atomic bombs or atom bombs or A-bombs.
2) **Fusion weapons or bombs:** These are based on nuclear fusion when light nuclei, usually isotopes of hydrogen such as deuterium and tritium combine together into heavier elements and release large amount of energy. Weapons which have a fusion stage, are also known as hydrogen bombs or H-bombs because of their primary fuel or thermonuclear weapons because fusion reactions require extremely high temperature to occur. The fusion reaction requires the nuclei involved to possess a high thermal energy and that is why, this reaction is also called thermonuclear. The extreme temperatures and densities necessary for a fusion reaction are generated with energy from a fission explosion. A pure fusion weapon that does not need a fission primary is hypothetical and no weapons of this sort have ever been developed.

Nuclear weapons which usually use nuclear fusion, have far greater yields than weapons, which use only fission, as fusion releases more energy per kilogram and can also be used as a source of fast neutrons to cause fission in depleted uranium.

Further, the light weight of the elements used in fusion makes it possible to build extremely high yield weapons which are still portable enough to deliver. Compared with large fission weapons, fusion weapons are cheaper and much less at risk of accidental nuclear explosion.

The distinction between these two types of weapons is blurred because they are combined in almost all advanced modern weapons. For example, a smaller fission bomb is first used to create necessary conditions of high temperature and pressure which are required for fusion. Similarly, fusion elements may also be present in the core of fission devices as well because they generate additional neutrons which increase efficiency of the fission reaction. Further, most of the fusion weapons derive substantial portion of their energy from a final stage of fissioning which is facilitated by the fusion reactions. The simplest nuclear weapons are pure fission bombs. They were the first type of nuclear weapons built during the American Manhattan Project and are considered as a building block for all advanced nuclear weapons.

Other specific types of nuclear weapons are commonly referred to by their names such as neutron bombs (enhanced radiation weapons), cobalt bombs and salted bombs. The atomic bomb was the first nuclear weapon to be developed, tested and used. It was developed under the direction of American physicist J. Robert Oppenheimer (1904–1967) and implemented toward the end of World War II. On August 6, 1945, an atomic bomb (nicknamed as '*Little Boy*') was dropped by an American B-29 bomber (Enola Gay) over Hiroshima, Japan instantly killing more than 70 000 people. On August 9, 1945, the USA dropped a second atomic bomb (nicknamed '*Fat Man*') killing some 40 000 people in Nagasaki, Japan. Because of this large-scale devastation, such nuclear explosive devices have never again been used in a war.

1.6.5.2 **Assembly**

There are two methods for assembling a supercritical mass: The first one brings two sub-critical masses together (gun method) whereas the second one compresses a sub-critical mass into a supercritical one (implosion method). Some salient features of these methods are:

1) **Gun method:** A simple technique for assembling a supercritical mass is to shoot one piece of fissile material as a projectile against a second piece as a target. This method was used in the '*Little Boy*' weapon which was detonated over Hiroshima. Gun method can only be used for U^{235} because of the relatively long time it takes to combine the materials. However, this method is now of only historical importance and is practically obsolete for technologically advanced nations.

2) **Implosion method:** Explosives are also used in nuclear weapons to generate the implosion required to bring the two halves of the radioactive device together. The implosion is achieved with the help of secondary explosives which surround the material and rapidly compress the mass to a supercritical state on their detonation. This encompasses two major assemblies: (i) com-

bined pit assembly consisting of pusher, tamper, reflector, neutron initiator and fissile material and (ii) explosive lenses made of secondary explosives with detonator or detonators. On actuation of the detonator or detonators, secondary explosive detonates giving rise to shock waves which are carefully shaped into a perfect sphere centered on the pit and traveling inwards. These shaped shock waves compress the mass of fissile material to a supercritical state leading to efficient and powerful explosion with simultaneous release of a large amount of energy. To derive an implosion, divergent detonation waves or shock waves are converted into a convergent one through three approaches: (i) multiple initiation points; (ii) advanced wave shaping techniques; and (iii) explosive lenses.

In approach (iii), the principle of refraction is used to shape a detonation wave, just as it is used in optics to shape a light wave. Optical lenses use combinations of materials in which light travels at different speeds. This difference in speed gives rise to refractive index which bends the wave when it crosses the boundary between materials. Similarly, explosive lenses use materials that transmit detonation or shock waves at different speeds. The original scheme used a hollow cone of an explosive with a high detonation velocity and an inner cone of an explosive with a low detonation velocity. The detonator initiates the high velocity explosive at the apex of the cone. A high velocity detonation wave then travels down the surface of the hollow cone, initiating inner explosive. The low velocity detonation wave lags behind, causing the formation of a concave (or planar) detonation wave.

The gun-type method is essentially obsolete and implosion technique is much more suitable in order to reduce weight of the weapon and consequently, increase weight of the fissionable material. Further, gun-type weapons also have some safety related problems.

1.6.5.3 **Fissile Materials and Explosive Lenses**

At this stage it is considered appropriate to describe some salient features of fissile materials and explosive lenses, before we discuss about the explosives and their formulations for nuclear weapons.

1) **Fissile Materials:** A fissile material is the one that can support a fission chain reaction. The production and procurement of weapon-grade fissile material is usually the most difficult part of a weapon development program. U^{235} and Pu^{239} are the fissile materials most often used in nuclear bombs. Several other isotopes have also been considered as potentially usable in fission weapons. As reported in the literature, neptunium^{237} can also be used for a nuclear explosive device. Test bombs using U^{233} have also been detonated by the USA and it is also thought to be a component of India's weapons program because of the availability of thorium in abundance in India (U^{233} is an artificially produced isotope from Th^{232} in a nuclear reactor). Pu^{239} has a higher probability for fission than U^{235} and a large number of neutrons are produced per fission event resulting in a smaller critical mass. The fissile properties of U^{233} are generally somewhat between those of U^{235} and Pu^{239}. The use of U^{233} as a

fissile material is considered a viable approach for countries which have thorium in abundance.

Most modern weapons use a hollow Pu core or pit with an implosion mechanism for detonation. Also low density Pu or delta-Pu is used due to its high compressibility. Modern pits may be composites of Pu^{239} and U^{235}. In view of chemical reactivity and toxic nature of Pu, it is a general practice to plate the completed pit with a thin layer of inert material – previously nickel and now gold.

2) **Explosive Lenses:** An explosive lens is a device composed of several explosive charges that are shaped in such a way so as to change the shape of the detonation wave passing through it. This is achieved by using a spherical shell closely fitting and accurately shaped bodies of explosives of different velocities of detonation to form explosive lenses. In an implosion nuclear weapon, an array of explosive lenses is used to change several approximately spherical diverging shock or detonation waves into a single spherical converging one. The converging wave is then used to collapse the various shells (tamper, reflector, pusher, etc.) and finally compresses the core (pit) of fissionable material to a supercritical state. Explosive lenses are usually machined from a plastic bonded explosive (PBX) and an inert insert (a dense foam or plastic), called a wave-shaper. Earlier explosive lenses did not include a wave shaper but used to employ two explosives that have significantly different velocities of detonation (VODs). The use of explosives having low and high VODs again results in a spherical converging detonation wave to compress the core. The *Fat Man* dropped on Nagasaki used Composition-B as a high VOD explosive and Baratol as a low VOD explosive.

The best combination of explosives is the fastest and slowest that are available. This provides greatest possible refractive index (in other words, greatest bending effect) and thus allows use of a wider lens angle. The fastest and slowest explosives generally reported are HMX (octogen) and Baratol respectively. HMX has a detonation velocity of $9110\,ms^{-1}$ (at a pressed density of $1.89\,g\,cm^{-3}$) while dense explosive Baratol (formulation: 76% barium nitrate + 24% TNT) has a detonation velocity of $4870\,ms^{-1}$ (at a cast density of $2.55\,g\,cm^{-3}$). Mixtures of TNT with glass or plastic microspheres have also been reported to be effective, light weight and economical slow explosives for explosive lenses in the recent unclassified literature.

During World War II, Los Alamos developed lenses using a combination of Composition B (or Comp. B) for the fast explosive (detonation velocity of $7920\,ms^{-1}$ at a cast density $1.72\,g\,cm^{-3}$) and Baratol for slow explosive. Later systems used very powerful explosive HMX as a fast explosive (mostly as a plastic bonded explosive). Plumbatol (formulation: 70% lead nitrate + 30% TNT, VOD – $4850\,ms^{-1}$ at a cast density $2.89\,g\,cm^{-3}$), a denser and slightly slower explosive, might have been used for some later lenses systems designs. Boracitol (Formulation : 60% boric acid + 40% TNT, VOD – $4860\,ms^{-1}$ at cast density $1.55\,g\,cm^{-3}$) is definitely known to have been used, probably in thermonuclear weapon triggers and perhaps in other types of weapons as well. The choice of explosives in an implosion system is driven by the desire for high performance, safety, ease of fabrication, or sometimes by special properties like slow detonation velocity needed in explosive lenses.

The desire for high performance leads to selection of highly energetic explosives that have very high detonation velocities and pressures. HMX is the commonly known explosive with highest performance. Using HMX as a main explosive provides greatest compression. HMX was widely used in US weapons from the late 1950s to 1970s, in a formulation called PBX-9404 (subsequently this formulation developed serious safety related problems). HMX is also known to be the principal explosive in many Soviet weapon designs as Russia is selling this explosive extracted from decommissioned warheads for commercial use. The chemically related RDX is the next powerful explosive which was the principal explosive used in most early US designs in the form of a castable mixture called Composition B.

1.6.5.4 **Explosives and Binders for Nuclear Weapons**

PBXs have replaced melt-castable explosives in almost all nuclear weapons. The PBX formulations that have been used include PBX-9010, PBX-9011, PBX-9404, PBX-9501, LX-04, LX-07, LX-09, LX-10, LX-11 and insensitive PBXs used for this purpose are PBX-9502 and LX-17.

As a result of a number of accidents in which HE detonation caused widespread plutonium contamination and also repeated fatal explosions during mixing, processing and fabrication, scientists have become more concerned with the weapon safety. Many of the high explosives such as RDX and HMX which are commonly used, are rather sensitive to shock and heat. This has led to the use of explosives such as TATB, HNS etc. that are insensitive to shock or fire. Safety is of paramount importance and is achieved by using TATB, a secondary high explosive which is very insensitive to friction and impact and has a very high ignition temperature. Insensitive explosive compositions/PBXs are all based on TATB as its chemical cousin DATB lacks this marked insensitivity. TATB is reasonably powerful, being a little less powerful than Composition-B. A formulation known as PBX-9504 has been developed where 15% of TATB is replaced by HMX resulting in a compromise between power and sensitivity [113–116]. Some explosives and binders used in nuclear weapons are given in Table 1.9 and the details of some explosive formulations and PBXs used in nuclear weapons are given in Table 1.10.

1.6.6
Miscellaneous Applications

In addition to applications of explosives for military, commercial, space and nuclear weapons, they are also reported to play an important role in the following fields.

1.6.6.1 **Agriculture**

Similar to the applications of explosives in mining, quarrying and construction work, explosives have a definite place in agriculture. As a power source, they enable

Table 1.9 Explosive and binder ingredients used in nuclear weapons.

Name	Application
Barium nitrate ($Ba[NO_3]_2$)	Heavy metal oxidizer used in slow explosive compositions (Baratol).
Boric acid (H_3BO_3)	Inert material used in slow explosive compositions (Boracitol).
Lead nitrate ($Pb[NO_3]_2$)	Heavy metal oxidizer used in slow explosive compositions (Plumbatol)
1,3,5-Trinitrotoluene (TNT)	Used as a main high explosive and also acts as a meltable binder.
Pentaerythritol tetranitrate (PETN)	Sensitive and powerful high explosive used in detonators
Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX, Cyclonite, Hexogen, Cyclotrimethylene trinitramine)	Powerful explosive used as a main high explosive
Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (β-HMX, Octogen, Cyclotetramethylene tetranitramine)	Very powerful explosive used as a main high explosive
Hexanitrostilbene (HNS)	Heat stable and relatively insensitive high explosive used in 'slapper' detonators.
1,3-Diamino-2,4,6-trinitrobenzene (DATB)	Thermally stable and insensitive main high explosive
1,3,5-Triamino-2,4,6-trinitrobenzene (TATB)	Thermally stable and very insensitive main high explosive. Special fine-grained TATB is used in boosters
Nitrocellulose (NC)	Solid explosive used as a binder
Kel-F (copolymer of chlorotrifluoroethylene and vinylidene fluoride) (3 : 1 ratio)	Inert binder for main high explosive compositions
2,2-Dinitropropyl acrylate (DNPA)	Solid explosive used as a binder
Viton-A (copolymer of hexafluoropropylene and vinylidene fluoride)	Rubbery solid used as a binder
Bis(2-fluoro-2,2-dinitroethyl) formal (FEFO)	Liquid explosive used as an energetic plasticizer
Bis(2,2-dinitropropyl)acetal/formal (BDNP A/F)	Liquid plasticizer mixture (50% BDNPA and 50% BDNPF) used in PBX compositions
Tris(chloroethyl)phosphate (CEF)	Plasticizer used for PBX Compositions

Table 1.10 Explosive formulations and PBXs used in nuclear weapons.

Name	Composition	Salient properties and applications
Baratol	76% $Ba(NO_3)_2$ + 24% TNT	Low VOD castable explosive used in early explosive lenses
Boracitol	60% H_3BO_3 + 40% TNT	Low VOD castable explosive used in later explosive lenses
Plumbatol	70% $Pb(NO_3)_2$ + 30% TNT	Low VOD castable explosive and its use is reported in U.S. Nuclear Weapons
Composition – B	63% RDX + 36% TNT + 1% wax	High VOD castable main explosive used in early nuclear weapons (e.g., Fat Man)
Cyclotol	75% RDX + 25% TNT	Basically modified Composition B with a higher RDX content for better performance. Used as a high VOD castable main explosive and also considered as a substitute for PBX-9404
LX-04	85% HMX + 15% Viton-A	High VOD PBX used as a main explosive
LX-07	90% HMX + 10% Viton-A	High VOD PBX used as a main explosive
LX-09	93% HMX + 4.6% DNPA + 2.4% FEFO	High VOD PBX used as a main explosive. The plasticizer was found to exude during storage.
LX-10 LX-10-1	95% HMX + 5% Viton-A 94.5% HMX + 5.5% Viton-A	High VOD PBXs used as a main explosive. Likely substitute for LX-09
LX-11	80% HMX + 20% Viton-A	High VOD PBX used as a main explosive
LX-17	92.5% TATB + 7.5% Kel-F 800	High VOD and insensitive PBX and it is one of the two IHEs in use
PBX-9010	90% HMX + 10% Kel-F 800	High VOD PBX used as a main explosive
PBX-9011	90% HMX + 10% Estane	High VOD PBX used as a main explosive
PBX-9404	94% HMX + 3% NC + 3% CEF	High VOD PBX widely used as a main explosive. Reported to have some safety related problems.
PBX-9501	95% HMX + 2.5% Estane + 2.5% BDNP F/A	High VOD PBX used as a main charge
PBX-9502	95% TATB + 5% Kel-F 800	High VOD and insensitive PBX. Principal IHE in recent nuclear weapons and is likely to replace earlier PBXs

the time-consuming and heavy work to be done in a fraction of time and also, at a lesser cost than by usual methods. The chief uses of explosives in agriculture are: removal of stumps and trees, tree planting, sub-soiling, digging pole holes, breaking boulders (blasting is the quickest and usually the most economical method of breaking up boulders or rock ledges and reducing them to a size that can be handled more easily), ditching and draining, log splitting (with the use of log splitting guns which use explosives and are available in the western countries and it is the most economical method for splitting logs up to a meter in diameter), well sinking (for drinking water and agricultural purposes) and orchard management (anti-hail rockets and anti-frost smoke for the protection of orchard crops to avoid the effects of disastrous weather conditions) etc. In addition, swamp drainage, land reclamation, canal construction, changing the course of rivers, stream diversion etc. are some other operations which may be executed successfully with the use of explosives [117].

1.6.6.2 **Medical Industry**

The use of nitroglycerine tablets has been known for several decades to dilate the blood vessels promptly thereby decreasing the blood pressure and thus giving instant relief from angina. However, the present trend is to use other esters of nitric acid such as erythritol tetranitrate, mannitol hexanitrate, PETN and other similar derivatives instead of NG for this purpose. These nitric acid esters being crystalline, are not assimilated readily and therefore, act more slowly but produce a longer lasting effect.

Presently explosives are being explored for their use in the area of medicines and surgery and two such important applications are:

1) Some Japanese researchers at the Kyoto University of Medicines have developed a new method for removal of large stones (mineral deposits) in kidney and bladder by using micro-explosive charges without any surgery [118–120]. Recently, applications of underwater shock waves have been extended to various clinical therapies for example, in orthopedic surgery for bone formation [121, 122], in cancer therapy, for enhancement of chemotherapeutic effects [123] and in drug delivery [124, 125].

2) While working on nitrocubanes (a new class of energetic materials), the researchers for ARDEC and Geo-Centers, USA were surprised to learn that cubane compounds might have biomedical applications as well because cubyl intermediates also show beneficial anti-viral, anti-AIDS and anti-cancer properties. Also, cubanes could be bound to monoclonal antibodies which may then be delivered specifically to pathogens or cancerous cells in the body. The energy released from the high energy cubanes is then used to destroy the cancerous cells. Thus cubanes may be regarded as tiny antipathogens or anticancer bombs. Further, it has also been established that cubanes are not inherently toxic and lipophilic platforms but biologically stable and innocuous.

1.6.6.3 **Food Industry**

The pyrotechnic formulations such as 50% $CaSi_2$ and 50% Fe_3O_4 which are relatively cool and gasless, have been extensively used in the past for the manufacture of self-heating food cans. The cool and gasless pyrotechnic formulation is held in a central tube with a $CaSi_2/Pb_3O_4$/clay formulation as the first fire formulation.

1.6.6.4 **Civil Engineering**

Explosives with high VOD have a blasting or shattering effect. As a result, explosives help us to construct tunnels and remove obstacles during road construction. In large-scale excavation work, a technique similar to those used in quarrying is employed. Explosives have been found useful in demolition work (dismantling and clearing of structures and buildings). Explosives have also been extensively used to demolish structures made of stone, brick, concrete, steel and timber. For cutting action, FLSCs have also been used whereas for demolition both conventional explosives (RDX, HMX etc.) and silent explosive (Acconex) have been used. 'Acconex' is a non-explosive demolition agent – a special type of expanding cement which produces cracks while setting, has been developed by one of the DRDO laboratories. The cement when mixed with 25–30% water forms a slurry which is poured into pre-drilled holes of about 65–70% of the size of the boulder, rock or target. The slurry sets in about 15 minutes and with the passage of time, it develops high expansive stresses due to the presence of special silicates in the composition. The phenomenon of demolition occurs with crack initiation. Propagation of cracks from hole increases in number. The process of cracking takes between 24 and 72 hours, depending upon nature and size of the target and the temperature. The most important feature of Acconex is that it demolishes rocks or concrete structures without any noise or adverse effect on neighboring structures. This is advantageous when demolishing is done in densely populated and built-up areas. Further, it does not cause any pollution as no gases are liberated.

1.6.6.5 **Automobile Industry**

Industries such as medical, food etc. rely on small explosive charges for a number of applications. Similarly in the automobile industry, the use of an explosive sodium azide which consists of interpenetrating lattices of ions of sodium and azide (a group of three chemically bound nitrogen atoms) is well-known for car airbags, a safety feature incorporated to absorb impact. An impact disrupts the lattice structure where the sodium combines with the oxygen while the nitrogen atoms regroup into pairs to form large quantities of nitrogen gas to fill the airbag in a little over 50 milliseconds. Automotive safety airbags which have to be inflated, require a pyrotechnic formulation that generates a large amount of gas quickly but does not cause fire or any more blast than necessary. A number of nitrogen-rich heterocycles called high nitrogen content-high energy materials (HNC-HEMs) have recently been reported in the literature which are likely to be useful for such applications [126–128].

1.6.6.6 **Oil and Gas Industry**

Nowadays, oil is considered to be the most important resource affecting the economy of many countries. For oil exploration, it is necessary to fix the location of actual oil bearing strata after drilling of exploratory holes. There are three segments in this industry where explosives are used extensively; (i) seismic exploration, (ii) well perforation and (iii) abandonment.

Seismic exploration is used to generate a prediction of underlying geology which can be interpreted by specialists to calculate the possibility of finding oil and gas bearing strata. Sound waves are reflected at the boundaries between the strata in the ground similar to the walls of buildings etc. The use of this principle is made in seismic prospecting by generating a shock wave with an explosive charge and observing the reflections by means of geophones located at suitable positions. This prospecting can be carried out either on land or at sea and enables a geological map of the substrata. Based on this geological map, the explorer is in a position to conclude the sites most likely to contain oil. Once oil bearing strata is located, a set of explosive devices, called 'shaped charges' (based on RDX with copper or steel as core material) are then fired electrically from the surface for *well perforation*. The jet formed from the shaped charges bore holes into the soil up to a depth of 2–3 meters and if the strata contains oil, it rushes to the surface. HMX-based shaped charges with more effective liner materials are also available for superior performance. The use of a thermally stable explosive such as PYX has also been reported for perforation of oil and gas wells (Chapter 2, Section 2.2.18.5).

In the oil and gas industry, the term '*abandonment*' generally refers to the activities undertaken to remove the structures used to sustain oil and gas production after the production is ceased. The structures range from a few tonnes of steel on the seabed to a complete platform constructed from around 30 000 tonnes of steel framework. The task of removal requires extremely detailed and careful planning as well as substantial resources. Explosives are very efficient tools for cutting steel underwater and have been the preferred choice of many offshore operators for over 40 years. Also explosives offer the flexibility of a single controlled cut or multiple simultaneous cuts for remote and safe toppling of very large structures [129].

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2
Status of Explosives

Several aspects of explosives: definition, classification, fundamental features, important characteristics including their applications in various fields have already been discussed in Chapter 1. During last 50 years, the number of explosives reported in the literature has increased exponentially and it is therefore proposed to discuss the status of current and future explosives in this chapter. Toward the end, some areas have also been identified for further research in the coming years by the high energy materials (HEMs) community.

2.1
Historical Aspects

Explosives are thought to have been discovered sometime in the seventh century by the Chinese. The first known explosive was black powder (also known as gunpowder) which was a mixture of charcoal, sulfur and saltpeter and burned violently. By around the tenth century, the Chinese had developed weapons which used black powder's energetic properties. The Arabs also took advantage of this discovery, presumably through trading routes. The first European mention of gunpowder was by the thirteenth century scientist and educator Roger Bacon (1220–1292) who recorded a recipe of 75% saltpeter (potassium nitrate), 15% charcoal and 10% sulfur. Charcoal and sulfur function as fuels in the powdered mixture whereas saltpeter acts as an oxidizer.

Black powder revolutionized warfare and also played a significant role in the overall development in the pattern of living throughout the world. The Chinese first used black powder as a gun propellant as early as 1130, placing it in bamboo tubes that were reinforced with iron to propel stone projectiles and arrows. The Chinese records also indicate that they used black powder in bombs for military purposes.

Until the discovery of fulminating gold in early 1600s, gunpowder was the only known explosive. Gunpowder remained in wide use until the mid 1800s, when the first two modern explosives, nitroglycerine (NG) and dynamite, were invented. Nitroglycerine was invented by an Italian chemist, Ascanio Sobrero (1812–1888) in 1847 and its potential for blasting was later demonstrated by the Swedish inventor Alfred B. Nobel (1833–1896).

High Energy Materials: Propellants, Explosives and Pyrotechnics. Jai Prakash Agrawal

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Around the same time, nitration of cellulose to produce nitrocellulose (NC also known as guncotton) was undertaken by different groups and finally the invention of NC was reported by Schonbein (Basel) and Bottger (Frankfurt) independently in 1846. Further, dynamite was invented by Alfred B. Nobel in 1866.

Since black powder is relatively low in energy, it leaves a large proportion of corrosive solids after explosion and absorbs moisture readily, it was succeeded in late 1800s by smokeless gunpowder and picric acid. The first smokeless powder, known as cordite, was invented by the English chemists Sir James Dewar and Sir Frederick Augustus Abel in 1889. It was made in two forms: a gelatinized nitrocellulose and a mixture of NC and NG with a small quantity of petroleum jelly added to act as a stabilizer. Smokeless powder soon became the primary ammunition for use in pistols.

As early as 1873, picric acid was detonated to produce explosion. Subsequently, it was found to be a suitable replacement for black powder. From 1888 into World War I, it was used as a basic explosive for military purposes. Because it required prolonged heating at high temperatures in order to melt and because it also caused shells to corrode in the presence of water, an active search for better explosives continued.

Trinitrotoluene (TNT) was the most commonly used conventional military explosive during the twentieth century. Although it had been used extensively in the dye industry during late 1800s, it was not adopted for use as a military explosive until 1902, when the German army used it to replace picric acid. TNT was first used in warfare during the Russo-Japanese War (1904–1905). The US Army began its use in 1912. After an economical process was developed for the nitration of toluene, TNT became the chief artillery ammunition in World War I (1914–1918). The most valuable property of TNT is that it can be safely melted and cast alone or with other explosives as a slurry.

With the advent of tanks, World War II (1939–1945) saw a return to maneuvering tactics, with artillery explosives continuing to provide the most destructive force on battlefields. Nitroguanidine, referred to as Gudol Pulver, was a primary explosive used during World War II. It produced very little smoke, had no evidence of a muzzle flash on firing and also increased the lifetime of gun barrels. Subsequently, pentaerythritol tetranitrate (PETN) and cyclotrimethylene trinitramine (RDX) were developed for filling hand and anti-tank grenades. A mixture of TNT, RDX, and wax was used to detonate bombs. A mixture of PETN and TNT was used to detonate demolition charges. Torpedo warheads were often made of cast mixtures of RDX, TNT, and aluminum powder.

2.2
Status of Current and Future Explosives

Explosives which are extensively used by the military currently are described in brief in the succeeding paragraphs. Some HEMs which have been reported recently and possess tremendous potential based on their properties for military applications, have also been included in this section.

2.2.1
Black Powder

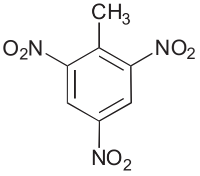
The first chemical explosive was invented in China around 1300 years ago and was originally used exclusively for military purposes. Black powder was not used industrially until the seventeenth century when it was adopted to blast out mines in Europe. In order to detonate black powder, it must be ignited by flame or intense heat.

The chief use of black- or gunpowder was as a propellant in guns and rockets. It is also an important material for the fabrication of fireworks. The main shortcoming of black powder is that it is hygroscopic. Attempts were made to improve black powder in this regard by replacing KNO_3 by ammonium nitrate or guanidine nitrate.

Special types of gunpowders which contain no sulfur are known as sulfurless gunpowders. They are used where any corrosion due to sulfur is undesirable. The powders for pyro-devices are often of the sulfurless variety.

2.2.2
Trinitrotoluene

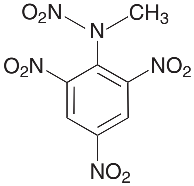
2,4,6-Trinitrotoluene (TNT) [$CH_3C_6H_2(NO_2)_3$: Structure (2.1)] is one of the most important high explosives and it has been the most common conventional military explosive during the twentieth century. First used in the Russo-Japanese war in 1905, it became the basis for most of the explosives used in subsequent wars. It is obtained by the nitration of toluene. It is a yellow crystalline solid with a m.p. 80.4 °C and velocity of detonation (VOD) 6700 ms^{-1} at 1.58 $g\,cm^{-3}$ density. It is insoluble in H_2O but dissolves in conc. HNO_3 or H_2SO_4 and is precipitated from their solutions on adding H_2O. It is non-hygroscopic and dissolves in practically all organic solvents. It is very stable to heat and on storage and has found wide application as a bursting charge explosive for shells, bombs and grenades etc. either alone or mixed with other explosives. It was used on a large scale in both world wars. To economize TNT, its mixtures with dry powdered ammonium nitrate (AN) were introduced in World War I under the name of Amatols which are less violent than TNT. Amatol 80/20 (AN/TNT) is in fact, a balanced explosive, that is, it has sufficient oxygen for the complete combustion of carbon and hydrogen to CO_2 and H_2O and thus gives little or no smoke. Amatol 50/50 (AN/TNT) was extensively used in shells. When a small quantity of aluminum powder is added to Amatols, the mixtures are known as Minols. Both Amatols and Minols



Structure (2.1): Trinitrotoluene (TNT) are suitable only when a blast effect is required as with aircraft bombs and not violent shattering and fragmentation of the explosive casing. TNT is most important as an explosive even today because it is simple and relatively safe to manufacture and above all, its high chemical stability and low sensitivity to impact and friction make it very safe to handle. Further, its toxicity is also low.

2.2.3
Tetryl

2, 4, 6-Trinitrophenylmethylnitramine [$(NO_2)_3\ C_6H_2N(CH_3)\ NO_2$: Structure (2.2)], also known as tetryl or composition exploding (CE) is made by the nitration of dimethylaniline with the use of large excess of HNO_3 (Sp. gr. 1.40). It is a yellow crystalline solid of m.p. 129 °C and VOD 7075 ms^{-1} at 1.53 g cm^{-3} density. It is more sensitive to initiation and finds use as a primer or booster along with high explosives in order to facilitate detonation of less sensitive high explosives. It is much more sensitive to mechanical impact than TNT and is used in admixture with TNT to increase sensitivity to initiation of the latter. Tetryl has been a widely used explosive since 1906. It is more powerful than TNT (110–130% of TNT). Its sensitiveness to impact and friction, particularly to rifle fire, is higher than that of TNT. Depending on its density, tetryl may explode or detonate with widely varying intensity and therefore with different heats of explosion or detonation.

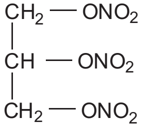


Structure (2.2): 2, 4, 6-Trinitrophenylmethylnitramine (tetryl)

In the USA, tetryl has not been considered for use in new explosive trains since 1973, however, it is still manufactured and used in Germany and India. On the contrary, it is no longer synthesized in the UK as both the material itself and its manufacture are considered to pose health hazards.

2.2.4
Nitroglycerine

Nitroglycerine [$NO_3CH_2CHNO_3\ CH_2NO_3$: Structure (2.3)] is prepared by reacting glycerine with a mixture of sulfuric and nitric acid under carefully controlled



$$\begin{array}{l} CH_2 - ONO_2 \\ | \\ CH - ONO_2 \\ | \\ CH_2 - ONO_2 \end{array}$$

Structure (2.3): Nitroglycerine (NG) conditions. It is a colorless oily liquid and it is transparent in pure form. It possesses density 1.6 g cm^{-3} and VOD 7700 ms^{-1} (calculated). It is very sensitive to mechanical shock and friction. NG became the basis of modern commercial blasting explosives and is considered as the first high explosive found suitable for practical applications. It is seldom used alone as an explosive but used extensively in propellant compositions and dynamites.

Nitroglycerine and dynamite succeeded black powder as the chief explosives. An Italian chemist, Ascanio Sobrero, invented NG in 1846 and the Swedish scientist Alfred Nobel invented dynamite in 1867,

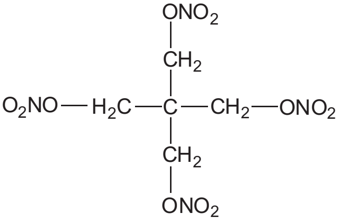
2.2.5
Dynamite

Dynamite, the modern blasting explosive was made by Alfred Nobel in 1867. The original dynamite was a mixture of 75% NG and 25% kieselguhr (a porous absorbent powder that yielded a dry, much less sensitive material). Although it may contain up to 75% NG, dynamite is a powdery material. It was found to be relatively safe for transportation, handling and was also called Nobel's Safety Powder. Dynamite is supplied in waxed paper wrapped cartridges about 2.5 cm in diameter and 20 cm long weighing 224 gm each. Similar packing is also used for other NG-based explosives so that the cartridges can be loaded in boreholes without opening.

Nobel developed gelatinous dynamite in 1875 by making a jelly from the dissolution of a collodion-type nitrocotton in NG, producing a more powerful explosive than the straight dynamite and one that proved to be safer. Later ammonium nitrate was also used in dynamite, which made it even safer and less expensive to produce.

2.2.6
Pentaerythritol Tetranitrate

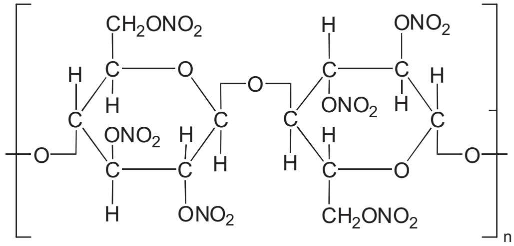
Pentaerythritol tetranitrate [$C(CH_2NO_3)_4$: Structure (2.4)] is made by nitrating pentaerythritol (PE) with nitric acid (d = 1.50–1.52 g cm^{-3}) at a temperature not exceeding 25 °C. It is a white crystalline solid with m.p. 140 °C and VOD 8000 ms^{-1} at 1.62 g cm^{-3} density. It is slightly more sensitive to mechanical shock and friction than CE. It has been used extensively with TNT under the name Pentolite (50:50::PETN:TNT) for loading of small-caliber projectiles and grenades as well as



Structure (2.4): Pentaerythritol tetranitrate (PETN) booster charges. When used alone as a filling in detonating fuse and detonators, PETN is always desensitized with 5%–10% paraffin wax.

2.2.7
Nitrocellulose

Nitrocellulose [Structure (2.5)] together with NG gave the strong foundation for modern gun propellants, finally outdating gunpowder as a propellant. It is prepared by the action of concentrated HNO_3 on cotton waste or cotton linters or wood pulp in the presence of H_2SO_4 as a dehydrating agent. By changing the acid composition and reaction conditions, a series of nitrocelluloses can be made, in which nitrogen content varies from 12.0%–13.5%. NC with lower nitrogen content is very stable and very insensitive to blows and friction. As the nitrogen content increases, the stability decreases slowly and NC becomes sensitive. NC is generally classified as NC Type A, NC Type B and NC Pyro. Various types of NCs mainly differ in terms of nitrogen content, solubility, and viscosity (molecular weight). The details are shown in Table 2.1.


Where `n' is the degree of polymerization

Structure (2.5): Nitrocellulose (NC)

It is seen from Table 2.1 that NC Type A contains nitrogen in the range of 12.1–12.3% and is soluble in an ether: alcohol (E:A:: 2:1) system. This may be used for solvent type propellants (gun propellants) as well as solventless type propellants (rocket propellants). The viscosity of NC must be high for solvent type propellants. NC Type B contains nitrogen in the range of 12.95–13.25% and is called gun cotton. Its solubility is less in an E/A system. This is mainly used for gun propellants, that is, solvent type propellants. Gun cotton was also used to some extent as an explosive charge in torpedoes, submarine mines and for demolition purposes; for these purposes, it has now largely been replaced by TNT. The nitrogen content of NC Pyro is in the range of 12.5–12.7%. This type of NC may be prepared either by direct nitration (also known as straight-cut) or by blending NC Type A and Type B. The solubility of NC Pyro (straight-cut) in E/A solvent system is poor compared with that of NC Pyro (blend). Similar to NC Type B, it is also used for gun propellants.

The stability and insensitiveness of NC (when dry) bear an inverse relation with nitrogen content. That is, as the nitrogen content increases, stability decreases slowly and NC becomes more sensitive. On the other hand, lower nitrates are very stable and insensitive to impact and friction. The stability and insensitiveness fall off rapidly above a nitrogen content of 12.8%.

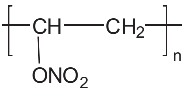
Table 2.1 Some salient properties of various types of nitrocellulose.

Property	Nitrocellulose		
	Type A	Type B	Pyro
Nitrogen content, %	12.2 ± 0.1	13.1 ± 0.15	12.6 ± 0.1
Solubility in ether: alcohol (2:1) solvent, % (at 15 °C)	95 plus	8–12	i) Straight-cut: Poor solubility ii) Blend: Better solubility
Viscosity of 1 % solution, centistokes (C/S) (at 25 °C) Solvent: Hercules solvent [toluene %–55, ethyl acetate %–20 and ethyl alcohol %–25] (by weight)	≈5–7 used for solventless type propellants (rocket propellants). ≈20 used for solvent type propellants (gun propellants)	≈20 used for solvent type propellants (gun propellants) and not for solventless type propellants (rocket propellants)	≈20 used for solvent type propellants (gun propellants)

With the advent of polymer chemistry in recent times, numerous efforts have been made to develop synthetic polymers containing nitro groups which may replace NC. In this regard, polyvinyl nitrate (PVN) needs some discussion.

2.2.8
Polyvinyl Nitrate

Polyvinyl nitrate [Structure (2.6)], originally thought to be a replacement for NC (at least partly), had been explored by a number of groups [1–3] who concluded that the propellants based on PVN (on replacement of NC by PVN) have the properties: comparable 'heat of explosion' and burning rate, decreased tensile strength, increased elongation and pressure exponent (n) and hence PVN is not acceptable as a replacement of NC [4].



$$\left[-\underset{\displaystyle ONO_2}{CH}-CH_2- \right]_n$$

Structure (2.6): Polyvinyl nitrate (PVN)

Some work was also done by Consaga *et al.* on cyclodextrin nitrates with a view to replacing NC [5]. The composites of this invention are mixtures of (i) a cyclodextrin nitrate or a mixture of cyclodextrin nitrates and (ii) an energetic organic nitrate plasticizer. These composites are useful as replacements for nitrocellulose (NC) because they are more thermally stable and less sensitive to impact and yet have comparable or greater energy content than NC. However, cyclodextrin nitrates are dry powders that are sensitive to electrostatic discharge (ESD).

The cyclodextrins can be nitrated using conventional techniques that are used for the preparation of NC where the degree of nitration is controlled by varying the nitration conditions. The energetic organic nitrate esters used for plasticization of cyclodextrin nitrates include 1,1,1-trimethylolethane trinitrate (TMETN), 1,2,4-butanetriol trinitrate (BTTN), triethylene glycol dinitrate (TEGDN), NG, 1,2-propylene glycol dinitrate (PGDN), pentaerythritol trinitrate (PETRIN), diethylene glycol dinitrate (DEGDN), or a mixture thereof. The preferred energetic organic nitrate ester plasticizers are TMETN, BTTN, DEGDN, NG or mixtures thereof. The most preferred plasticizer is TMETN. Further, when enough plasticizer is used to convert a powdery cylodextrin nitrate to a rubbery composite, ESD is decreased to about that of the plasticizer while the impact sensitivity remains as low as that of a cyclodextrin nitrate. However, the present status of this polymer as a replacement of NC is not available in the literature.

2.2.9
Mercury Fulminate

Mercury fulminate (MF) is the oldest initiatory explosive known.

$$(\mathrm{C} \overset{\longleftarrow}{\equiv} \mathrm{NO})_2\ \mathrm{Hg}$$

It was invented by the British scientist N. Howard in 1799 and was first used in 1814, in percussion caps for gunpowder charges in British Service cap compositions. Alfred Nobel invented its use in detonators in 1867. Mercury fulminate is prepared by the reaction of mercury, ethyl alcohol and nitric acid in an all-glass apparatus. It is white in color when pure and grayish-yellow when slightly impure. Its crystal density is 4.42 $\mathrm{g\,cm^{-3}}$. Extremely sensitive to impact and friction, it burns fiercely if unconfined but detonates if confined. The most important property of this compound is that its burning at a moderate rate, started by ignition, impact or friction can easily be converted into detonation. The grayish product has a bulk density of 1.7 $\mathrm{g\,cm^{-3}}$ and has a loading density of 3.5 to 4.0 $\mathrm{g\,cm^{-3}}$ when pressed into detonators. The VOD is 4740 $\mathrm{m\,s^{-1}}$ at 3.96 $\mathrm{g\,cm^{-3}}$ loading density. Further compression gives 'dead-pressed' material which is less sensitive to initiation. It is not hygroscopic in the presence of moisture but may react with metals specially aluminum.

Its use has now been abandoned in most of the countries.

2.2.10
Lead Azide

Lead azide [$\mathrm{Pb(N_3)_2}$] (LA) is a salt of hydrazoic acid ($\mathrm{N_3H}$, highly poisonous) and is prepared by reacting solutions of sodium azide and lead acetate or nitrate. This exists in two forms: the α form (orthorhombic and stable) and β form (monoclinic) which has a tendency to revert back to the α form. The β form is much more sensitive. The two forms differ in their rate of decomposition when heated. Crystalline LA is stored in dry conditions because it becomes more sensitive when stored under water due to the increase in the size of crystals. Lead azide is less sensitive to impact having a 'Figure of Insensitiveness' (F of I) of 20, but it is highly friction-sensitive. It is comparatively insensitive to flash and therefore, it is always used in conjunction with lead styphnate. It is unstable in the presence of moisture and carbon dioxide giving out hydrazoic acid. It is not compatible with copper and its alloys since hydrazoic acid liberated from LA forms dangerous copper azide. In view of its stability, cost and availability, it is preferred over MF and is extensively used in military ammunition and commercial blasting caps. The most important drawback of LA is that it cannot easily be ignited. At the same time, the most important attribute is that it passes from burning to detonation very rapidly. When used in very small amounts, it is capable of initiating detonation in other explosives. It is therefore considered suitable for use in detonators but not in caps. It detonates when subjected to a flame or spark and its VOD is $4500\,\mathrm{ms}^{-1}$ at $3.8\,\mathrm{gcm}^{-3}$ loading density. Lead azide is a more efficient detonating agent than MF.

The introduction of LA into commercial detonators resulted in an unacceptably high level of explosions during manufacture and use and hence its use was discontinued until it could be prepared in less sensitive form. A number of methods have been used to prepare LA in a less sensitive form. The main control of properties is by synthesis rather than by any other approach. Lead azide compositions RD 1343 (improved CMC co-precipitated LA), RD 1352 (improved dextrinated LA) and Service lead azide (SLA) illustrate some modified LAs which are used depending on the requirements. Different processes developed for the modification of LA may be summarized as follows:

- **Service lead azide (SLA):** SLA is prepared by double decomposition of lead acetate and sodium azide in the presence of sodium carbonate and acetic acid. In this process, LA crystals grow around the lead carbonate nucleus and as a result, formation of larger and sharp needle-shaped crystals is prevented, making it comparatively less sensitive than pure LA. SLA is still sensitive to friction and sometimes causes accidents. However, it is used in the absence of any other alternative.

- **Dextrinated lead azide (DLA):** An amorphous form of LA was made in the USA in 1930 and was found to be safe during manufacture and handling. It was prepared by slowly adding a slightly alkaline solution of sodium azide to a solution of lead nitrate and dextrine. It is hygroscopic and has poor cohesive properties. Dextrine prevents the formation of large sensitive crystals of LA and regulates their shape.

- **Improved lead azide (Co-precipitated Na-CMC):** For this form of LA, precipitation is carried out using sodium carboxy methyl cellulose (Na-CMC). The product obtained has lower bulk density than SLA. The use of sodium amylose offers some advantages over both Na-CMC and dextrine [6].

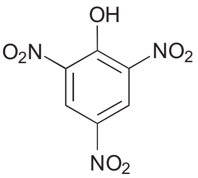
- **Gelatin, azide, molybdenum disulfide (GAM) form of lead azide:** GAM was developed and introduced during 1967. It is manufactured by the precipitation of LA from a solution containing gelatin and a suspension of molybdenum disulfide. MoS_2 is incorporated in the crystal agglomerate to obtain the desired combination of cohesion and electrical properties. The electrical properties of the modified product thus obtained are excellent, however, the bulk density and power of GAM lead azide are lower than those of DLA.

2.2.11
Picric Acid, Lead Picrate and Ammonium Picrate

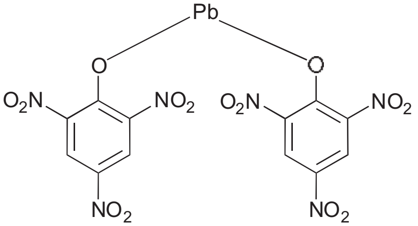
The presence of nitro groups in phenol and resorcinol enhances their acidic properties and that is why trinitrophenol is commonly known as picric acid while trinitroresorcinol is known as styphnic acid.

2,4,6-Trinitrophenol [picric acid, $HOC_6H_2(NO_2)_3$: Structure (2.7)], which is obtained by the action of nitric acid on phenol in the presence of sulfuric acid, was the earliest high explosive used as a bursting charge in artillery shells. It was also used as an explosive in detonating fuses and an ingredient of pyrotechnic compositions. It is a yellow, crystalline solid of m.p. 121 °C and VOD of 7100 ms^{-1} at 1.69 gcm^{-3} density. It forms highly sensitive initiatory explosives if contaminated with metals, especially lead. Lead picrate is more sensitive than any other metal picrate and because of this hazard, it has now been replaced by more modern and superior explosives. Lead picrate [Structure (2.8)] is extremely sensitive to impact and is considered too dangerous for practical use.

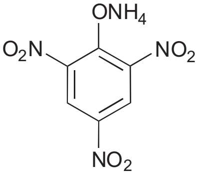
Ammonium picrate [also known as Explosive D: Structure (2.9)] was used as a military explosive to fill armor-piercing shells because of its relative insensitiveness to impact. It was also used in admixture with KNO_3 as a substitute for black powder or gunpowder. Ammonium picrate in conjunction with TNT [Picratol-52/48 (Ammonium picrate/TNT)] was also formulated and used.



Structure (2.7): Picric acid



Structure (2.8): Lead picrate

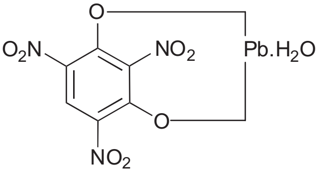


Structure (2.9): Ammonium picrate

Other well-known initiating explosives are: lead trinitroresorcinate (lead styphnate), diazodinitrophenol (DDNP), tetrazene and mercuric-5-nitrotetrazole (MNT).

2.2.12
Lead Styphnate (Lead-2,4,6-trinitroresorcinate)

Normal lead styphnate (LS) [Structure (2.10)] was first reported by Von Herze in 1914, although its basic salt, that is, basic LS was prepared by Griess [7] way back in 1874, by the reaction of acidified magnesium styphnate with lead nitrate/acetate in hot aqueous solution. It is precipitated as monohydrate and consists of reddish-brown rhombic crystals. It is filtered off, washed with water, sieved through a stainless steel sieve and dried. Like other initiatory explosives, it is kept in wet conditions until used.

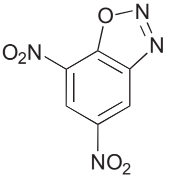


Structure (2.10): Lead styphnate (LS)

The crystal density of LS is 3.02 g cm^{-3} but its bulk density is 1.4–1.6 g cm^{-3}. It is sparingly soluble in acetone and ethanol but soluble in ether, chloroform and carbon tetrachloride. Its ignition temperature is 250 °C and explodes at 267–268 °C. Lead styphnate is a very stable initiator. It is less sensitive to impact than MF or DDNP but is more brisant. It is also less sensitive to friction than MF or LA. It is a relatively poor initiating agent but because of its ease of ignition, it is used as a cover charge for LA and also as an ingredient of primary compositions. Normal LS presents considerable static risk during handling and is therefore made under conditions of high relative humidity with adequate earthing of buildings and equipment [8].

2.2.13
Diazodinitrophenol

Diazodinitrophenol (DDNP or Dinol) [Structure (2.11)] or 4,6-dinitrobenzene-2-diazo-1-oxide was first prepared by Griess [9] in 1858 but was developed commercially as a detonating agent 70 years later. It is prepared by the diazotization of

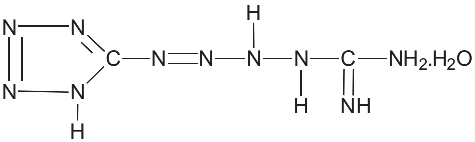


Structure (2.11): Diazodinitrophenol (DDNP) picramic acid by means of sodium nitrite and hydrochloric acid. It occurs as yellow needles which decompose without melting on heating to 188 °C. DDNP is less sensitive to impact than MF, LA or LS [10]. It is more stable and brisant than MF and is used in blasting caps, loading fuse detonators and in priming compositions for military use. The initiating power of DDNP is slightly less than that of LA. Some investigators are of the opinion that DDNP alone is not suitable as an initiating material for detonators because it requires too long a path to change from burning to detonation and hence it is necessary to add another initiating material such as LA. DDNP does not become dead pressed even under a pressure of 9140 kg cm^{-2} which is considered a great advantage for an initiating material. Russians have recently reported a method for preparing free-flowing DDNP by diazotization of magnesium picramate with sodium nitrite and hydrochloric acid [11].

It has good storage properties and is a preferred initiating explosive particularly in the USA and Japan as it is relatively insensitive to impact and friction compared with other initiating explosives. Its VOD is 6900 ms^{-1} at a density of 1.58 g cm^{-3}.

2.2.14
Tetrazene

1-(5-Tetrazolyl)-4-guanyl tetrazene hydrate (shortened to tetrazene) [Structure (2.12)], was first prepared by Hoffmann and Roth in 1910 by the reaction of aminoguanidine and nitrous acid [12]. Subsequently, Patinkin *et al.* ascribed the following structure to tetrazene [13].

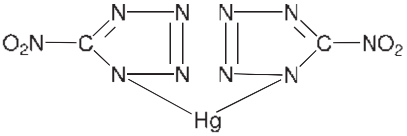


Structure (2.12): 1-(5-Tetrazolyl)-4-guanyl tetrazene hydrate (tetrazene)

Tetrazene is a colorless to pale yellow fluffy material which is practically insoluble in water, alcohol, ether, benzene and carbon tetrachloride and its bulk density is 0.45 g cm^{-3}. It explodes when subjected to a temperature of 160 °C for 5 s. It is not stable at temperatures above 75 °C. Tetrazene is as sensitive to impact as MF and DDNP. When exposed to a flame, it undergoes a mild explosion with the production of black smoke. When subjected to high pressure, it becomes 'dead-pressed'. As the density increases, its brisance falls off. Its power is slightly higher than that of MF but it does not have sufficient initiating efficiency to permit its use alone as an initiatory explosive. It can however, act as a good sensitizing agent to other initiating explosives and mixtures and hence, it finds extensive use in cap compositions. In spite of this disadvantage, tetrazene is used in cap compositions where as little as 2% in the composition results in an improved uniformity of percussion sensitivity. Tetrazene, though unstable, is used as a sensitizer in cap compositions and no other suitable alternative has been found so far.

2.2.15
Mercuric-5-nitrotetrazole

Mercuric-5-nitrotetrazole [Structure (2.13)] was prepared according to the methods reported by Gilligan *et al.* [14] and Redman and Spear [15]. Thus, 5-aminotetrazole was treated with sodium nitrite and copper sulfate to obtain $Cu(NT)_2HNT \cdot 4H_2O$ (where NT: nitrotetrazole). The copper salt was subsequently converted to the ethylene diamine complex; MNT was then obtained by treating the complex with mercuric nitrate in HNO_3 medium. The precursors and final product were air dried. The synthesis of these compounds is carried out in a fume hood behind a protective polycarbonate shield in a stainless steel reaction vessel.



Structure (2.13): Mercuric-5-nitrotetrazole (MNT)

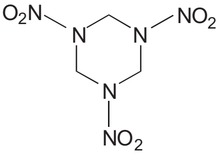
The intermediate used in the preparation of nitrotetrazole salt is sodium salt, purity of which markedly affects some of the properties of the mercuric salt. The 'temperature of ignition' and 'dead pressing level' are increased with increasing purity of the sodium salt. Unlike the silver salt, it does not exhibit polymorphism. Bates *et al.* reported higher yields of MNT by altering the reaction parameters [16]. It is also reported that MNT has shown to be a very effective single component detonant with greater output than LA [17–19]. It is also claimed that in contrast to LA, MNT possesses advantage of excellent inflammability even in a moist environment [20]. Further, its stability is not influenced by the presence of carbon dioxide and it may be stored without deterioration in tropical climates. Its sensitivity to electrostatic initiation is also relatively less than that of the primary explosives in use. Unlike MF, MNT does not get dead pressed.

Silver and mercury salts of 5-nitrotetrazole were also investigated as possible replacements for LA and at the end of the investigation, it was concluded that MNT is very effective in small detonators with a superior performance than LA.

Despite the fact that LA, LS and tetrazene suffer from serious drawbacks, they are still being used in detonators and cap compositions for military and civil applications. Thus LA, LS and tetrazene are the most commonly used primary explosives at present and research is in progress in order to find out suitable substitutes free from such drawbacks. The aim of research in initiatory explosives has all along been to get less sensitive, more compatible, more stable and more efficient material so that safety in manufacture and handing is ensured.

2.2.16
Research Department Explosive

The chemical name for research department explosive (RDX) is cyclotrimethylene trinitramine or 1,3,5-trinitrohexahydro-*sym*-triazine [Structure (2.14)]. Because of



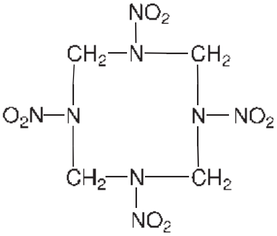
Structure (2.14): Research department explosive (RDX)

its cyclic structure and cyclonic nature, it is also known as ‘cyclonite’ in the USA. The Germans call it ‘Hexogen’ while the Italians ‘T_4’. It is prepared mainly by two processes. In the Woolwich or direct nitrolysis process, it is prepared by treating hexamethylene tetramine (hexamine) directly with a large excess of strong HNO_3 (density: 1.52 g cm^{-3} and purity: 99%) at a temperature of 20–25 °C. In this process, hexamine is added slowly in small portions at a time [21, 22]. On the other hand, in the Bachmann or Combination Process, the reaction mixture contains nitric acid, ammonium nitrate, acetic anhydride and acetic acid. The product is obtained in higher yields and is known as RDX(B) which contains ≈10% HMX. It is a white crystalline solid, m.p. 202 °C–204 °C and density 1.82 g cm^{-3}. It is insoluble in water, alcohol, ether; very slightly soluble in hot benzene; readily soluble in hot aniline, phenol and nitrobenzene and moderately soluble in hot acetone. It is conveniently recrystallized from acetone.

Cyclonite is a very important explosive. The outstanding properties of RDX as an explosive are: high chemical stability, not much lower than aromatic nitro compounds and high explosive power which considerably surpasses that of aromatic nitro compounds such as TNT and picric acid. RDX has a detonation velocity of 8600 ms^{-1} and a detonation pressure of 33.8 GPa at a density of 1.77 g cm^{-3}. RDX is used in mixtures with TNT (Hexotols, Cyclotols, Compn. B); wax (Composition A); aluminum (Hexals); aluminum and TNT (HBX, Hexotonal, Torpex) etc.

2.2.17
High Melting Explosive (or Her Majesty’s Explosive)

High melting explosive or Her Majesty’s explosive (HMX) is chemically known as cyclotetramethylene tetranitramine or 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane [Structure (2.15)]. It is also known as octogen. It was first discovered by Bachmann in 1941 by modifying the Bachmann or Combination Process which was originally discovered for RDX. The main product is HMX and subsequent purification



Structure (2.15): High melting explosive or Her Majesty’s explosive (HMX) removes RDX and converts HMX into its β form. It is prepared by the nitration of hexamine dissolved in glacial acetic acid using ammonium nitrate dissolved in nitric acid (98% min.) in the presence of excess of acetic anhydride and *p*-formaldehyde as a catalyst.

HMX is a white crystalline substance and exists in four polymorphic modifications, the β form being most stable and least sensitive. The α and γ forms exist at room temperature but all forms transform to δ polymorph above 160 °C. Octogen is usually obtained in the β form which is less sensitive to impact and has a density of 1.91 $\mathrm{g cm^{-3}}$ and m.p. of 291 °C. HMX and RDX are almost alike in chemical reactivity. It is non-hygroscopic, insoluble in water and soluble in organic solvents similar to RDX. They differ only in that:

- HMX is more resistant to the action of NaOH than RDX and this is the reaction which is the basis for their separation;
- HMX is more easily soluble in 55% HNO_3 than RDX.

HMX/octogen is a superior explosive than RDX/cyclonite because of its higher chemical stability, higher density, higher VOD and higher ignition temperature and is used where its advantages of higher m.p., higher density and higher VOD outweigh its higher cost and higher sensitiveness. It is the most brisant military explosive in current use. At a density of 1.90 $\mathrm{g\,cm^{-3}}$, β-HMX has a detonation velocity of 9100 $\mathrm{m s^{-1}}$ and a detonation pressure of 39.5 GPa. HMX is used in mixtures with TNT (octols) or bonded with plastics (PBXs). It may also be phlegmatized with wax etc.

Both RDX and HMX are stable, crystalline solids somewhat less sensitive to impact than PETN. Both RDX and HMX are substantially desensitized by mixing with TNT to form cyclotols (RDX) and octols (HMX) or by coating with waxes, synthetic polymers and elastomeric binders.

A huge number of HEMs have been synthesized, studied for their properties and used for different applications in the light of their characteristics vis-à-vis requirements needed for that particular application. In order to make the description simpler and more clear and precise, HEMs are classified as follows:

1) 'Heat-resistant' or 'thermally stable' explosives.
2) High performance explosives, that is, high density and high VOD explosives.
3) Melt-castable explosives.
4) Insensitive high explosives (IHEs).
5) Energetic binders and plasticizers for explosive compositions or formulations.
6) Energetic materials synthesized using dinitrogen pentoxide (N_2O_5).

2.2.18
'Heat-Resistant' or 'Thermally Stable' Explosives

Explosives with improved high-temperature properties are usually termed 'heat-resistant' or 'thermally stable' explosives [23–25]. Some specific applications of explosives for drilling deep oil-wells, space exploration etc., demand 'heat-resistant' or 'thermally stable' explosives. This was a new line of research which is still being actively pursued worldwide with the aim of producing explosives or explosive compositions which are safer, more reliable and stable at high temperatures.

For this purpose, nitro compounds have received special attention because of their ability to withstand high temperatures and low pressures encountered in space environments. The research on heat-resistant explosives was reviewed first by Dunstan [26] followed by Urbanski and Vasudeva [27], Lu [28], recently by Agrawal [29, 30] and Sikder [31].

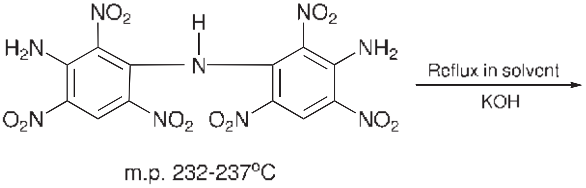
2.2.18.1 General Approaches for the Synthesis of TATB, HNS, PATO etc.

The analysis of the structures of well-known thermally stable explosives clearly brings out that there are four general approaches to impart thermal stability to explosive molecules.

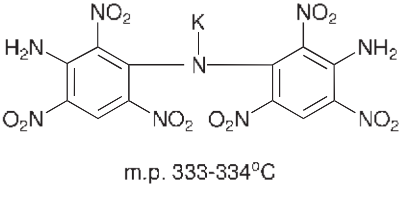
- salt formation;
- introduction of amino groups;
- introduction of conjugation;
- condensation with a triazole ring.

Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine or cyclotetramethylene tetranitramine (HMX) with a m.p. of 291 °C, is also regarded as a heat-resistant explosive in some countries [32, 33] and its safe working limit is 225 °C.

Salt Formation Thermal stability is enhanced by the salt formation [34] which may be illustrated by the following example [Structures (2.16) and Structure (2.17)]

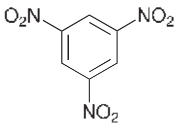


Structure (2.16): 3,3′-Diamino-2,2′,4,4′,6,6′-hexanitrodiphenylamine



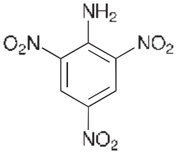
Structure (2.17): Potassium salt of 3,3′-diamino-2,2′,4,4′,6,6′-hexanitrodiphenylamine

Introduction of Amino Groups The introduction of an amino (–NH_2) group (in ortho position) into a benzene ring already having a nitro (–NO_2) group is one of the simplest and oldest approaches to enhance thermal stability of explosives [35–37]. This is evident from the study of the effect of introduction of amino groups in trinitrobenzene (TNB) [Structure (2.18)] to form monoamino-2,4,6-



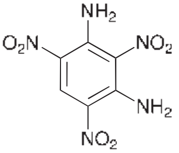
m.p. 122°C

Structure (2.18)



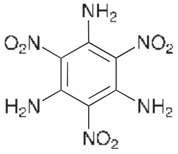
m.p. 192°C

Structure (2.19)



m.p. 286°C

Structure (2.20)



m.p. >350°C

Structure (2.21)

Figure 2.1 Structures of mono, di and tri amino derivatives of trinitrobenzene(TNB).

trinitrobenzene (MATB) [Structure (2.19)], 1,3-diamino-2,4,6-trinitrobenzene (DATB) [Structure (2.20)] and 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) [Structure (2.21)], where the order of thermal stability is MATB < DATB < TATB [38–40] (Figure 2.1).

DATB and TATB have already qualified as heat-resistant explosives among various nitro derivatives of benzene [41, 42]. DATB is fairly stable with a m.p. of 286 °C but it transforms into a crystalline form of lower density at 216 °C which represents the limit of its utility. The use of DATB in explosive compositions has been described in several patents [43, 44] and it was of practical value for various space applications. On the other hand, TATB has excellent thermal stability in the range 260–290 °C which represents its upper temperature limit at which it may be used. TATB is an explosive with unusual insensitivity, heat resistance and respectable performance, which places it first in the list of thermally stable and safe explosives. These properties are attributed to several unusual features of its structure, that is, extremely long C–C bonds in the benzene ring, very short C–N (amino) bonds and six furcated hydrogen bonds. In addition, there is an evidence of strong inter-and intra-molecular hydrogen bonds in TATB [45]. The net result is that TATB lacks an observable m.p. and has a low solubility in all solvents [46] except concentrated H_2SO_4

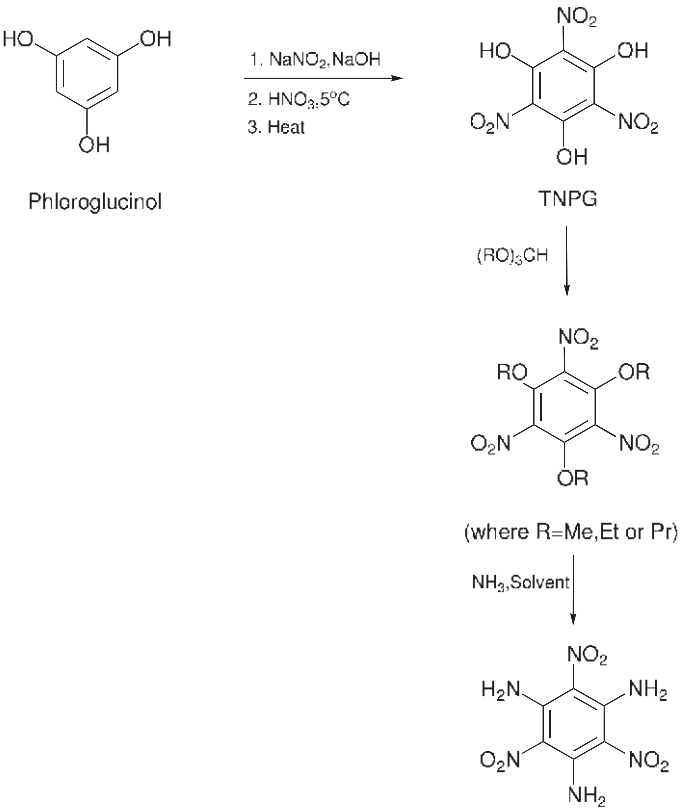
Several methods have been reported in the literature for the synthesis of TATB [24]. Considering the ease of synthesis, purity and yield of the resulting TATB, its synthesis from symmetrical trichlorobenzene (sym.-TCB) is regarded as a method of choice for scaling-up and now almost all countries follow this method for its large scale manufacture. However, sym.-TCB is a little expensive and also not domestically available in several countries. Further, use of sym.-TCB also raises some environmental concerns. In view of all these issues, the following two methods for synthesis and manufacture are gaining importance.

1) Mitchell recently reported that 1,1,1-trimethyl hydrazinium iodide (TMHI) allows amination of nitroarenes at ambient temperature via vicarious nucleophilic substitution (VNS) of hydrogen. Thus TMHI reacts with picramide in the presence of a strong base (NaOMe or *t*-BuOK) to give TATB in over 95% yield. The starting materials, that is, TMHI [obtained by the alkylation of 1,1-dimethyl hydrazine/unsymmetrical dimethyl hydrazine (UDMH) by methyl iodide or directly from hydrazine and methyl iodide] and picramide (obtained from Explosive D) can be obtained from either inexpensive starting materials or surplus energetic materials available from demilitarization activities. It is reported that UDMH (used as a liquid propellant) and Explosive D (used as an explosive filling) are available in large quantities for disposal in many advanced countries like USA, UK, Germany, France, ex-USSR etc. and may be used for the manufacture of TATB [47–49]. Lawrence Livermore National Laboratory (LLNL), under the direction and sponsorship of the US Army Defense Ammunition Center (DAC) has developed a process for the conversion of picric acid to TATB on a small scale which is being scaled-up to larger scale [50].
2) During the synthesis of TATB from sym.-TCB, both nitration and amination steps require drastic conditions. In this process, all chlorine in the starting material, that is, sym.-TCB is converted to chlorinated waste which is not desirable in view of the existing environmental regulations. Bellamy *et al.* have recently reported a method to get TATB from 1,3,5-trihydroxy benzene (phloroglucinol) by a 3-stage route involving nitration, alkylation and amination. The overall yield is ≈87% when the trimethoxy derivative is used. DATB and picramide have also been synthesized in high yields by analogous routes [51].

American scientists at LLNL have studied all aspects of scaling-up followed by optimization of parameters and it appears that TATB would be manufactured by them in future by following the TMHI route. However, a new method proposed by the UK scientists is still at the laboratory scale in UK. According to a recent report in the literature, ATK Thiokol, Inc, USA has performed considerable route development for an alternate TATB process starting with phloroglucinol via Scheme 2.1.

The process has been successfully scaled-up to pilot plant level and the product characteristics are: yield > 98%, purity 95–99% and particle size 40–60 µm. At the same time, this process reduces the environmental impact of TATB production as compared with the traditional TCB Route [52].

Following the discovery of TATB, it is now preferred to DATB. It is of special interest for warheads of high speed guided missiles. By using TATB, energy is sacrificed but handling safety is gained [53, 54]. TATB is extensively used in the USA and a number of pilot plants are available for its manufacture [55].



Structure (2.21) : TATB

Scheme 2.1 Synthesis of TATB.

The use of insensitive high explosives (IHEs) significantly improves safety and survivability of munitions, weapons and personnel as they are remarkably insensitive to high temperatures, shock and impact. TATB is considered as the most important IHE for use in modern nuclear warheads because its resistance to heat and physical shock is greater than that of any other known explosive of comparable energy. A study conducted by Buntain at 250 °C and 300 °C using a drop-weight impact machine with a 2.5 kg weight shows a slight increase in the impact sensitivity of TATB with temperature. However, 50% drop height ($h_{50\%}$) for both temperatures is still greater than 320 cm maximum test height available on the machine (Los Alamos National Laboratory, Los Alamos, 1991). The high stability of TATB also favors its use for civilian applications in addition to military applications.

Americans used TNT, RDX and HMX for nuclear weapons in the initial years but their use posed additional hazard of aerosolized-plutonium dispersal. The scattering of this long-lived isotope poses a great danger to human life as well as to the environment. Therefore, the US Department of Energy and Department of Defense switched over to IHEs like TATB-based formulations in their nuclear arsenals. TATB formulations are particularly attractive for use in modern ordnance, space and nuclear applications because they satisfy requirements of high temperature and also resistance to accidental initiation. TATB is also found to have a critical diameter smaller than TNT, which means that it sustains a high-order, steady-state detonation more easily and at the same time, its response to deflagration-to-detonation transition (DDT) is poor [56].

The US Department of Energy currently maintains an estimated five year supply of TATB for its 'Stockpile Stewardship and Management Program' which is designed to ensure the safety, security and reliability of the US nuclear stockpile. The Department of Defense is also studying the possible use of TATB as an insensitive booster material because even with its safety characteristics, a given amount of this explosive has more power than an equivalent volume of TNT.

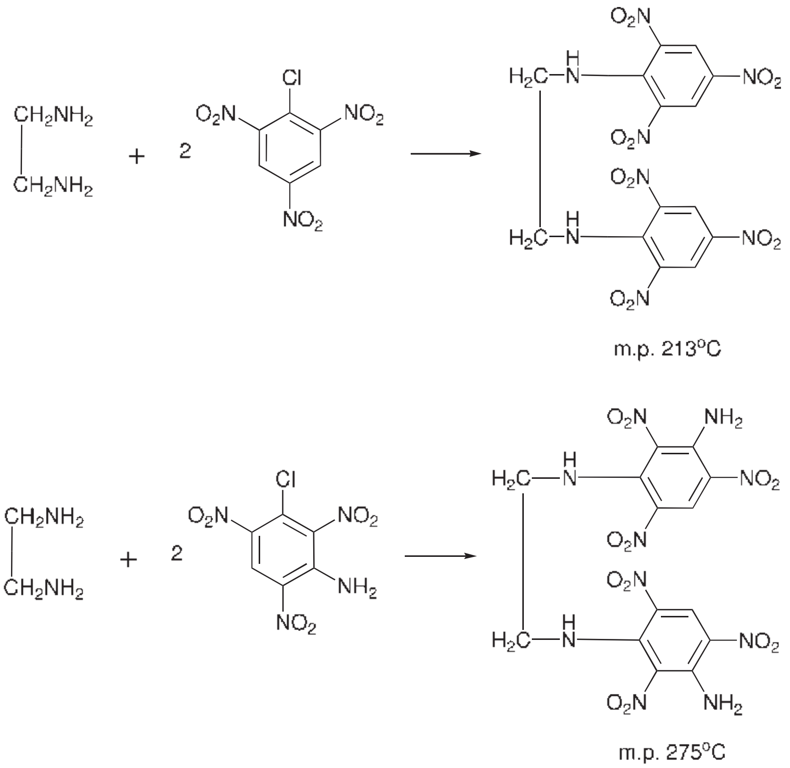
The high stability of TATB favors its use in military and civilian applications where insensitive high explosives are required. In addition to its applications as a HE, TATB is also used to produce the important intermediate benzenehexamine which has been used in the preparation of ferromagnetic organic salts and in the synthesis of new heteropolycyclic molecule such as 1,4,5,8,9,12-hexaazatriphenylene (HAT) that serves as a strong electron acceptor ligand for low-valence transition metals.

Further, TATB has been proposed for use as a reagent in the manufacturing of components of lyotropic liquid-crystal phases for use in display devices, which is the subject of a German patent. There is also interest in employing this explosive in the civilian sector for deep oil-well exploration where heat-insensitive explosives are required. Despite its broad potential, the high cost of manufacturing TATB has limited its use. Several years ago, TATB produced on an industrial scale in the USA was priced at \$90–\$250 per kg. Today, it is available to customers outside Department of Energy (DoE) for about \$200 per kg. The Lawrence process (VNS) should be able to produce TATB for less than \$90 a kg on an industrial scale in about 40% less manufacturing time. The process also offers significant advantages over the current method of synthesis in respect of environmental concerns, that is, by eliminating the use of chlorinated starting material.

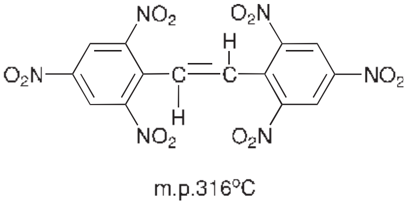
The concept of enhancing thermal stability by the introduction of amino groups is further supported by Chinese work [28]. Some typical examples are shown under Schemes 2.2–2.4.

These examples of explosives show beyond doubt that the m.p. is raised by the introduction of amino group/s. Further, data on thermal decomposition show that the thermal stability is associated with high melting point and low vapor pressure [57] and therefore, it proves beyond doubt that thermal stability increases with the introduction of amino group/s. Hexanitrostilbene (HNS) [Structure (2.22)] is an explosive with excellent heat-resistance which is further enhanced by the introduction of amino group/s (5,5′-diamino-HNS) [Structure (2.23)].

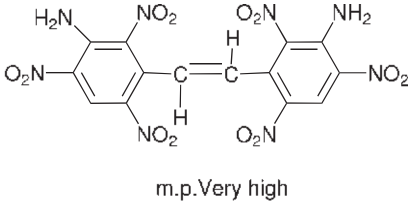
High molecular mass polynitroarylenes often show increased thermal stability which is further enhanced when amino functionality is positioned adjacent to nitro groups.



Scheme 2.2 Synthesis of di(trinitrophenyl)ethylenediamine and its diamino derivative.



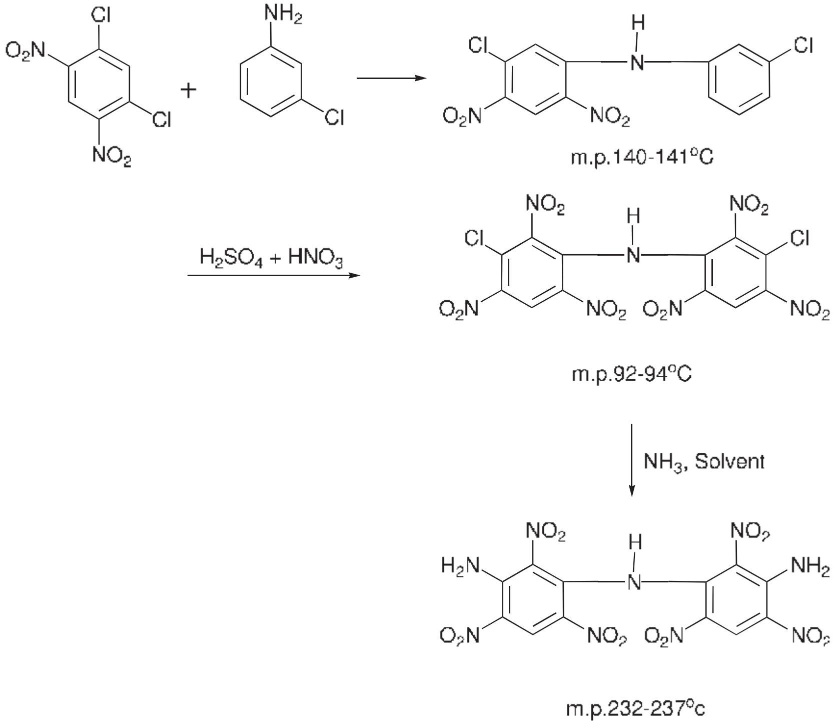
Structure (2.22): 2,2′,4,4′,6,6′-Hexanitrostilbene (HNS)



Structure (2.23): 5,5′-Diamino-HNS

Introduction of Conjugation The best example of imparting higher thermal stability through the introduction of conjugation in explosive molecules is hexanitrostilbene (HNS), synthesized by Shipp [58, 59] of the US Naval Ordnance Laboratory (NOL) in 1964. Plants for full-scale production exist in the UK and China, based on the method of Shipp [60]. It has proved its efficiency as a heat-resistant explosive as well as a component of heat-resistant formulations employed in the Apollo spaceship and for seismic experiments on the moon [61]. HNS has also been reported for use in achieving stage separation in space rockets.

Similarly,

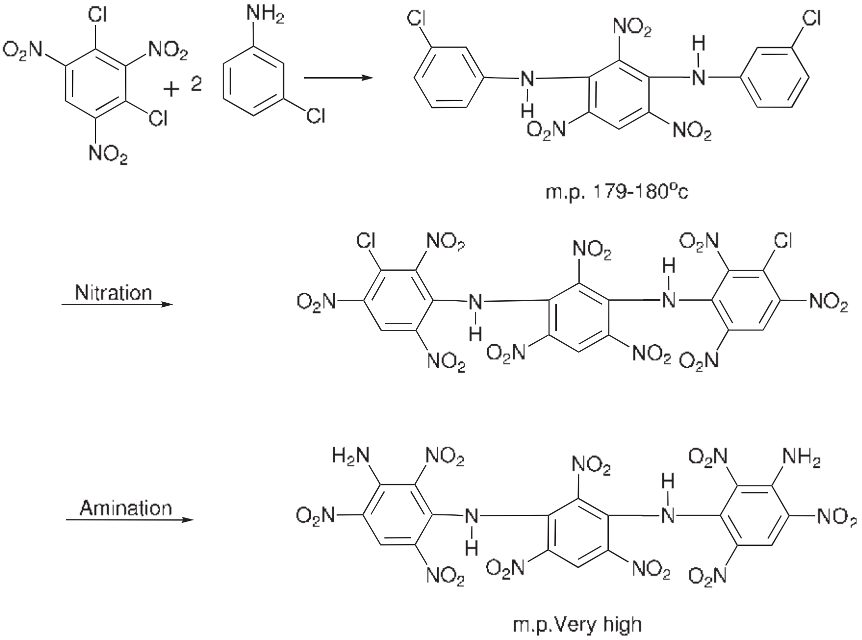


Scheme 2.3 Synthesis of 3,3′-diamino-2,2′,4,4′,6,6′-hexanitrodiphenylamine.

Similar to HNS, conjugation exists in hexanitroazobenzene (HNAB) and hexanitrotetrachloroazobenzene (HNTCAB). They are interesting explosives from the point of view of thermal stability [62]. HNAB is of interest because of its m.p. and relative insensitiveness compared with PETN and HNS [63] whereas HNTCAB is a high temperature-resistant explosive (m.p. *ca.* 308–314 °C) in addition to its likely use as an intermediate for the synthesis of other high temperature-resistant explosives. It is possible that HNTCAB, on reaction with picramide, DATB, TATB or other amino nitro derivatives, could give rise to a new series of high temperature-resistant explosives.

In an effort, to study the effect of introduction of –C=C– on thermal stability of polynitroaromatics, Feng and Boren designed 3,3′-bis((2,2′,4,4′,6,6′-hexanitrostilbene) and azo-3,3′-bis (2,2′,4,4′,6,6′-hexanitrostilbene), synthesized and studied their structural aspects by infrared (IR), NMR, elemental analysis and mass spectrometry [64]. These explosives are expected to have high m.p. and thermal stability in view of their large molecular masses and better molecular symmetry. Further, DSC study of these explosives also proves that thermal stability of an explosive is associated with its m.p. Also decomposition rate is accelerated

Also

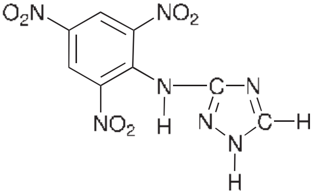


Scheme 2.4 Synthesis of 1,3-di(3′-amino-2′,4′,6′-trinitrophenylamino)-2,4,6-trinitrobenzene.

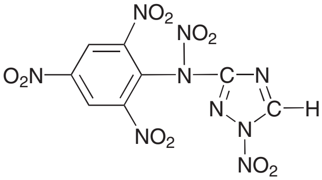
when it exists in a molten state. In this series, there is one more explosive, that is, sym.-2,2′,4,4′,6,6′-hexanitro-3-methyl nitroaminostilbene, which has also been claimed as a heat-resistant energetic material [65]. HNS is used in artillery ammunition filling as an anti-crack additive in TNT-based formulations, in booster charges, in perforating charges for oil and gas industry, in space and military pyrotechnical devices (cap relays, detonating cords, transmission cords etc.) and in exploding foil igniters.

Condensation with Triazole Ring/s Coburn and Jackson studied in detail the synthesis of various picryl and picrylamino-substituted 1,2,4-triazoles and 3,3′-bi-l,2,4-triazolyls by condensing appropriate 1,2,4-triazole or amino-l,2,4-triazole with picryl chloride and established their structures with IR and proton nuclear magnetic resonance (^{1}H-NMR) [66]. Based on the data of thermal stability and impact sensitivity, 3-picrylamino-l,2,4-triazole (PATO) [Structure (2.24)] which is more thermally stable than the parent compound was selected. Its crystal density is 1.94 g cm^{-3}, calc. VOD 7850 ms^{-1}, Chapman–Jouguet pressure (P_{CJ}) 30.7 GPa and impact sensitivity with 2.5 kg weight more than 320 cm. It is relatively inexpensive and was originally considered as one of the potentially useful thermally stable explosives. At the same time, it is as insensitive as TATB. It was initially thought that it would replace TATB in future applications but its performance is inferior to TATB [67].

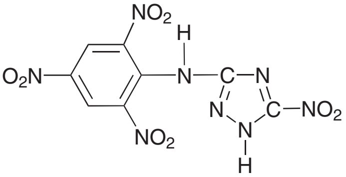
PATO has also been synthesized by a Chinese team [68] by the condensation of tetryl with 3-amino-l,2,4-triazole and their data on its thermal stability is in agreement with American investigators [69]. Chinese researchers have also reported two nitro derivatives of PATO with the following structures based on IR and NMR [68].



Structure (2.24): 3-Picrylamino-1, 2,4-triazole (PATO)

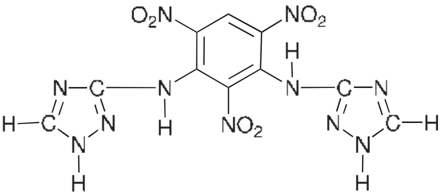


Structure (2.25): Nitro derivative of PATO-I



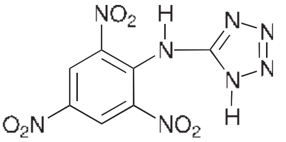
Structure (2.26): Nitro derivative of PATO-II

A comparison of their properties with PATO reveals that the thermal stability of these derivatives is not as good as that of the parent compound, that is, PATO. Some experimental and predicted properties of the nitro derivative of PATO-I [Structure (2.25)] reported by the Chinese are: density ≈ 1.92 $g cm^{-3}$, m.p. *ca* 103 °C, calc. VOD ≈ 8590 $m s^{-1}$ and P_{CJ} ≈ 34.5 GPa. This compound has also been synthesized [70] in HEMRL, Pune, India and the properties are similar to those reported by the Chinese investigators. Indian scientists determined its impact sensitivity also which is $h_{50\%}$ ≈ 28 cm. Further work is needed to evaluate its suitability for practical applications as this explosive possesses high density, respectable performance (comparable to RDX) and low m.p. and may prove to be a melt-castable explosive similar to TNT and TNAZ. The nitro derivative of PATO-II is shown in Structure (2.26). Similarly, a new explosive called 1,3-bis(1,2,4-triazolo-3-amino)-2,4,6-trinitrobenzene (BTATNB) [Structure (2.27)] has also been prepared by the condensation of styphnyl chloride with 3-amino-1,2,4-triazole by Agrawal *et al.* [71] and characterized for its structural aspects, thermal and explosive properties.

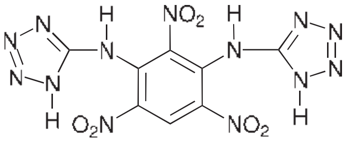


Structure (2.27): 1,3-Bis(1,2,4-triazolo-3-amino)-2,4,6-trinitrobenzene (BTATNB)

The data indicate that BTATNB is slightly more thermally stable (m.p. 320 °C as compared with 310 °C for PATO) coupled with better insensitivity toward impact and friction. Similarly, 5-picrylamino-1,2,3,4-tetrazole [72] (PAT) [Structure (2.28)] and 5,5′-styphnylamino-1,2,3,4-tetrazole [73] (SAT) [Structure (2.29)] have been synthesized by condensing picryl chloride and styphnyl chloride respectively with 5-amino-1,2,3,4-tetrazole in methanol. A comparison of thermal and explosive properties of newly synthesized PAT (deflagration temperature ≈ 203 °C and calc. VOD ~ 8126 ms^{-1}) and SAT (deflagration temperature ≈ 140 °C and calc. VOD ~ 8602 ms^{-1}) reveals that PAT is more thermally stable than SAT but more sensitive to impact and friction.



Structure (2.28): 5-Picrylamino-1,2,3,4-tetrazole (PAT)

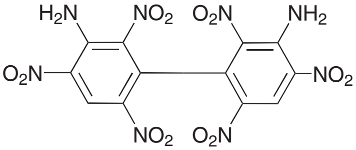


Structure (2.29): 5,5′-Styphnylamino-1,2,3,4-tetrazole (SAT)

In addition to these heat-resistant explosives, there are some well-known thermally stable explosives which have some additional features and are described in following section.

2.2.18.2 3,3′-Diamino-2,2′,4,4′,6,6′-hexanitrodiphenyl

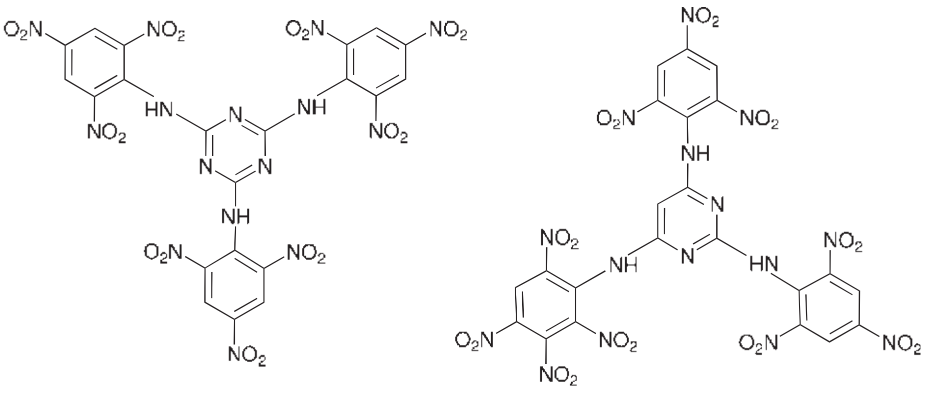
3,3′-Diamino-2,2′,4,4′6,6′-hexanitrodiphenyl (DIPAM) [Structure (2.30)] is extremely insensitive to electrostatic discharge, requiring more than 32 kJ for initiation. In addition, it has good thermal stability (m.p. ca. 304 °C) and has been used to achieve stage separation in space rockets and for seismic experiments on the moon in a manner similar to HNS [74].



Structure (2.30): 3,3′-Diamino-2,2′,4,4′6,6′-hexanitrodiphenyl (DIPAM)

2.2.18.3 N^2,N^4,N^6-Tripicrylmelamine or 2,4,6-Tris(picrylamino)-1,3,5-triazine Series of Explosives

N^2,N^4,N^6-Tripicrylmelamine (TPM) [Structure (2.31)] has been reported to be a moderately thermally stable explosive with performance a little better than that of TNT [75]. Subsequently, heterocyclic nitrogen atoms of TPM were systematically replaced [76, 77] with the C-nitro function to give nitro-substituted tris(picrylamino) derivatives of pyrimidine [Structure (2.32)], pyridine [Structure (2.33)] and benzene [Structure (2.34)] given in Figure 2.2.

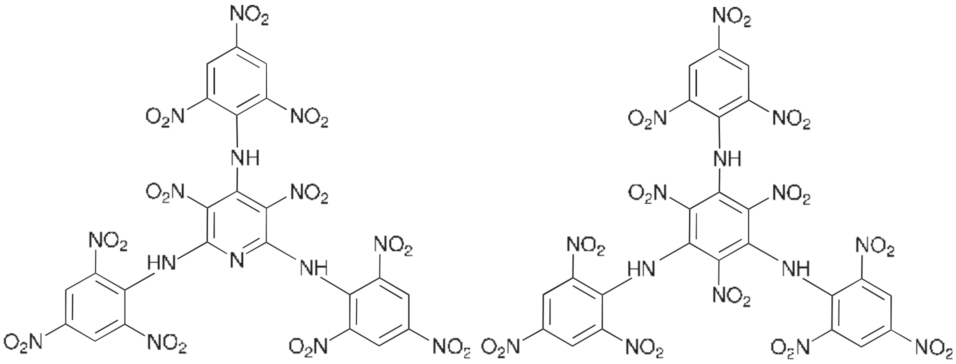


m.p.316°C

Structure (2.31) I

m.p.334°C

Structure (2.32) II



m.p.276°C

Structure (2.33) III

m.p.234°C

Structure (2.34) IV

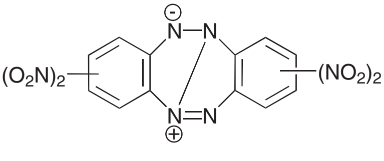
Figure 2.2 Structures of TPM or 2,4,6-tris(picrylamino)-1,3,5-triazine series of explosives.

The m.p. data show that II is more thermally stable than I. However, thermal stability decreases with further substitution of C-nitro for heterocyclic nitrogen to give III and IV in spite of increased resonance stabilization of the parent ring. The decrease in thermal stability appears to be the result of increased steric crowding about the ring as we proceed from II to IV. This is supported by the fact that when the bulky 4-picrylamino group is removed from III, it yields PYX, one of the most thermally stable explosives [78].

Hercules Inc., USA manufactures TPM on a large scale for about the same cost as hexahydro-l,3,5-trinitro-l,3,5-triazine or RDX. China is also reported to have a low-cost newer manufacturing technology for TPM but has a limited production capability. l,3,5-Trinitro-2,4,6-tripicrylaminobenzene (IV) is a readily-detonatable thermally stable secondary explosive synthesized by the reaction of 1,3,5-trichloro-2,4,6-trinitrobenzene (sym.-TCTNB) and picramide in the presence of activated copper powder. Its m.p. is only 234 °C but it is still used in booster cup or bridgewire detonators for example, for oil-well perforation [79, 80].

2.2.18.4 **Tetranitrodibenzo-l,3a,4,4a-tetraazapentalene**

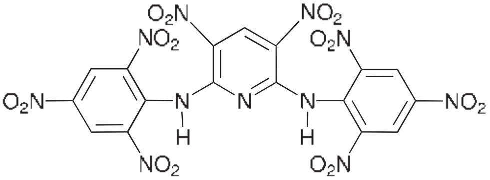
Tetranitrodibenzo-l,3a,4,4a-tetraazapentalene (TACOT) [Structure (2.35)], a new Du Pont explosive, is a mixture of isomers with 2-nitro groups substituted in different positions in each benzene ring. As these isomers have similar explosive and thermal properties, they are not separated while formulating explosive compositions. It is an explosive with unusual and outstanding high-temperature stability [81–83] and its activation energy (292 kJmol^{-1}) was found to be around 1.5 times that of benchmark thermally stable explosive TATB (200 kJmol^{-1}) [84]. Thermal stability of TACOT is attributed to the presence of pentalene moiety in it. Its ignition temperature (*ca.* 494 °C) is the highest registered for an explosive. However, its DTA curve shows that it is stable up to 354 °C, after which a slight exothermic reaction starts which builds into a very rapid deflagration exotherm at 381 °C. Its explosive power (VOD-7250 ms^{-1} at a density of 1.64 gcm^{-3}) is equal to 96% of 2,4,6-trinitrotoluene (TNT) and 80–85% of RDX. It is highly insensitive to impact and electrostatic charge but is readily initiated by a LA primer with as little as 0.02–0.03 g of $Pb(N_3)_2$. Further, TACOT continues to function effectively even after long exposure to high temperatures. It is available in the form of high-density charges, plastic bonded explosives (PBXs), core lead in explosive cords like mild detonating fuse (MDF) and flexible linear shaped charge (FLSC). TACOT is also reported to be used for the manufacture of high-temperature resistant detonators. 1,3,5,7-Tetranitroadamantane (TNA) with a m.p. of *ca.* 350 °C, has also been reported and is likely to be of value as a heat-resistant explosive. Similar to TACOT, it is very insensitive to impact [85].



Structure (2.35): Tetranitrodibenzo-1,3a,4,4a-tetraazapentalene (TACOT)

2.2.18.5 **2,6-Bis(picrylamino)-3,5-dinitropyridine**

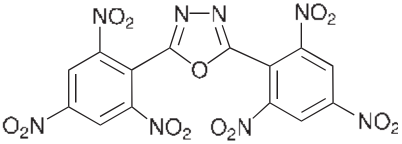
2,6-Bis(picrylamino)-3,5-dinitropyridine (PYX) [Structure (2.36)] is produced in high yields from relatively inexpensive starting materials and possesses properties: crystal density 1.75 gcm^{-3}, m.p. 460 °C, VOD 7450 ms^{-1}, P_{CJ} 24.2 GPa and impact sensitivity 63 cm. PYX has already been commercialized in America and Chemtronics Inc. is currently producing it under license from Los Alamos for use in thermally stable perforators for oil and gas wells [86, 87]. It is increasingly being used as a substitute for HNS and is gradually replacing HNS for most commercial thermally stable explosive applications.



Structure (2.36): 2,6-Bis(picrylamino)-3,5-dinitropyridine (PYX)

2.2.18.6 **2,5-Dipicryl-1,3,4-oxadiazole**

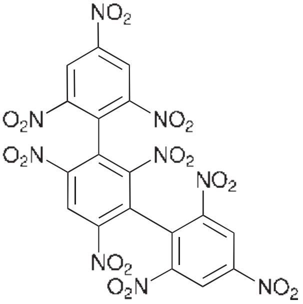
A renewed interest in thermally stable but shock-sensitive explosives for use in detonation transferring formulations has given rise to 2,5-dipicryl-1,3,4-oxadiazole (DPO) [Structure (2.37)] which possesses a unique combination of impact sensitivity ($h_{50\%} = 20\,\text{cm}$) and thermal stability [88]. According to Sitzmann, its high impact sensitivity is attributed to the N–N bond of the oxadiazole ring which provides a trigger linkage [89]. DPO is generally considered as a thermally stable substitute for PETN.



Structure (2.37): 2,5-Dipicryl-1,3,4-oxadiazole (DPO)

2.2.18.7 **2,2′,2″,4,4′,4″,6,6′,6″-Nonanitroterphenyl**

2,2′,2″,4,4′,4″,6,6′,6″-Nonanitroterphenyl (NONA) [Structure (2.38)] is produced by the condensation of 2 moles of picryl chloride with 1,3-dichloro-2,4,6-trinitrobenzene (styphnyl chloride)in the presence of copper dust at 210 °C using nitrobenzene as a medium (Ullmann's Condensation) [90]. It has a density of $1.78\,\text{g}\,\text{cm}^{-3}$ and exceptional heat stability, melting at 440–450 °C with decomposition which together with a low volume of split-off gases render it as an interesting explosive for booster explosives in space technology [91].



Structure (2.38): 2,2′,2″,4,4′,4″,6,6′,6″-Nonanitroterphenyl (NONA)

Ritter and co-workers have recently reported a new class of explosives known as polynitropyridines: 2,4,6-trinitropyridine oxide (I); 2,4,6-trinitropyridine (II) and

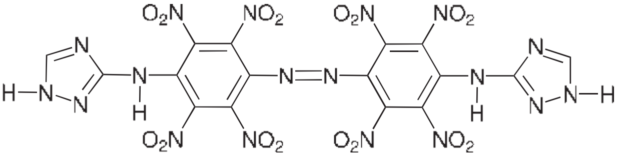
2,6-diazido-4-nitropyridine-1-oxide (III), and characterized them by spectroscopic and thermoanalytical methods. II has a heat-resistance comparable to TNB and impact-sensitivity comparable to RDX. These are high explosives with performance superior to sym. trinitrobenzene (TNB) and TNT [92].

2.2.18.8 **3,5-Diamino-2,6-dinitropyridine-*N*-oxide**

3,5-Diamino-2,6-dinitropyridine-*N*-oxide (DADNPO) is more heat resistant than HNS but its performance is equal to HNS. It is used for oil-well completions at higher depth than HNS shaped charges.

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**

Agrawal and co-workers have reported the synthesis of *N,N′*-bis(1,2,4-triazol-3-yl)-4,4′-diamino-2,2′,3,3′,5,5′,6,6′-octanitroazobenzene (BTDAONAB) [Structure (2.39)] via nitration–oxidative coupling of 4-chloro-3,5-dinitroaniline followed by nucleophilic displacement of the chloro groups with 3-amino-1,2,4-triazole. BTDAONAB has the unique distinction of being the most thermally stable explosive reported so far (DTA exotherm ~ 550 °C) as compared with well-known thermally stable explosives such as TATB (~360 °C), TACOT (~410 °C), NONA (~440–450 °C) and PYX (~460 °C) [25].



Structure (2.39): *N,N′*-Bis(1,2,4-triazol-3-yl)-4,4′-diamino-2,2′,3,3′,5,5′,6,6′-octanitroazobenzene (BTDAONAB)

The most promising thermally stable explosives and their properties are given in Table 2.2.

The data suggest that PYX is impact sensitive and therefore, is not suitable. The synthesis of TACOT involves five steps and at the same time, the resulting TACOT is a mixture of isomers with 2-nitro groups substituted in different positions in each benzene ring. This synthetic route involving five steps makes its production expensive. It is an explosive with unusual and outstanding high temperature stability but its performance, that is, VOD is lower than that of TATB. On the other hand, TATB is a most thermally-stable explosive of this group with excellent impact insensitivity and reasonable performance. The explosive BTDAONAB reported recently has a unique distinction of being the most thermally stable explosive reported so far when compared with other well-established thermally stable explosives. However, its process of synthesis has to be scaled-up and it needs to be exhaustively evaluated before its use for large-scale applications.

The literature suggests that thermally stable explosives such as HNS were employed for seismic experiments on the moon [61]. This is probably due to safety considerations while handling explosives for such applications on the lunar surface.

Table 2.2 Most promising thermally stable explosives and their properties.

Name	Melting point/°C	Density/ gcm^{-3}	Impact sensitivity ($h_{50\%}$)/cm	VOD/$m s^{-1}$	Salient properties and applications
1,3,5-Triamino-2,4,6-trinitro benzene (TATB)	>350	1.94	Very insensitive	8000	Explosive with unusual insensitivity, heat resistance and respectable performance. Used for space, nuclear and special military applications (high speed guided missiles)
Tetranitro dibenzo-1,3a,4,4a-tetraazapentalene (TACOT)	494 (Ignition)	1.85	Very insensitive	7250	Stable up to 354 °C and very impact insensitive. Used for FLSC and high temperature resistant detonators
2,6-Bis (picryl amino)-3,5-dinitro pyridine (PYX)	460	1.75	63	7450	Slightly impact sensitive. Regarded as a substitute for HNS. Used for thermally stable perforators for oil and gas wells.
N,N′-Bis(1,2,4-triazol-3-yl)-4,4′-diamino-2,2′,3,3′,5,5′,6,6′-octanitroazobenzene (BTDAONAB)	Does not melt/ show any change up to 550 and gives exotherm at 550.	1.97	87	8321	Most thermally stable explosive reported so far. Reported recently on a laboratory scale. Needs further evaluation.
2,2′,2″,4,4′,4″,6,6′,6″-nonanitroterphenyl (NONA)	440–450 (with decomposition)	1.78	–	–	It is of interest for booster explosives in space technology
Polynitropolyphenylenes (PNPs)	286–294	1.8–2.2	–	–	Thermally stable binder for pyrotechnic formulations.

In order to understand it, knowledge of some facts about the lunar surface and its atmosphere is considered necessary which is given in the next paragraph.

The moon is the closest and best-known object in the sky and is also earth's constant companion. It was considered a battered and forbidden place. Valiant efforts and voluminous research conducted by various astronomers and scientists specially after the landing of American astronauts Neil Armstrong and Buzz Aldrin on July 20, 1969 on the surface of the moon, suggest that its surface is extremely rough and consists of millions of rocks and craters. The rocks are igneous which contain silicate materials, Ti, Zr and radioactive isotopes of K and have solidified from their molten state. Further, the large craters have been produced by meteoritic hitting of the lunar surface at high velocity whereas the small ones by explosive volcanic activity. There is practically no atmosphere on the moon, mainly due to considerably less gravitational force at its surface (one sixth of the earth's gravitational force). Also there is no surface water or rain. However, on September 23, 2009, Indian and American scientists have reported the presence of molecules of water and hydroxyl as very fine films on dust particles over the lunar surface. At the most, the atmosphere is believed to be an extremely diffuse halo of electrically charged particles. With practically no atmosphere to shield it, the moon is unprotected against the violence of space. Further, solar radiation strikes it at full strength with X-rays and ultraviolet (UV) light. The effect of solar radiation is further aggravated as the lunar days are longer compared with days on the earth (one lunar day is ≈29 days at the earth). The cumulative effect of all such factors leads to high temperature on the lunar surface [93, 94]. Since the sensitivity of explosives increases with an increase in temperature, use of conventional explosives such as TNT, RDX and HMX etc is considered hazardous and as a natural consequence, thermally stable explosives are used for seismic experiments on the lunar surface.

Similarly, another thermally stable explosive such as PYX has been used for perforation of oil and gas wells [86]. High temperatures are also encountered during the perforation of oil and gas wells and drilling of exploratory holes for oil perforation. As a result, use of conventional explosives is not considered safe for such applications.

2.2.19
High Performance (High Density and High VOD) Explosives

It has always been the aim of explosive technologists to achieve higher performance for their product applications. An increase in density improves performance without increasing sensitivity as detonation pressure (P_{CJ}) is proportional to density [95, 96], that is, (Equation 2.1):

$$P_{CJ} = (1/4).\rho D^2 \tag{2.1}$$

where P_{CJ} is detonation pressure in Pascals
ρ is density of the formulation in $g\,cm^{-3}$
D is VOD in ms^{-1}.

It is also clear from this relationship that higher detonation velocity and density lead to higher performance as well. On the other hand, an increase in oxygen balance (OB) and 'heat of formation' generally increase performance as well as sensitivity of an explosive [97]. The recently developed crystal-density predictive methods have been very valuable in directing research efforts toward high-density explosives. However, these methods predict unusually high densities for two general classes of compounds, that is, hydrogen-free nitro heterocycles and polynitro cage compounds.

2.2.19.1 **General Synthetic Approaches for High Performance Explosives (HNIW/CL-20 etc.)**

There are three general approaches to enhance density and thus performance of explosives:

1) replacement of the nitro group by furoxano group;
2) introduction of pentafluorosulfonyl (SF_5) group into nitro compounds;
3) formation of cage-like structures.

Replacement of the Nitro Group by Furoxano Group A new area of interest and activity in recent years is the development of new explosives with increased performance coupled with increased stability and insensitivity [98]. In order to meet these requirements, several Chinese investigators have reported that replacement of the $–NO_2$ group by furoxano group results in an increase in density and detonation velocity [99]. The introduction of $–NH_2$ group in explosive molecules is also reported to increase density in addition to heat resistance, as discussed earlier. By exploiting this concept, a new explosive [*N,N′*-bis(2,4-dinitrobenzofuroxan)-1,3,5-trinitro-2,6-diaminobenzene] has been prepared [100] by the method in Scheme 2.5.

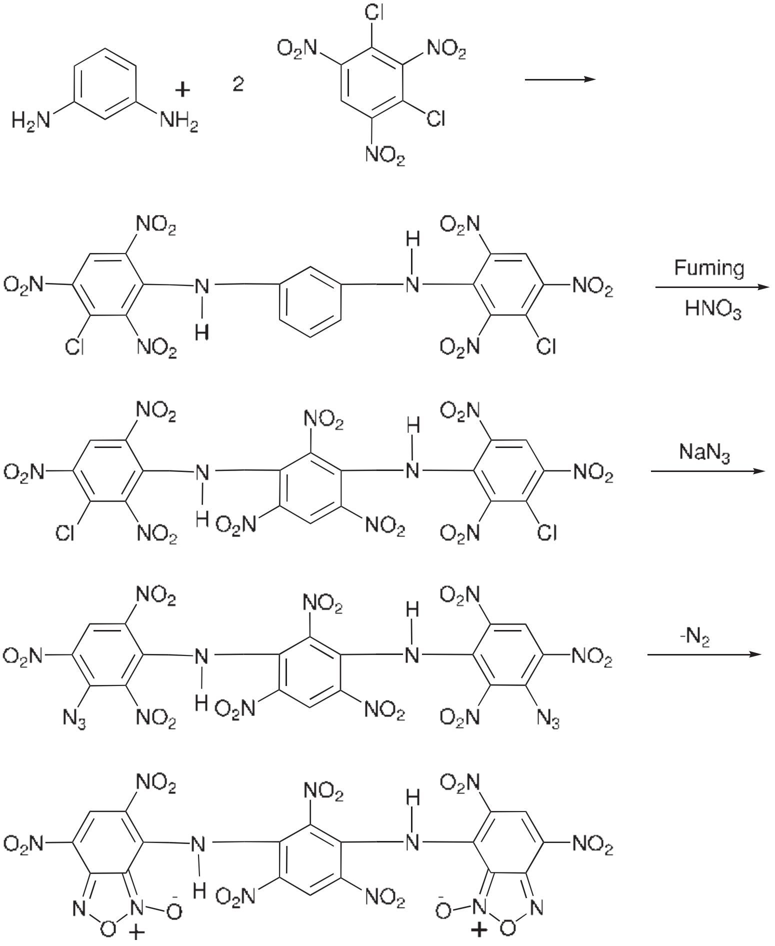
This compound possesses a density of 1.92 $g cm^{-3}$ and VOD ≈ 8570 $m s^{-1}$ without any loss of weight at 100 °C for 48 h. The density of this explosive is higher than those of PYX [101] and 2,4,6-tris(picrylamino)-1,3,5-triazine [75]. Further, the cost of production is also likely to be low because of the inexpensive starting materials.

Another interesting explosive in this class is 5,7-diamino-4,6-dinitrobenzofuroxan (DADNBF) which is synthesized [102] by the method in Scheme 2.6.

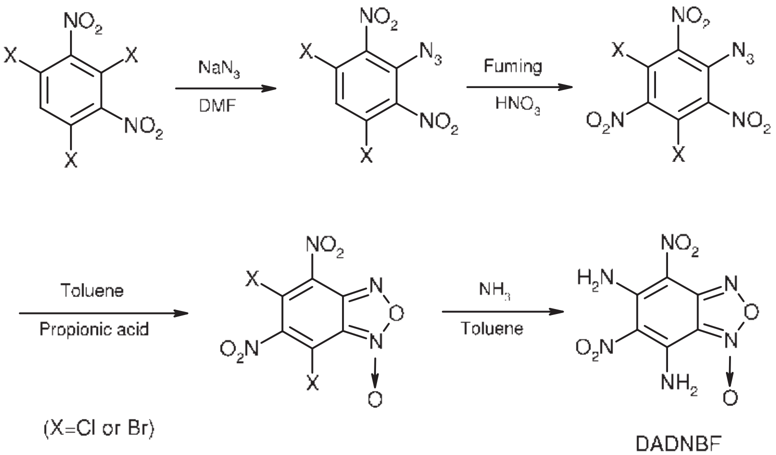
The authors have claimed that density of this explosive is high (1.91 $g cm^{-3}$) and it is more powerful (VOD ≈ 8050 $m s^{-1}$) than TATB (VOD ≈ 8000 $m s^{-1}$) and at the same time, it is insensitive [103]. A comparison of TATB and DADNBF shows that the performance of this explosive in terms of density and VOD is almost similar to TATB. Similarly, introduction of pyridine in addition to a $–NH_2$ group further increases density, heat resistance and impact insensitivity. Accordingly, explosive *N,N′*-bis(2-nitrobenzodifuroxanyl)-3,5-dinitro-2,6-diamino pyridine has been designed, synthesized (Scheme 2.7) and characterized by elemental analysis, IR, ^{1}HNMR and mass spectroscopy and studied for its explosive properties (density ≈ 1.91 $g cm^{-3}$, calc. VOD ≈ 8630 $m s^{-1}$ and m.p. *ca.* 231 °C) [104]. This explosive is better than PYX in terms of density as well as VOD and the yield is also reported to be higher.

Naixing and co-workers have also reviewed research on benzofuroxan-based explosives and reported a high-energy and low-sensitivity explosive: *N,N′,N″*-tris(2-nitrobenzodifuroxanyl) melamine [105]. The data on its explosive properties (density ≈ 1.90 $g cm^{-3}$, calc. VOD ≈ 8695 $m s^{-1}$ and m.p. *ca.* 316 °C) show that it is a high performance as well as a thermally stable explosive.

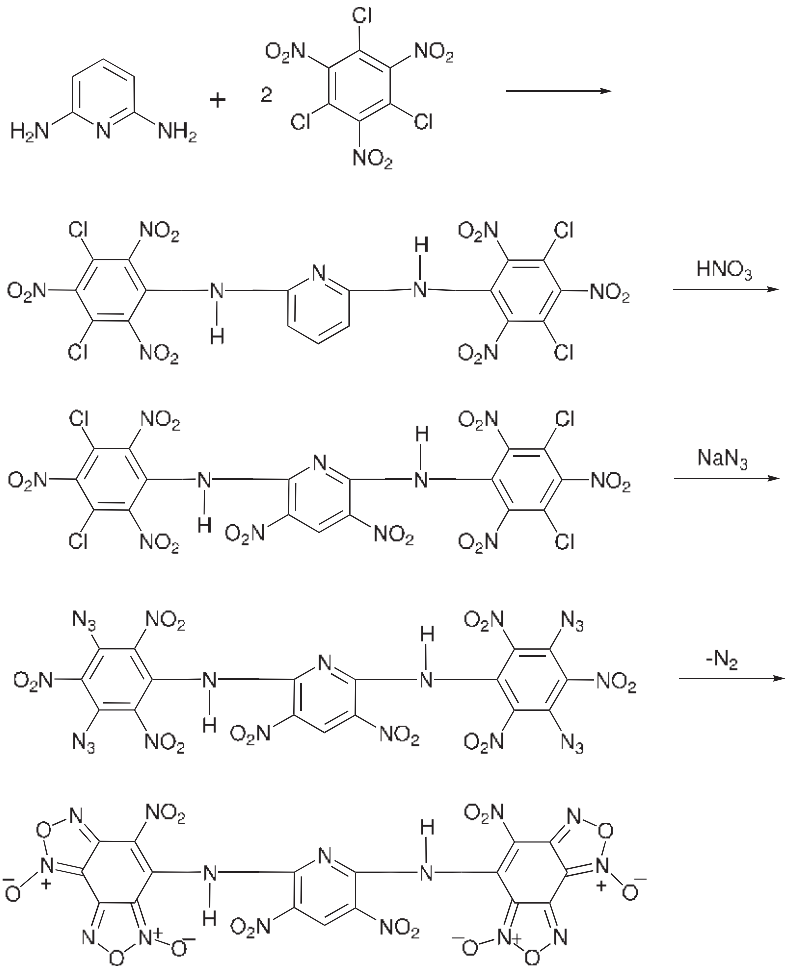
It is evident from the foregoing discussions on thermally stable and high performance explosives that the introduction of an amino group may be regarded as



Scheme 2.5 Synthesis of *N,N′*-bis(2,4-dinitrobenzofuroxan)-1,3,5-trinitro-2,6-diaminobenzene.



Scheme 2.6 Synthesis of 5,7-diamino-4,6-dinitrobenzofuroxan (DADNBF)



Scheme 2.7 Synthesis of *N*,*N*′-bis(2-nitrobenzodifuroxanyl)-3,5-dinitro-2,6-diaminopyridine.

the simplest approach for enhancing melting point (thermal stability) as well as the density of nitro aromatic compounds. This is attributed to its ability to undergo strong hydrogen bonding with neighboring nitro groups and also its ability to strengthen the –C–NO_2 bond of an ortho or para nitro group. At the same time, it decreases impact sensitivity or in other words, increases impact insensitivity [106]. Similarly, introduction of pyridine also increases density, heat resistance and impact insensitivity.

Introduction of SF_5 Groups into Nitro Compounds As a part of continuing research for energetic materials that combine high performance with low vulnerability toward accidental detonation, the effect of introduction of the pentafluorosulfonyl (SF_5) group on the properties of explosive nitro compounds has been reported [107]. This is based on the fact that more energy is released due to the formation of HF in the detonation of SF_5 explosives (S–F bond energy: 79 kcal mol^{-1}, that of H–F 136 kcal mol^{-1} whereas Al–F bond energy: 158 kcal mol^{-1}). It is also well-established that substitution of H by F in hydrocarbons leads to a significant increase in density [108]. It implies that SF_5 group would provide nitro explosives with higher density or, in other words, improved performance [109]. Based on these assumptions, some polynitro SF_5 explosives have been designed and their performance predicted which is in agreement with their actual performance. The initial experiments of Sitzmann *et al.* support the hypothesis that SF_5 group may provide explosives with improved properties: increased density, increased insensitivity and increased energy coupled with better thermal stability – a unique combination of properties. Some examples of dense, thermally stable, impact insensitive polynitroaliphatic explosives with SF_5 groups are:

$SF_5CH_2COO\ CH_2\ C(NO_2)_2\ F$	density 1.86 gcm^{-3}
$SF_5CF_2CF_2CF_2SF_5$	density 2.04 gcm^{-3}
$(SF_5)_2NCF_2CH_2SF_5$	density 2.13 gcm^{-3}

Some preliminary work employing this approach was reported by American investigators in early 1990s but subsequently there is no further report regarding research in this area.

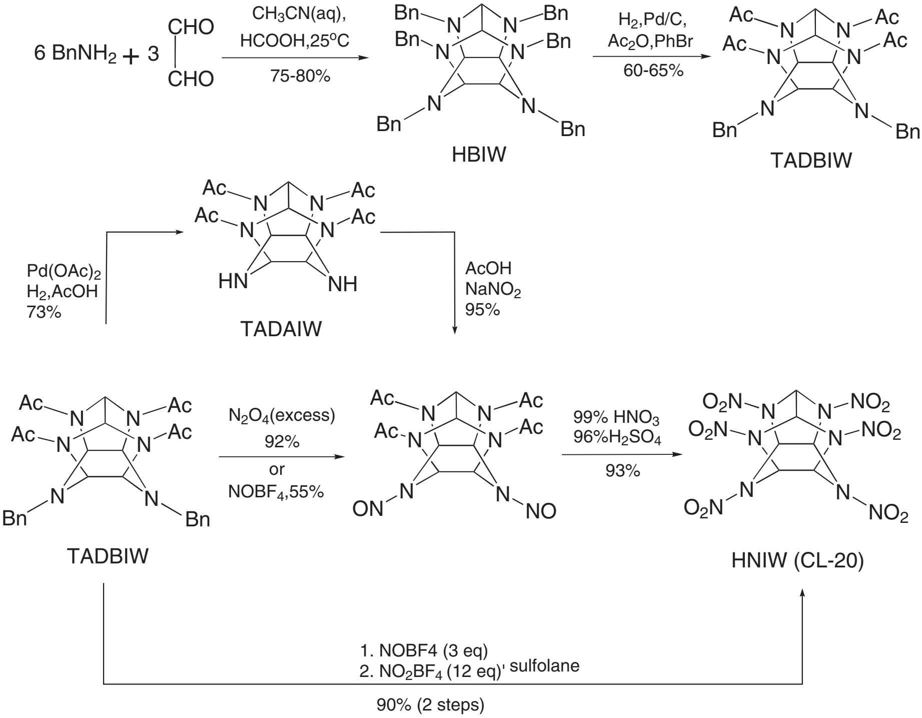
Strained and Cage Compounds Energetic materials of the strained-ring and cage families constitute a promising new class of explosives. This is based on the fact that the compounds of this family have high strain energies locked in the molecules (high strain energy means increased positive heat of formation compared with a corresponding unstrained molecule) and it is released as an additional energy on detonation. The compounds of this family also possess rigid and highly compact structures resulting in increased density. Thus more mass of polynitro polycyclic strained cage compounds is accommodated in a given volume which, along with their high molecular strain energies, results in a better performance on detonation.

Considerable current interest and sustained research efforts of some groups in the USA and other countries have been aimed at the synthesis and chemistry of strained energetic compounds. According to Marchand and co-workers, polynitro polycyclic cage compounds are important members of this class [110].

ARDEC has also made significant contributions in this field and synthesized a number of cage compounds with an optimum number of nitro groups which are more powerful than HMX. This is attributed to their high crystal densities combined with high strain-energies of cage compounds [111]. The synthesis of l,4-dinitrocubane has also been reported through various routes by other groups [112, 113]. The multi-nitrated caged explosive (3,7,9-trinitronoradamantane) which is highly strained, has been reported by Zajac and claimed to be highly energetic [114]. The evaluation of polynitro polycyclic cage compounds for their explosive performance characteristics indicates that this class of explosives is both relatively powerful and shock-insensitive. As a result, it is thought that polynitro polycyclic cage compounds may be valuable for use as explosive and propellant ingredients in many military applications in the near future.

Extensive research on cage compounds has resulted in the invention of 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (HNIW, popularly known as CL-20). It is regarded as the most celebrated product of many years of research at the Naval Air Warfare Center (NAWC) by Neilsen and co-workers on the synthesis of novel nitramines and related energetic materials [115, 116]. It exists in five polymorphic forms α, β, γ, δ (not fully established) and epsilon (ε) due to the presence of different molecular conformations and arrangements in the lattice. Epsilon (ε), α, β, and γ forms of CL-20 can be prepared by recrystallization techniques and generally mixture of polymorphs is present in the product. Currently the epsilon (ε) form is found most suitable as a high performance explosive. The first member of the hexaazaisowurtzitane family is hexabenzyl hexaazaisowurtzitane (HBIW) which is further elaborated to HNIW.

Subsequent to Neilsen and coworkers, a number of researchers have synthesized and characterized CL-20 on a laboratory scale [117] all over the globe and a most up-to-date review is given in the book of Agrawal and Hodgson [118] which is as follows (Scheme 2.8).



Scheme 2.8 Synthesis of 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (HNIW or CL-20).

The Thiokol Corporation, USA, has modified the original route discovered by Neilsen and scaled-up to pilot scale [119]. Its attributes of great interest are: density 2.04 g cm^{-3}, VOD 9400 ms^{-1}, DSC decomposition temperature 228 °C and heat of formation, $\Delta H_f \approx 100$ k cal mol^{-1} compared with βHMX – 1.91 gcm^{-3}, 9100 ms^{-1}, just after 280 °C (a sharp endothermic peak at 280 °C corresponds to melting which is immediately followed by a strong exothermic peak due to the self-decomposition of HMX) and 17 k cal mol^{-1} respectively [120]. The high performance of CL-20 is due to the presence of a strained cage structure carrying six –NO_2 substituents. CL-20 is reported to be compatible with nitramines, nitrate esters, azidopolymers, poly(ethylene glycol) (PEG), hydroxy-terminated polybutadiene (HTPB), ammonium perchlorate (AP), ammonium nitrate (AN), etc. and has a high potential as a high-performance explosive as well as an ingredient in propellant formulations. As regards sensitivity to impact and friction, there is a difference of opinion. Simpson *et al*. reported that CL-20 exhibits impact sensitivity (ε CL-20: $h_{50\%} \approx 12$–21 cm) and friction sensitivity (insensitive up to 61–71 N) as against 32 cm and 114 N respectively for β-HMX [121, 122]. Agrawal and co-workers have also studied impact sensitivity of ε CL-20 and β-HMX with a drop weight machine coupled with a high speed camera and found that CL-20 was slightly more sensitive [123]. On the other hand, Dudek *et al*. found that the impact sensitivity ($h_{50\%}$) of ε CL-20 ≈ 28 cm is comparable to that of β-HMX ($h_{50\%} = 30$ cm) [124]. Agrawal *et al.* have not only given impact sensitivity of CL-20 but also the mechanism of initiation on impact leading to its detonation. This is in line with the mechanism of initiation by 'hot spot' formation on impact followed by detonation similar to other secondary explosives [125].

A critical appraisal of all synthetic routes of CL-20 vis-à-vis yield, purity and ease of scaling-up had been carried out by Sanderson and coworkers [126] and the gist of their conclusions is:

1) The original route to synthesize CL-20 from the precursor tetraacetyldinitroso isowurtzitane (TADNIW) may give very pure CL-20 but it is not the most economical route [127]. In this method, it is either necessary to isolate and handle a nitrosamine or to do one-pot nitrosation followed by nitration; the latter is possible in the laboratory but does not appear practical for bulk production.

2) The second route uses tetraacetyldiformal isowurtzitane (TADFIW) as a precursor which on direct nitration yields CL-20. However, it was experienced during experimentation that it is difficult to replace formyl groups compared with acetyl groups. As a result, some mono- or di-formal (≈2–3%) are likely to be left in CL-20 and may give rise to higher crystal sensitivity. Complete removal of formyl groups from TADFIW takes a longer time under vigorous nitration conditions, which is not advisable from the safety point of view especially during bulk-production. The important attribute of this method is that the yield from TADFIW is almost quantitative.

3) CL-20 had also been synthesized with another precursor, that is, tetraacetal diamine isowurtzitane (TADAIW) by nitration with a conventional nitrating agent, that is, mixture of nitric acid and another strong acid (HNO_3 and H_2SO_4). As TADAIW contains no formyl groups, there is no formylated impurity in the CL-20. Further, nitration of TADAIW is relatively faster than TADFIW. On the other hand, contrary to TADFIW method, yield is very high in this method but not quantitative.

In summary, it appears that the following route:

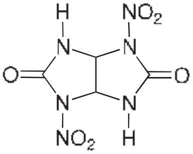
$$BA \rightarrow HBIW \rightarrow TADBIW \rightarrow TADAIW \rightarrow HNIW\ (CL\text{-}20)$$

may be a suitable route for further scale-up and large scale manufacture.

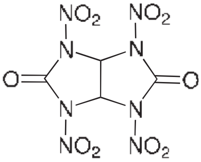
In addition to these approaches for the synthesis of high-performance explosives, there are some other explosives reported in the literature which need a brief description.

2.2.19.2 **1,3,4,6-Tetranitroglycoluril**

1,4-Dinitroglycoluril (DINGU) [Structure (2.40)] is a starting material for 1,3,4,6-tetranitroglycoluril (TNGU Sorguyl, French) [Structure (2.41)] which is categorized as a high-performance explosive. DINGU, on nitration with a nitrating mixture consisting of 80% HNO_3 and 20% N_2O_5, gives TNGU which has a density of 1.94 $g\,cm^{-3}$, VOD 9070 $m\,s^{-1}$, decomposition temperature of *ca.* 200 °C and is stable up to 100 °C. The density, VOD and brisance are at par with HMX. TNGU is, however, readily decomposed by water and polar solvents even at a temperature [128] of 10–15 °C indicating that it may not be useful for any practical application. Its thermal decomposition has also been reported by Brill and co-workers [129].



Structure (2.40): 1,4-Dinitroglycoluril (DINGU)

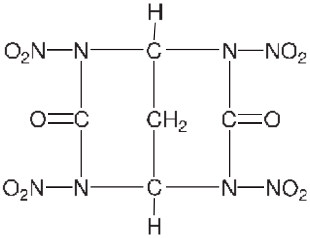


Structure (2.41): 1,3,4,6-Tetranitroglycoluril (TNGU)

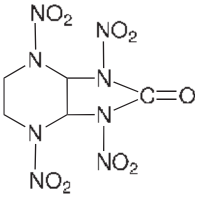
2.2.19.3 **Tetranitropropanediurea**

Another interesting explosive reported recently is tetranitropropanediurea (TNPDU) [Structure (2.42)] with a density of 1.98 $g\,cm^{-3}$ and good thermal stability.

It is synthesized by the nitration of propanediurea (a condensation product of 1,1,3,3-tetraethoxypropane with urea in an acidic medium) with HNO_3-$(CH_3CO)_2O$ nitrating agent. Its explosive properties indicate that it is superior to TNGU and has a potential for a variety of applications. TNPDU is sensitive to both impact and friction but has high thermal stability. There is a substantial decrease in sensitivity (impact as well as friction) on coating it with paraffin wax. Further, in order to improve hydrolytic stability of explosives containing carbonyl groups, the explosive 2,5,7,9-tetranitro-2,5,7,9-tetraazabicyclo [4.3.0] nonane-8-one (TNABN) [Structure (2.43)] was prepared and evaluated for its preliminary explosive properties. It was observed that TNABN possesses better properties in terms of impact and friction sensitivity than those of TNPDU. It was also recorded that both TNPDU and TNABN are significantly more resistant to hydrolytic destruction [130] than tetranitroglycoluril (TNGU). However, these explosives need exhaustive evaluation to establish their superiority and use for practical applications [131].



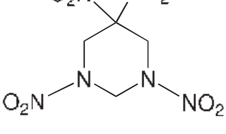
Structure (2.42): Tetranitropropanediurea (TNPDU)



Structure (2.43): 2,5,7,9-Tetranitro-2,5,7,9-tetraazabicyclo [4.3.0] nonane-8-one (TNABN)

2.2.19.4 **1,3,5,5-Tetranitrohexahydropyrimidine**

French researchers have reported a new explosive called 1,3,5,5-tetranitrohexahydropyrimidine (DNNC French abbreviation) [Structure (2.44)] which may also find application as an oxidant for propellant and pyrotechnic formulations [132] in addition to its use as a filling for warheads, shells and bombs. It was first synthesized in 1982 and has properties [133]: m.p. 151–154 °C, density $\approx$ 1.82 g cm^{-3}, VOD $\approx$ 8730 ms^{-1} and $P_{CJ} \approx$ 34 GPa. The opinion of American researchers is that it is an excellent oxidant (OB $\approx$ 6%) with very low impact sensitivity and may be used as an oxidizer for explosive, pyrotechnic or rocket propellant formulations [134]. DNNC with a six-membered ring is a unique heterocyclic molecule which combines chemical structural features found separately in energetic geminal dinitroalkane compounds and cyclic RDX nitramine. This hybrid molecular structure of DNNC produces an energetic compound with impact initiation sensitivity much



Structure (2.44): 1,3,5,5-Tetranitrohexahydropyrimidine (DNNC) lower than that of RDX and more like that exhibited by TNT. In the opinion of Shackelford and Goldman, DNNC is an inherently thermally stable and insensitive high-energy oxidizer that could be a potential replacement candidate for cyclic six-membered RDX nitramine in explosive and propellant formulations [135].

Because of their favorable elemental compositions, heteroaromatic nitro compounds represent explosives of high performance (oxygen balance, density, heat of formation and VOD) compared with analogous aromatic explosives [136–138]. With this objective, Licht and co-workers have synthesized some methylnitramine substituted pyridines and triazines, established their structures and characterized them for thermal and impact sensitivities [139]. The data on impact sensitivity, however, indicate that tetryl may not be replaced by these explosives.

2.2.20
Melt–Castable Explosives

Explosives such as RDX (hexogen) and HMX (octogen) are important military explosives and generally a binder is used along with these explosives for two reasons:

1) It improves safety in processing, handling, transportation and storage.
2) It also imparts mechanical integrity to the explosive charge.

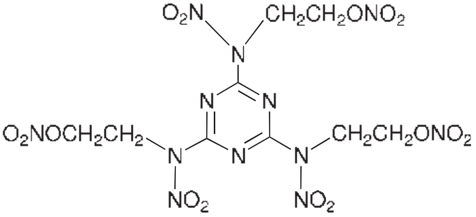
However, the use of such binders (usually inert polymers) brings down the overall energy of the systems; this can be improved by the use of an energetic binder such as TNT, which is a low melting explosive and also has the capability of binding explosive particles.

2,4,6-Trinitrotoluene (α-TNT) is by far the most commonly used high explosive. It has been widely used as a military explosive since World War I and still retains an important place in the explosive industry. TNT derives its virtues from its relative insensitivity to shock, high chemical stability and low melting point (80.4 °C). As it can be melted with steam, it may be safely cast into shells etc. TNT is usually used in conjunction with other high explosives such as RDX and HMX where it acts as an energetic binder in addition to explosive. As the melting point of TNT is low (convenient for melting with steam) and the temperature of decomposition is high ≈ 300 °C and also has the capability of binding explosive particles, it is termed a melt-castable explosive or explosive binder. Such explosives, except for TNT, are of recent origin and only a few explosives have recently been reported in the literature for such application.

2.2.20.1 Tris-X and Methyl Tris-X

Millar *et al.* have synthesized two heterocyclic trinitramines (Tris-X and its homolog 'Methyl Tris-X'), established their structures by elemental analysis, IR, NMR (^{1}H and ^{13}C) and mass spectroscopy and studied their explosive properties [140]. Some properties of Tris-X [Structure (2.45)] are: crystal density 1.73 g cm^{-3}, calc. $P_{CJ} \approx 30.0$ GPa, calc. VOD ≈ 8700 ms^{-1}, F of I ≈ 57 (F of I of RDX = 60) and m.p. *ca.* 68–69 °C. These can be easily synthesized in large yields using N_2O_5 technology.

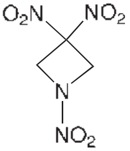
The low m.p. indicates its suitability as a melt-castable explosive using steam processing. However, its thermal stability (by DSC and chemiluminescence) is only marginally acceptable suggesting that this family of explosives is unlikely to be used for munitions.



Structure (2.45): 2,4,6-Tris(2-nitroxyethylnitramino)-1,3,5-triazine (Tris-X)

2.2.20.2 **1,3,3-Trinitroazetidine**

Another potential explosive in this class is 1,3,3-trinitroazetidine (TNAZ) [Structure (2.46)] reported by Iyer and his team [141]. This is a new strained-ring energetic material with a m.p. of 101 °C, density (X-ray) of 1.84 gcm^{-3} and thermal stability [142] of over 240 °C. Similar to 'Tris-X', it is also a melt-castable explosive and may be processed with steam. Further, it has many added advantages over known explosives. Unlike HMX, TNAZ is soluble in molten TNT, and is compatible with aluminum, steel, brass and glass. Also, it is not hygroscopic and does not pose processing problems. It provides up to 10% increased energy relative to RDX in the low-vulnerability ammunition (LOVA) XM-39 gun propellant formulations [143]. A comparison of the energetics in XM-39 type formulations is: RDX 1069 Jg^{-1}, HMX 1063 Jg^{-1} and TNAZ 1160 Jg^{-1}. Based on these properties, it may safely be concluded that TNAZ is a steam-castable explosive which is attractive as an explosive or as a near-term candidate component for explosives or propellants with low sensitivity, good stability and enhanced performance (high energy and density) over existing military formulations.



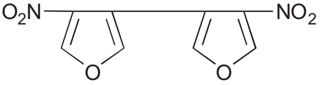
Structure (2.46): 1,3,3-Trinitroazetidine (TNAZ)

Australians have recently reported data on thermal study, hazards and performance assessment of neat and formulated TNAZ (60:40 RDX/TNAZ designated as ARX-4007) [144] and their data is not in agreement with Americans' [145]. Thermal analysis data suggest TNAZ to have high volatility and as a result, it rapidly evaporates from the liquid phase (>101 °C). The hazards assessment data suggest TNAZ to have an increased sensitivity over TNT while ARX-4007 shows sensitivity levels similar to Pentolite. TNAZ castings appear to solidify from the melt to give layered plates and form large number of shrinkage voids leading to non-reproducible mechanical properties. However, performance assessment of

ARX-4007 suggests it as a general purpose metal accelerating explosive with excellent VOD ($8660\,ms^{-1}$) and P_{CJ} (33.0 GPa). ARX-4007 (RDX/TNAZ 60/40), the analog of Composition 'B' (RDX/TNT 60/40) has comparable viscosity and gives performance improvement of approximate 11% over Composition 'B'. Its main drawbacks at the moment are its high production cost and slight volatility. When production cost for TNAZ is reduced through synthetic process refinement and its volatility is improved, TNAZ is likely to find applications in every system that now uses TNT.

2.2.20.3 **4,4′-Dinitro-3,3′-bifurazan**

4,4′-Dinitro-3,3′-bifurazan (DNBF) [Structure (2.47)] was reported by Coburn [146] as having properties: m.p. 85 °C, thermal stability (DTA) 254 °C, impact sensitivity 12 cm, calc. crystal density $1.92\,g\,cm^{-3}$, VOD $8800\,ms^{-1}$ and P_{CJ} 35.6 GPa. The low m.p. and predicted high performance make it a very attractive melt-castable explosive. It is however, very sensitive to impact demanding stringent safety measures during synthesis, handling, transportation and storage.



Structure (2.47): 4,4′-Dinitro-3,3′-bifurazan (DNBF)

It is well-known that the introduction of SF_5 groups has a strong tendency to lower melting points of nitro explosives [107]. Therefore, introduction of SF_5 groups into nitro explosives may also prove to be advantageous for the synthesis of melt-castable explosives or low melting energetic plasticizers, an area which is currently being explored and receiving world wide attention.

Russians have recently proposed a new approach to bring down the melting points of explosives by the replacement of picryl (Pic) by nitrofurazanyl (Nif) moiety. The incorporation of 'Nif' in place of 'Pic' in a molecule decreases melting point in the range of 50–200 °C. In addition, density of 'Nif' derivatives as a rule is $0.1–0.2\,g\,cm^{-3}$ greater than for 'Pic' analogs. At the same time, 'Nif' explosives possess high positive 'heat of formation', high VOD and high detonation pressure etc. They have validated their approach by synthesizing some explosives of this series. A comparison of 'Pic' and 'Nif' analogs (Table 2.3) supports their contention [147].

2.2.21
Insensitive High Explosives

Common explosives like TNT, RDX and HMX were considered adequate for all weapon applications, but these explosives have now become less attractive due to a number of accidents involving initiation of munitions by impact or shock aboard ships, aircraft carriers and ammunition trains. So there is a trend of current research worldwide to synthesize explosives which have high performance coupled with low sensitivity.

Table 2.3 Some important properties of Pic and Nif analogs.

Property	Pic derivative	Nif derivative
Molecular mass	439.21	341.15
Oxidant Balance (OB_{100})	(–) 1.14	(–) 0.29
Nitrogen, %	22.33	28.74
m.p., °C	249	180
Density, g cm^{-3}	1.64	1.81
Heat of formation, kcalkg^{-1}	18	128
Velocity of detonation, ms^{-1}	7150	7750
Detonation pressure, kbar	269	287
Heat of explosion, kcalkg^{-1}	985	1033

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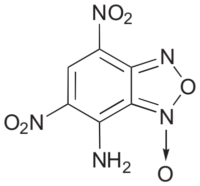
The conventional NC- and NG-based gun propellants are highly prone to accidental initiation as a result of external stimuli (fire, shock wave and impact). The range of threats to gun ammunition depends on the system in which it is placed. Such threats may be due to shaped charge jets, kinetic energy penetrators or hot spalls. In fact, NC-NG-based propellants are more sensitive than high explosive warheads especially when they are stored inside battle tanks or other fighting vehicles. Due to the sensitive nature of NC-NG-based gun propellants, there is always a risk of accidental loss of not only stored ammunition but also of crew members and their vehicles. In order to reduce this risk, low vulnerability ammunition (LOVA) propellants are an attractive alternative for conventional NC-NG-based gun propellants. Also, the problem of warhead vulnerability has become acute in the recent past. The first solution offered to this problem was invention and use of PBXs which consist of a plastic matrix encasing a conventional granular explosive, thereby offering some immunity to fire and bullet impact. Subsequently, it was observed that use of PBXs alone is no longer sufficient. As a result, this originated an idea of using intrinsically less sensitive explosives leading to the invention of another class of explosives (thermostable explosives with low-impact sensitivity) which was called insensitive high explosives (IHEs). TATB is the first member of this class and is considered a reference explosive for invulnerable explosives. TACOT, DINGU, TNAD, ADNBF, NTO, ANTA and DANTNP are some other explosives of this class.

TATB is well-known for its insensitivity and is currently employed as an IHE for some applications. TATB is however, inferior to RDX and HMX in performance. Therefore, a need exists for the research and development of explosives that are powerful yet resistant to accidental and sympathetic initiation.

Norris and co-workers, while working on 5-chloro-4,6-dinitrobenzofuroxan, had an intuition that 7-amino-4,6-dinitrobenzofuroxan (ADNBF) [Structure (2.48)] may be an IHE which proved to be correct at the end of the investigation [148, 149].

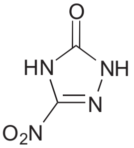


Structure (2.48): 7-Amino-4,6-dinitrobenzofuroxan (ADNBF)

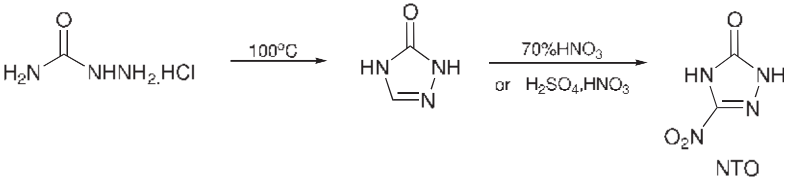
ADNBF is one of the early IHEs equal to TNT in impact insensitivity, with a calc. VOD slightly less than that of TATB. It is a fairly dense and easily-prepared explosive with the properties: density ≈ 1.902 $\mathrm{g\,cm^{-3}}$ m.p. *ca.* 270 °C with decomposition, calc. VOD ≈ 7910 $\mathrm{m\,s^{-1}}$, calc. P_{CJ} ≈ 28 GPa, impact sensitivity ($h_{50\%}$) ≈ 53 cm (TNT = 54 cm), and heat of formation ≈ +36.79 $\mathrm{kcal\,mol^{-1}}$. The work of Norris *et al.* was supported by other researchers who established that introduction of an $-NH_2$ group into 4,6-dinitrobenzofuroxan (DNBF) has a remarkable effect upon almost all physical and explosive properties: that is, m.p., density and calc. VOD all increase significantly while impact sensitivity is reduced drastically [150, 151].

2.2.21.1 **Oxynitrotriazole or Nitrotriazolone**

3-Nitro-1,2,4-triazol-5-one (NTO) [Structure (2.49)] or oxynitrotriazole (ONTA)has been reported as another IHE coupled with better performance [152–157]. Almost all aspects of NTO – synthesis, structural aspects, chemical and explosive properties including thermal behavior have been investigated [158–161]. NTO exists in two polymorphic forms, that is, α-form and β-form. It has been established that α-NTO is the stable and dominating form whereas β-NTO is only found in the product on recrystallization of NTO from a methanol or ethanol/methylene chloride mixture [162]. French researchers have recently reported its evaluation as an explosive for warhead filling without a binder and also as a PBX [155]. Further, synthesis of NTO is easy consisting of only two steps (Scheme 2.9) and uses inexpensive starting materials.



Structure (2.49): Nitrotriazolone (NTO) or Oxynitrotriazole (ONTA)



Scheme 2.9 Synthesis of nitrotriazolone (NTO).

The crystal density of NTO ≈ 1.93 g cm^{-3} and its VOD and P_{CJ} are equal to those of RDX. At the same time, it is far less sensitive than RDX and HMX. It is more stable than TNT and RDX but its sensitivity to ignition is slightly higher than TNT. NTO or NTO/RDX or HMX have been reported as fillings to get insensitive munitions (IM) [155]. A comparison of PBXs based on TATB and NTO further confirms the same sensitivity levels while VOD of the NTO-based PBX is slightly higher. The salient feature of NTO as a raw material for PBXs is that it may be obtained in particle sizes much larger than TATB, that is, 300–500 μm as against 9–30 μm for TATB. This implies that TATB may be processed by only pressing technique [155] whereas NTO may be processed by pressing as well as casting technique.

The synthesis and structural aspects of metal salts of NTO, that is, K, Cu and Pb NTO reveal that they have special characteristics and may find applications in several fields including ballistic modification of rocket propellants. The study of their thermal behavior with differential scanning calorimetry (DSC) suggests that: (i) NTO decomposition consists of one step (ii) Cu and K NTO salts decompose in three stages: dehydration, ring breakage and formation of metal oxides and (iii) Pb NTO decomposes in only two steps as it contains no water of crystallization. The structural aspects and thermal decomposition mechanisms of some alkaline earth salts of NTO have also been reported and their mechanism of decomposition is similar [163, 164].

The Chinese have recently reported preparation and characterization of nano-NTO and the data indicate that it decomposes at a lower temperature and is less sensitive to impact stimuli [165] compared with micro-NTO.

American investigators have reported development of a new IHE called Picatinny Arsenal Explosive-2 (PAX-2, a nitramine-based PBX) which possesses reduced sensitivity to sympathetic detonation in cannon caliber ammunition [166] and is considered as a substitute for existing PBXN-5. In this series, PAX-2A which retains all the requisite performance capabilities of PAX-2 but possesses less sensitivity to initiation by outside stimuli, has also been developed. This is regarded as the US Army's first high performing IM explosive.

NTO continues to receive attention from both defense and civilian sectors in the USA and other countries as a potential new-generation IHE. It has been used by Navy as an insensitive component to replace RDX as a bomb fill and as a major ingredient by Morton International Inc. to replace sodium azide for the auto air bag system [167].

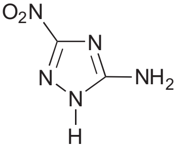
2.2.21.2 **Dinitroglycoluril**

Some years ago, French scientists reported DINGU [Structure (2.40)] as an insensitive explosive but subsequently lost interest in it due to its poor performance (VOD: 7580 ms^{-1} and density: 1.99 g cm^{-3}). It is easy to prepare DINGU (by nitration of the condensation product of glyoxal with urea) at a low cost which makes it very attractive [168]. Based on their studies, Coburn and co-workers called this an IHE. It is of course, somewhat more sensitive than TATB but it is much less sensitive than HMX [169]. The data of Coburn and co-workers are in agreement with the findings of Chinese workers who prepared PBXs of DINGU, TNT and

RDX using polymer G_{505} as a binder and studied VOD, impact and jet sensitivities. The DINGU-based PBXs possess high explosion energy, good physico-chemical stability and outstanding low vulnerability and are comparable [170] to TATB-based PBXs. As the method of preparation of DINGU is very simple and uses inexpensive starting materials compared with TATB, DINGU-based PBXs have a definite edge over TATB-based PBXs in terms of cost.

2.2.21.3 **Aminonitrotriazole**

As discussed in Section 2.2.18.1, the combination of $-NH_2$ and $-NO_2$ substituent groups particularly in the ortho position to each other provides inter- and intra-molecular hydrogen bonding that stabilizes molecules and increases their crystal densities. The heterocyclic substrates are included in order to add density, compared with the corresponding aromatic analogs and, also in many cases, contribute to a more positive heat of formation. It is with this background that 5-amino-3-nitro-1*H*-1,2,4-triazole (ANTA) [Structure (2.50)] has been tailored and synthesized by three routes [171, 172]. The best one involves diazotization of 3,5-diaminotriazole followed by reduction with hydrazine. The structure has been established with the help of IR and NMR. The thermal behavior and explosive properties – impact, friction and spark sensitivities including VOD have also been studied. The performance of small-scale tests indicates that ANTA is very insensitive (its impact sensitivity is too low to be determined with a 180 cm impact height limit machine). This new explosive has been found to be generally insensitive in all sensitivity tests but it is of low energy compared with TATB (calculated performance is however, comparable to TATB). ANTA (French abbreviation ANT) on treatment with a commercially available compound, 4,6-dichloro-5-nitropyrimidine (DCNP) yields a new IHE, that is, 5-nitro-4,6-bis(5-amino-3-nitro-1H-l,2,4-triazole-l-yl) pyrimidine (DANTNP) [Structure (2.51)] which was studied extensively by French researchers [173]. Its synthesis is shown in Scheme 2.10.



Structure (2.50): 5-Amino-3-nitro-1*H*-1,2,4-triazole (ANTA)

The characteristics of this explosive are: calculated density (X-ray diffraction) ≈1.865 $g\,cm^{-3}$, impact sensitivity ($h_{50\%}$ for 5 kg weight) ≈70 cm, friction sensitivity ≈ insensitive, temperature of decomposition (DSC) *ca.* 350 °C and VOD ≈ 8200 $m\,s^{-1}$. The data confirm that DANTNP is slightly more powerful while its impact insensitivity is of the order of TATB [174].

2.2.21.4 **Trans-1,4,5,8-tetranitro-1,4,5,8-tetraazadecalin**

Trans-1,4,5,8-tetranitro-1,4,5,8-tetraazadecalin (TNAD) [Structure (2.52)] has been obtained by the reaction of trans-1,4,5,8 tetraazadecalin with $NaNO_2$ and HCl to

$$C_2H_5OH + Na \longrightarrow C_2H_2ONa + 0.5H_2$$

$$C_2H_2ONa + ANT \longrightarrow ANT.Na + C_2H_5OH$$

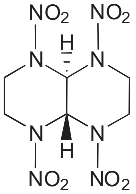
$$ANT.Na + DCNP \longrightarrow DANTNP + NaCl$$

Structure (2.51) : DANTNP

Scheme 2.10 Synthesis of 5-nitro-4,6-bis(5-amino-3-nitro-1H-1,2,4-triazole-1-yl) pyrimidine(DANTNP).

obtain its nitroso derivative followed by its nitration [175]. It has a better thermal stability than RDX and is less sensitive to impact than either RDX or HMX. Its density is equal to that of RDX but its calculated VOD is slightly lower. TNAD is also regarded as an IHE because of its improved insensitivity.

Some TNT-based formulations have been tailored, made and tested for sensitivity and ballistic performance. When TATB, DINGU and nitroguanidine (NQ) are incorporated in these formulations, they become IHEs. Further details of these formulations are available in the literature [176].



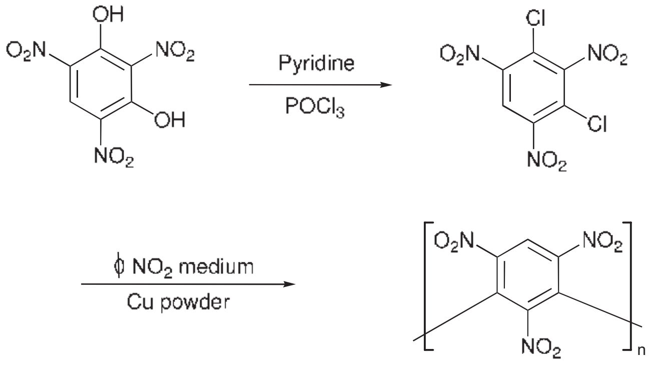
Structure (2.52): Trans-1,4,5,8-tetranitro-1,4,5,8-tetraazadecalin (TNAD)

2.2.22
Energetic Binders and Plasticizers

2.2.22.1 **Energetic Binders**

There are a number of inert binders such as polyester, epoxy, polysulfide, polyurethane which have been reported as binders for composite propellants and plastic bonded explosives (PBXs). At present, hydroxy-terminated polybutadiene (HTPB) is regarded as the state-of-the-art workhorse binder for such applications. However, the recent trend is to use energetic binders such as poly [3,3-bis(azidomethyl oxetane)] [poly(BAMO)], poly (3-azidomethyl-3-methyl oxetane) [poly(AMMO)], PNP, GAP diol and triol, nitrated HTPB(NHTPB), poly(NiMMO), poly(GlyN) and nitrated cyclodextrin polymers poly(CDN) for PBXs and composite propellants in order to get better performance.

Polynitropolyphenylenes (PNPs) [Structure (2.53)] describe a class of compounds with aromatic C–NO_2 groups in a chain of benzene units interlinked by



Structure (2.53) : PNPs

where `n' is the degree of polymerization which is in the range of 11-19

Scheme 2.11 Synthesis of polynitropolyphenylenes (PNPs).

aromatic C–C bonds. They may be synthesized from *m*-dichloro trinitrobenzene (styphnyl chloride) and copper powder in nitrobenzene medium, according to Ullmann's reaction [177, 178] (Scheme 2.11).

The structure of this polymeric material has been established on the basis of ^{1}H-NMR, ^{13}C-NMR (proves the presence of C–C-linked aromatic nitrated benzene rings) and molecular weights $\overline{M}_n$ and $\overline{M}_w$ (by GPC). PNP is of green-brownish yellow to dark brown color and is soluble in many common organic solvents. The properties are: deflagration temperature 286–294 °C, explosion energy 3300 Jg^{-1}, density 1.8–2.2 gcm^{-3}. Also it is insensitive to impact and friction. Further, PNPs are non-crystalline, thermally stable and are considered as high-temperature resistant binders together with inert binders and/or softeners. Some pyrotechnic formulations which use PNP as a binder have been reported recently [179, 180]. The polymer does not melt and is coated on to fillers by an acetone–ethanol solution. This may also find use as a heat resistant binder for propellant and explosive formulations.

Due to recent advances in polymer chemistry, efforts have been made to synthesize polymers containing nitro groups (C-nitro, O-nitro and N-nitro) and azide group ($-N_3$) and use them as binders for explosive or propellant formulations. A number of energetic polyurethanes based on nitro aliphatic diisocyanates with nitroaliphatic diols have been reported [181]. The energetic polyurethanes are of academic interest and none of them has been found to be a useful binder in explosive formulations. C-nitropolymers from monomers with a vinyl group are another class of energetic polymers which may find applications as binders for explosives. Nitroethyl acrylate ($CH_2{=}CH \cdot COO \cdot CH_2 \cdot CH_2 \cdot NO_2$) monomer, on polymerization under the action of benzoyl peroxide(BPO) at 100 °C in an inert atmosphere, gives a soft polymer. In contrast, the polymer of methacrylate is hard [182]. The polymer of dinitropropyl acrylate (DNPA) (with a VOD of 6100 ms^{-1}) has also been suggested as a binder for explosive formulations [183].

The chemistry and properties together with applications of other energetic binders such as GAP, NHTPB, poly (NiMMO), poly (GlyN) and poly (CDN) will be described in Chapter 4 on propellants because of their extensive use in that segment of explosive industry.

2.2.22.2 Energetic Plasticizers

NG, EGDN, DEGDN, TEGDN, BTTN, MTN/TMETN, K-10, BDNPF, BDNPA and Bu-NENA, azidoplasticizer (low molecular wt. GAP), low molecular wt. poly (NiMMO) and poly (GlyN) are some of the energetic plasticizers which have been reported in the literature to improve the performance of PBXs and gun and rocket propellants. Further, a lot of data has been generated by using these materials in explosive and propellant formulations in India as well as in other countries. These will also be described in Chapter 4 along with energetic binders.

2.2.23
Energetic Materials Synthesized Using Dinitrogen Pentoxide

Explosives are usually synthesized with the use of conventional nitrating agents. However, European countries and the USA have moved toward a novel nitration methodology based on dinitrogen pentoxide (N_2O_5). The development and perfection of this new nitration methodology is mainly due to sustained research in UK [184]. Nitration with N_2O_5 has several advantages over conventional nitrating agents and may be used to prepare all types of explosives, that is, C-nitro explosives (TNT etc.), N-nitro explosives (RDX, HMX, etc.) and O-nitro explosives (NG etc.) Some salient features are: (i) it is significantly faster than conventional nitrating agents; (ii) yields are higher ≈ 80–90%; (iii) purity is better; (iv) ease of temperature control as reactions are not generally exothermic; (v) absence of waste acids for disposal; (vi) it is a universal nitrating agent which can be used to prepare all three types of explosives, that is, C-nitro, O-nitro and N-nitro explosives.

In fact, N_2O_5 was reported as early as 1849 but its use was neglected until 1925; mainly because of the difficulty in preparing it in a pure form and problems associated with its storage due to its poor thermal stability [185–187]. It is prepared by: (i) electrolysis [188] of HNO_3 in the presence of N_2O_4; (ii) ozonation [189] of N_2O_4; (iii) dehydration of HNO_3 with P_2O_5. It is generally stored at −60 °C and used for nitration in two ways:

1) **N_2O_5 in pure HNO_3:** Unselective nitration system akin to mixed acids system.
2) **N_2O_5 in organic solvents:** Chlorinated solvents encompass a much wider range of nitrations and permit synthesis of polynitrated species directly without the formation of acidic by-products (an important environmental consideration). It is also suitable for the nitration of strained-ring heterocyclic skeletons.

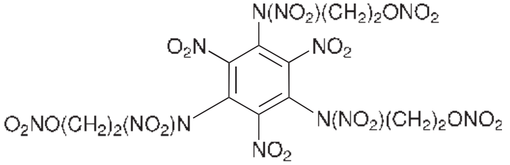
Using this new nitration methodology, Millar and co-workers have reported synthesis of 'Tris-X' and its methyl analog [140] 'methyl Tris-X'. Similarly, French researchers [190] have reported synthesis of 1,3,4,6-tetranitroglycoluril [TNGU or Sorguyl (French)] using N_2O_5. Furthermore, a new series of energetic binders and oxidizers regarded as major ingredients of explosive or propellant formulations, has also recently been reported in the literature. The nitrated hydroxy-terminated polybutadiene (NHTPB) synthesized by selective nitration using N_2O_5 from cheap precursors, has undergone scale-up and evaluation trials in UK [191]. The data suggest its suitability for binder applications [192]. The low molecular weight poly (NiMMO) and poly(GlyN) (potential plasticizers) and high molecular weight poly(NiMMO) and poly(GlyN) (very promising binders) are also available with the use of N_2O_5. Ammonium dinitramide, (ADN), an eco-friendly and high performance oxidizer for composite propellants, is also synthesized with the use of this new nitration methodology. All these materials are of recent origin and are regarded as next generation materials; they have been synthesized with the use of novel materials and techniques followed by their characterization and evaluation for intended applications. Some of them are considered very promising and are at various stages of scaling-up and large scale application. The details are included in Chapter 4.

2.2.24
Newly Reported Explosives

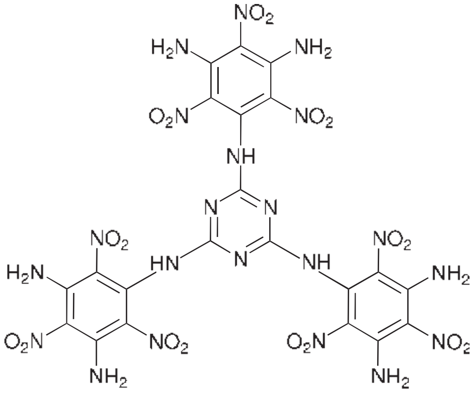
A number of explosives for various applications have been synthesized, characterized for structural aspects, thermal and explosive properties by us in India and are being evaluated [193–198] for their intended end-use. The evaluation of BTATNB [Structure (2.27)] indicates that it is slightly more thermally stable than PATO [Structure (2.24)] coupled with better insensitivity toward impact and friction [71]. The data on thermal and explosive properties of some aromatic nitrate esters suggest that 1,3,5-tris(2-nitroxyethyl nitramino)-2,4,6-trinitrobenzene [Structure (2.54)] is a potential substitute of PETN [193]. An explosive called 2,4,6-tris (3′,5′-diamino-2′,4′,6′-trinitrophenylamino)-1,3,5-triazene [designated as PL-1: Structure (2.55)] is a new thermally stable and insensitive explosive which on comparison with TATB suggests that it is slightly inferior to TATB [Structure (2.21)] in terms of thermal stability (m.p., °C: TATB ≈ 350 and PL-1 ≈ 336) and calculated VOD, ms^{-1} (TATB ≈ 8000 and PL-1 ≈ 7861) but it is better in respect of density (density, gcm^{-3}: TATB ≈ 1.94 and PL-1 ≈ 2.02) whereas sensitivity to impact and friction is comparable [194]. Another study on 3-amino-5-nitro-1,2,4-triazole (ANTA) [Structure (2.50)] and its derivatives concludes that ANTA and 4,6-bis (3-amino-5-nitro-1H-1,2,4-triazole-1-yl)-5-nitropyrimidine (DANTNP) [Structure (2.51)] may find application in propellant or explosive formulations where insensitivity coupled with thermal stability is of prime importance [195]. The study on 4-picrylamino-2,6-dinitrotoluene (PADNT) [Structure (2.56)] leads to the conclusion that its handling is safe and at the same time, it possesses a good thermal stability [196]. PADNT may also be an attractive option as a new energetic ingredient for the development of safe and insensitive explosive or propellant formulations. The compound 2,5,7,9-tetranitro-2,5,7,9-tetraazabicyclo(4,3,0) nonane-8-one (TNABN) [Structure (2.43)] possesses a promising blend of explosive properties and insensitivity to impact and friction [197, 198].

We have also reported a new explosive called, *N,N′*-bis(1,2,4-triazol-3-yl)-4,4′-diamino-2,2′,3,3′,5,5′,6,6′-octanitroazobenzene (BTDAONAB) [Structure (2.39)], prepared on a laboratory scale and characterized for its thermal and explosive characteristics [25]. This explosive possesses a remarkable thermal stability which is better than the most thermally stable explosive, TATB and at the same time, its VOD is more than that of TATB. The chemical structures of some newly reported explosives are depicted in Figure 2.3.

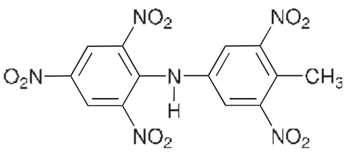
Further, some important properties of these explosives vis-à-vis their comparison with benchmark explosives are given in Table 2.4.



Structure (2.54)



Structure (2.55)



Structure(2.56)

Figure 2.3 Structures of some newly reported explosives.

Table 2.4 Important properties of some newly reported explosives.

Name	Melting point/°C	Density/ $g cm^{-3}$	Impact sensitivity/cm	VOD/$m s^{-1}$ (calculated)	Remarks
PL-1	336	2.02	170	7861	Slightly inferior to TATB in terms of thermal stability and VOD but better in respect of density
ANTA	240	1.82	>170	8460	May be useful for formulations where insensitivity coupled with thermal stability is required
DANTNP	>330	1.84	>170	8120	–
PADNT	198-201	1.85	135	6628	Useful for safe and insensitive explosive/ propellant formulations
2,5,7,9-tetranitro-2,5,7,9-tetraazabicyclo (4,3.0) nonane-8-one (TNABN)	>230	1.92	115	9015	Promising blend of explosive properties and insensitivity to impact and friction
BTDAONAB	>550	1.97	87	8321	DTA exotherm appears at 550 °C. It is better than TATB in respect of density, thermal stability and also VOD.

2.2.25
Important Formulations Based on TATB, CL-20 and NTO

In supersonic missiles where warheads are subjected to aerodynamic heating, conventional explosives cannot be used and thermally stable explosives like TATB, TACOT, HNS and PYX, etc. are necessary for such systems. Some formulations based on these explosives are HNS/Kel-F800 95/5 (developed by Atomic Weapons Research Establishment, Aldermaston, UK) and AFX 521 (PYX/Kel-F800 95/5 – developed by Los Alamos National Laboratory, USA). Their shock sensitivities lie in the region required for boosters. HNS/Teflon explosive charges have also been used for the Apollo 17 seismic experiments [199].

2.2.25.1 TATB-based Formulations

A study has been conducted on PBXs based on TATB using various binders such as polyurethane (Estane 5703–Goodrich), Viton-A (copolymer of vinylidene fluoride and hexafluoropropylene: Du Pont), silicone resin (Chemlok), Kel-F800 [copolymer (3:1) of chlorotrifluoroethylene and vinylidene fluoride: 3M Company] and Teflon [poly (tetrafluoroethylene), PTFE: Du Pont] etc. and it was concluded that

TATB/Kel-F800 (90/10 wt.%) is best in terms of thermal stability coupled with a respectable performance [200]. Similarly, PBXs based on TATB, HMX and Kel-F800 are available, and sensitivity data on TATB/HMX-based PBXs clearly show that insensitivity rapidly decreases with increasing HMX content, even at relatively low levels of HMX. Evidently, some trade-off must be made between VOD and safety [201] (Table 2.5). Further, sensitivity and thermal test data (Table 2.6) also indicate that TATB-based formulations rank as the most insensitive explosive formulations [202].

These PBXs have relatively high thermal stability and sufficient power for certain applications where size of container is not severely restricted. For example, warheads of large rockets, large bombs etc.

Polymers such as Estane 5702-F1 and Kel-F800 are considered to be good binders for TATB. However, decomposition of Estane binder has cast doubts on the long-term stability of TATB/Estane formulations. Polymer Estane-5702 is known to undergo hydrolytic degradation which is evidenced by reduction in intrinsic viscosity due to hydrolysis of the ester linkage and fragmentation into low molecular weight segments. Thermal degradation is another problem during storage and degradation mechanism which probably involves both the reaction of isocyanate with hydroxyl ends of neighboring chains and the cleavage of these

Table 2.5 Some TATB/HMX Based PBXs and their properties.

Composition	**TATB**	**HMX**	**Kel-F 800**	**Density/g cm^{-3}**	**VOD/m s^{-1}**	**Impact sen. ($h_{50\%}$ for 11 kg wt.)/cm**
PBX-9502	95.0	0	5.0	1.895	7706	–
X-0344	71.25	23.75	5.0	1.894	8046	–
PBX-9501	0	95.0	5.0	1.832	8802	–
–	0	90.0	10.0	1.869	–	<30
–	20.0	70.0	10.0	1.873	–	~60
–	40.0	50.0	10.0	1.878	–	>1920

Table 2.6 TATB based PBXs with different binders and their properties.

Formulation Property	**TATB/PU 95/5**	**TATB/Viton/ Chemlok95/2.5/2.5**	**TATB/Kel-F800 90/10**
Impact (5 kg/200 cm)	No reaction	No reaction	No reaction
Friction	No reaction	No reaction	No reaction
DTA/°C	340	330	330
VOD/m s^{-1}	7500	7970	7534

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nascent segments from the longer repeat unit [203]. TATB/Kel-F 800 and TATB/Viton formulations appear to be stable and attractive for long-term use [46, 204].

Several formulations based on TATB have been reported as main-charge explosives. PBX-9502 (TATB 95% and Kel-F 800 5%) is a main-charge explosive formulation with very low explosiveness and shock sensitivity; RX-26-AF (HMX 49.3%, TATB 46.6% and Estane 4.1%) is another main-charge explosive formulation with low explosiveness but increased shock sensitivity; PBX-9503 (TATB 80%, HMX 15% and Kel-F 800 5%) was developed as a booster formulation for PBX-9502. PBXW-7 (TATB 60%, RDX 35% and PTFE 5%) is also a booster formulation which originated from the Naval Surface Weapons Center, Whiteoak (USA) as a result of their investigation to produce a material of low explosiveness but with sufficient shock sensitivity. This formulation is used in cook-off resistant boosters. The following booster explosive (BX) formulations have also been investigated and shock sensitivity data on these formulations suggest that all these formulations are sufficiently shock sensitive.

BX1: TATB 60%, Nitramine 35% and Kel-F800 5%
(Nitramine = RDX 95% and HMX 5%)
BX2: TATB 60%, Nitramine 35% and PTFE 5%
(Nitramine = RDX 95% and HMX 5%)
BX3: TATB 60%, Nitramine 35% and Kel-F800 5%
(Nitramine = RDX 90% and HMX 10%)
BX4: TATB 60%, Nitramine 35% and PTFE 5%
(Nitramine = RDX 90% and HMX 10%)

The manufacturing process of BX4 was found to be more favorable than that of BX3. The detonation pressure and test of their ability to initiate a secondary explosive have shown that BX4 is the most powerful of these formulations and therefore, it is considered the most promising booster formulation. Another attribute of BX4 is that it could be converted into a blast formulation by the addition of aluminum powder and this modified formulation may find application as a main-charge blast formulation.

2.2.25.2 **CL-20-based Formulations**

Some properties of GAP and CL-20-based propellants are: I_{sp} 257.6 s, density 1.73 $\mathrm{g\,cm^{-3}}$ and burn-rate 13.4 $\mathrm{mm\,s^{-1}}$ as against 249.7 s, 1.67 $\mathrm{g\,cm^{-3}}$ and 7.2 $\mathrm{mm\,s^{-1}}$ respectively for GAP and HMX-based propellants. Some CL-20-based explosive formulations which possess promising calculated performance have also been reported in the literature [205]. The calculated performance of these formulations along with two commonly used HMX-based formulations is given in Table 2.7.

The data suggest that the CL-20-based explosive formulations have considerably more energy than the analogous HMX formulations. Typical processes (mix-cast, melt-cast, pressing and molding) used to manufacture explosive formulations containing RDX/HMX may also be used for CL-20-containing formulations, but initiability and detonability of CL-20-containing formulations are reported to be greater. Further, sensitivity data suggest that safety characteristics of CL-20-based

Table 2.7 Comparison of calculated performance of CL-20 and HMX based explosives.

Formulation	Density (99%TMD)/g cm^{-3}	Detonation velocity/m s^{-1}	ERL impact sensitivity/cm	BAM friction sensitivity/N	ESD sensitivity/J
PAThX-1 (CL-20 based)	1.944	9370	35.4	211.9	>8
PAThX-2 (CL-20 based)	1.923	9220	32.5	211.9	>8
PAThX-3 (CL-20 based)	1.958	9500	24.6	Not tested	>8
PAX-2A (HMX based)	1.773	8420	–	–	–
LX-14 (HMX based)	1.835	8800	30-38	235.4	>8

formulations are comparable with those of LX-14 (HMX/Estane). The results of some researchers indicate that CL-20-containing formulations are more sensitive to mechanical and shock factors than the RDX and HMX-based formulations. However, an in-depth study and exhaustive R&D programs should be undertaken to optimize the I_{sp} and VOD of CL-20-based formulations, without penalty on vulnerability in view of their emergence as an effective solution to future needs.

The formulation LX-19 which is a volume analog to LX-14 (HMX/Estane) consisting of 95.8 wt.% ε CL-20 and 4.2 wt.% of Estane binder has recently been reported by Murphy *et al.* [206]. As a result of their extensive work on different warhead configurations (trumpet lined shaped charge, a hemispherical lined shaped charge, an EFP charge and a fragmentation warhead), they concluded that CL-20 impact sensitivity is similar to PETN and the formulated materials are significantly less sensitive with impact values close to those of HMX-based formulations. Further, formulation LX-19 is one of the most powerful metal pushing explosive formulations, which produces performance improvement when compared with octol, LX-14 and Composition A6. Today, it is considered to be the most powerful explosive formulation. In view of its superior performance, CL-20 is regarded as a HEM of the next generation and promises to be in the vanguard of many new energetic materials for explosive, propellant and pyrotechnic applications.

CL-20 was evaluated in both propellant and explosive formulations. A large number of CL-20-based PBXs are reported in the literature. A comparison of their VOD with that of the corresponding HMX-based formulations reveals a 12–15% higher energy potential of CL-20-based formulations. CL-20 is also a superior alternative to RDX and HMX for application in low-signature rocket propellants. CL-20-based propellants offer burn-rates much higher (≈35–110%) than those of HMX-based propellants. The performance of CL-20-based propellants in terms of I_{sp} is found to be higher than those of RDX-based propellants.

Golfier *et al.* reported CL-20 and GAP-based propellants to have I_{sp} = 251 s, in comparison to that of 242 s for the corresponding RDX-based propellants [207]. CL-20 is also a potential component of gun propellants having a superior impetus and high burning rate. Mezger *et al.* while continuing their research on explosives, formulated compositions with 85–90% of CL-20 as an alternative to today's most widely used HMX-based formulation LX-14. They also projected applications of CL-20-based PBX [208] in explosively formed projectiles (EFP).

Eiselle and Menke reported the probability of application of CL-20-based formulations in rocket motors for highly accelerating guided tactical missiles and high velocity ballistic missiles [209]. Harris *et al.* recommended Hytrel [thermoplastic copolyester ethers consisting of an aromatic polyester, polybutylene terephthalate (hard/crystalline segment) and polyether glycol (soft/amorphous segment) manufactured by DuPont] and copolymer of BAMO (bis-azidomethyl oxetane) and AMMO (azidomethyl methyl oxetane) containing CL-20 propellants as a superior alternative to the M30 gun propellant [210].

CL-20-based propellant formulations based on NC plasticized with BDNPA/F or EPX (a nitramine plasticizer) are reported to be safe for testing in a 40-caliber gun simulator [211]. Lewis *et al.* studied a CL-20-based pyrotechnic gas-generating formulation that burns down to produce one or more reaction products that suppress fire [212]. Sato and Kodama studied CL-20 as a base charge for detonators [213] and as a filling of detonation cords [214].

2.2.25.3 **NTO-based Formulations**

Nitrotriazolone and TATB are explosives of relatively low sensitivity compared with conventional secondary explosives but their performance levels are not high. The VOD for NTO is $8510\,\mathrm{ms^{-1}}$ and density is $1.91\,\mathrm{gcm^{-3}}$ whereas for TATB, VOD is $8000\,\mathrm{ms^{-1}}$ and density is $1.94\,\mathrm{gcm^{-3}}$. Further, NTO can easily be obtained in particle size much larger than TATB, that is, 300 μm to 500 μm (NTO) as against 9 μm-3 μm (TATB).

Though NTO was first prepared in 1905, research into its explosive properties was not fully undertaken until the 1980s. It is a high-energy explosive with low-vulnerability and high stability which can be used in many types of explosive fillings: melt-cast, cast-cured PBXs and pressed PBXs. Many countries: France, USA, UK, Norway, South Africa and Switzerland etc. have formulated so many formulations containing NTO and in general, most of the formulations show a marked reduction in vulnerability in comparison to nitramine (RDX, HMX) and TNT/nitramine-based formulations.

The NTO/TNT formulation is characterized by a lower vulnerability than RDX/TNT and Composition B. NTO is also used to produce pressed PBXs with thermoplastic binders and cast PBXs with thermosetting binders for IMs. NTO is an explosive with calculated performance near that of RDX but with insensitivity approaching that of TATB. Possible use of NTO is as an alternative to RDX in formulations where a lower sensitivity is desired or as an alternative to TATB where better performance is required without a large increase in sensitivity [123, 152, 153, 215]. The formulations based on NTO/binder (FPC-461, Viton-A, Kel-F800, Estane-5702 and Kraton G) in 95/5 (mass percent concentrations) have also been tested for compatibility and none of the NTO/binder formulations showed evidence of incompatibility.

PBXs such as X-0483(95/5 mass%, NTO/FPC-461) and X-0489 (50/50 mass%, NTO/TNT) have been reported for some specific applications. Société Nationale des Poudres et Explosifs, France, (SNPE) has reported B-2214 based on an inert binder, HMX and NTO (12% and 72% respectively) as a substitute for industrial French PBX (filled with 86% HMX and designated as ORA 86) for a French missile warhead. Based on data on bullet impact, ignition by a shock wave, shaped charge jet and sympathetic detonation, it is evident that B-2214 is less sensitive than Composition B (Hexol 60/40) or ORA 86. It is also possible with NTO to obtain 1.6 classed PBXs insensitive to sympathetic detonation [215]. Another NTO-based formulation X-0489 (50/50 mass% NTO/TNT) was cast and radiographed and showed minimal shrinkage and bubbles. The performance data are: density, $g\,cm^{-3}$: 1.720, Pressure, kbar: 242 and detonation velocity, ms^{-1}: 7225 as against calculated values of $1.720\,gcm^{-3}$, 246 kbar and $7560\,ms^{-1}$ respectively [153].

The US Air Force formulation designated as AFX 644 (based on TNT and NTO and also referred to as TNTO IV) is used for low-vulnerability General Purpose (GP) bomb. AFX-644 is a melt-cast, wax desensitized nitrotriazolone (NTO)-based explosive formulation which employs TNT as an energetic binder and aluminum powder to enhance blast performance. TNT, NTO, wax and Al powder are mixed in proportions of 30,40,10 and 20% respectively and meets the United Nations' (UN) criteria for extremely insensitive detonating substances (EIDS) and full-scale testing requirements for fast cook-off, slow cook-off and bullet impact [216]. However, mixed results were obtained in the full-scale detonation testing of this formulation. MK-82 pressure arena tests for AFX-644 yielded performance parameters similar to those obtained for tritonal-filled bombs. A reformulation strategy for TNTO IV (AFX-644) was developed to minimize exudation, improved processing parameters and improved survivability for sympathetic detonation scenarios. These efforts resulted in AF-644 Mod 0 (extremely insensitive but poor performing explosive) and AFX-645. This new formulation AFX-645 eliminates the poor processing characteristics of baseline AFX-644 formulation and also improves upon the performance of AFX-644 Mod 0. AFX-645 also provides proper balance of insensitivity, performance and initiability required for safe storage, handling, reliability and lethality in operational environments [217]. The US Air Force has also developed AFX-757, explosive fill used in Joint Air-to-Surface Stand-off Missile (JASSM), as a replacement of tritonal in the Miniature Munition Technology Program. Lockheed Martin also chose AFX-757 for their warhead because of its increased blast energy and potential insensitivity. Giat, France offers a MURAT (Munitions à Risques Attenues) version of its LU211 155 mm HE projectile (LU211-M) filled with 9 kg of XF13 153 melt cast of this formulation (TNT 30%, Al 20%, wax 10% and NTO 40%). This ammunition is designated as one-star MURAT IM with VOD [218] $\approx 6880\,ms^{-1}$. Also, CPX-413 [based on poly(NiMMO)/HMX/NTO/K-10 Plasticizer) matches the performance of Composition B while passing the UN Series-7 tests ranking it as an EIDS [219]. Presently, this formulation is not optimal but should prove a suitable candidate for further research.

2.2.26
Insensitive Munitions and Some New Insensitive Explosives/Formulations

The safety of munitions received increased attention after the adoption of Insensitive Munition Policy by the US military. The IM Policy stipulated that all in-service munitions should exhibit a response no greater than burning to a range of impact and thermal stimuli by the year 1995. This was a very exacting and stringent requirement as some of the effects of accidental stimuli are not far removed from those of the intentional initiating stimuli. The implementation of IM Policy by the target date did not appear to be achievable for most munitions without an appreciable decrease in performance which is unacceptable. But research is still continuing apace in the USA, UK and many other developed countries so that all in-service munitions conform to this ideal standard in the near future.

A formal international requirement for insensitivity was raised as far back as 1984 by NATO's Conference of National Armament Directors (CNAD) AC/310 Partnership Group on 'Safety and Suitability for Service Munitions and Explosives'. As a result, a pilot NATO Insensitive Munitions Information Center (NIMIC) was set-up in the USA in 1988. Subsequently, after a couple of years when technologies for production of most ammunition of insensitive types were available and implementation and fielding was more important, the name NIMIC was changed to NATO's Munitions Safety Information Analysis Center (MSIAC) in December 2004. The advantages derived as a result of implementation of IM Policy are briefly described in Chapter 6 (Section 6.8).

Organizations such as Giat (France), Denel (South Africa) and US Army's Picatinny Arsenal continue their efforts to develop IMs based on melt-cast TNT. It is acceptable for artillery ammunition (not for high performance warheads required for missiles) being cheaper in production than either pressed or cast-cured PBXs.

2.2.26.1 **ROWANEX Class of PBXs**

The UK Royal Ordnance in collaboration with UK Defence Research Agency has developed a new series of PBXs called ROWANEX (stands for Royal Ordnance Waltham Abbey New Explosive) for use in IMs and this program was conducted in accordance with the guidelines defined by NATO authorities [220] under STANAG 4170. At the end of this investigation, ROWANEX 1001 was concluded to be the PBX of their choice for this purpose. This is a vacuum castable, curable, HMX-based formulation, which has a total solids loading of 88 m/m (77.8% v/v) and 12% polyurethane binder derived from HTPB, IPDI, DOA (to improve processibility), an anti-oxidant and dibutyltin dilaurate catalyst. The details of nominal formulations along with their performance are given in Table 2.8 and compared with octol 75/25, Composition B (60/40) and TNT. ROWANEX 1001 with reduced vulnerability and comparable performance is primarily meant for shaped charge and fragmenting warhead main charge applications. This is likely to be available to users as a fully approved explosive in near future [221].

Some explosive formulations based on HMX, HMX and NTO, HMX and TATB (by wt.) and binder have been studied for density, VOD, IAD (number of cards), initiation sensitivity, ignition temperature and other explosive properties. The data given in Table 2.9 and Table 2.10 show a significant decrease in sensitivity, IAD (number of cards) and initiation sensitivity of explosive formulations with an increase in the proportion of NTO as well as TATB. However, performance of the NTO-based formulation is slightly better [222].

Table 2.8 Some formulations and their performance data[a].

Parameter	Explosive formulations			
	ROWANEX 1001	**Octol 75/25**	**Comp B**	**TNT**
Solids loading, % (wt./wt.)	88.0	75.0	60.0	–
Solids loading, % (v/v)	77.8	70.9	57.9	–
Theoretical max. density, $\mathrm{g cm^{-3}}$	1.68	1.81	1.74	1.65
VOD, $\mathrm{m s^{-1}}$	8320 (8340[b])	8460	8042	7000
Detonation pressure, GPa	29.4	32.2	28.1	20.3
Gurney velocity, $\mathrm{m s^{-1}}$	2749	2820	2712	2391
Heat of detonation, $\mathrm{kJ\,g^{-1}}$	5.4	6.09	5.9	5.41
Gas evolved on detonation, $\mathrm{cm^3\,g^{-1}}$	800	710	681	567

a) Theoretical data unless stated otherwise.

b) Experimental result.

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Table 2.9 Some properties of pressed explosives with 92.5%HMX, HMX/TATB and HMX/NTO (Kel-F binder 7% and graphite 0.5%).

Formulation (mass, %)	Reference HMX	HMX/TATB	HMX/NTO
HMX	92.5	37.0	37.0
TATB	–	55.5	–
NTO	–	–	55.5
Density/$\mathrm{g\,cm^{-3}}$	1.89	1.90	1.89
Detonation velocity/$\mathrm{m\,s^{-1}}$	8690	8100	8360
Friction sensitivity (FSC)/N	210	10% at 353 N	326
Impact sensitivity (ISC)/J	3.6	12.5	8.8

2.2.26.2 **SNPE's PBXs**

The SNPE has designed PBXs for different applications and their data confirm that all given below are EIDSs.

- GP bombs B 2214;
- penetrators B 2214, B 2211;
- mines or torpedoes B 2211, B 2245;
- missile warheads B 2248, B 2237;
- shaped charges B 3021.

The Table 2.11 summarizes some characteristics of these PBXs and their responses to UN Test Series-7.

Table 2.10 Some properties of composite explosives with 80.6 % HMX, HMX/NTO and HMX/TATB.

Formulation (mass, %)	Reference Formulation		
Binder	19.4	19.4	19.4
HMX	80.6	21.9	21.9
NTO	0	0	58.7
TATB	0	58.7	0
Density/g cm^{-3}	1.621	1.624	1.620
Detonation velocity/m s^{-1}			
30 mm dia	8000	N.D.	N.D
50 mm dia	8050	7270	DS
IAD (number of cards)	160	130	110
Initiation sensitivity	BRISKA	BRISKA+ 8 g of plastic	BRISKA + 20 g of plastic
Spontaneous ignition temperature by gradual heating/°C	240	240	240

N.D.: No detonation; D.S.: Detonation stopped.
BRISKA: Detonator with a force equivalent to 0.8 g of PETN

Table 2.11 Characteristics of some EIDSs and their responses to UN Series-7 tests.

PBX	B 2211	B 2214	B 2237	B 2245	B 2248	B 3021
Ingredients	**HTPB/RDX AP/Al**	**HTPB/HMX NTO**	**HTPB/HMX AP/Al**	**HTPB/RDX NTO/AP/Al**	**HTPB/HMX NTO**	**Energetic binder HMX/NTO**
ρ/g cm^{-3}	1.803	1.63	1.71	1.81	1.685	1.765
D/m s^{-1}	5500	7495	7330	5150	8050	8100
Cap test 7a	–	–	–	–	–	–
Gap test 7b	–	–	–	–	–	–
Friability test 7 c,d	–	–	–	–	–	–
Bullet impact test 7d	–	–	–	–	–	–
External fire test 7e	–	–	–	–	–	–
Slow cook-off (SCO) test 7f	–	–	–	–	–	–
EIDS	Yes	Yes	Yes	Yes	Yes	Yes

(–) means that acceptance criterion is met.
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2.2.26.3 **FOI's Explosives**

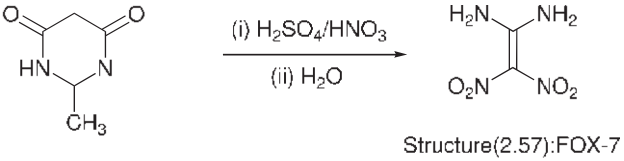
The Swedish Defence Research Agency [SDRA, Swedish abbreviation FOI (ex-FOA)] and Bofors (now part of European Energetics Corporation, EURENCO) have developed FOX class of explosives and there are two main explosives under development and evaluation.

FOX-7 FOX-7 or 1,1-diamino-2,2-dinitroethylene, (DADE/DADNE) [Structure (2.57)] is manufactured on a pilot-plant scale in Sweden by the nitration of 2-methyl-4,6-pyrimidinedione with mixed acids followed by aqueous hydrolysis. The outline of the method is as follows (Scheme 2.12) where the yield is around 80%.

Its solubility is poor in common organic solvents and water but readily soluble in dipolar aprotic solvents such as dimethyl formamide (DMF), dimethyl sulfoxide (DMSO) and *N*-Methyl pyrrolidinone (NMP). It is usually recrystallized from water containing acid. It may also be recrystallized from DMF or NMP [223, 224].

It is a new interesting energetic material with a density of 1.885 g cm^{-3}, drop hammer height 72 cm (HMX-32 cm), OB same as that of HMX and performance 85% of HMX [225]. Ostmark *et al.* determined the compatibility of FOX-7 with a number of materials: binders including HTPB and GAP, isocyanate (HMDI), energetic plasticizers (K-10, Bu-NENA) and explosive such as TNT (1:1 mixture) and concluded its excellent compatibility with these materials suggesting that FOX-7 may be used in PBXs and also in TNT-based melt-cast formulations [226]. FOX-7 has also been studied for impact, friction, electrostatic discharge, shock and thermal sensitivities by Swedish and Australian researchers [227, 228] and the gist of their findings is as follows:

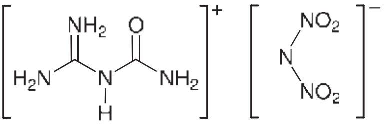
- **Impact sensitivity:** 126–159 cm for recrystallized FOX-7 compared with 38 cm for RDX [BAM Apparatus, Drop weight 2 kg).
- **Friction sensitivity:** >350 N for purified FOX-7 (RDX-120N) as recorded on a Julius Peters apparatus.
- **Electrostatic discharge sensitivity:** Ignition occurs at 4.5 J but not at 0.45 J for both FOX-7 and RDX.
- **Shock sensitivity:** Low sensitivity to shock stimuli (NOL Small Scale Gap Test)
- **Thermal sensitivity:** Temperature of ignition of FOX-7 is 215 °C as against 220 °C for RDX (Wood's metal bath). Further, excellent thermal stability is indicated by vacuum stability test for both FOX-7 as well as RDX.



Scheme 2.12 Synthesis of 1,1-Diamino-2,2-dinitroethylene (FOX-7).

It may however, be noted that these values for different parameters are influenced by purity, morphology and particle size of the sample. The calculated values of VOD for FOX-7 and RDX are 9090 ms^{-1} and 8940 ms^{-1} respectively (Cheetah Thermochemical Code). Based on these results, it was concluded that FOX-7 is better than RDX which is used as a benchmark explosive for comparison with other explosives. Consequently, it is an attractive ingredient for application in high performance IM compliant explosive formulations. FOX-7 also increases the burning-rate in propellants and as a natural consequence, is of interest for high performance propellants.

FOX-12 FOX-12 (*N*-guanylurea dinitramide, GUDN) [Structure (2.58)] is prepared by the reaction of an aqueous solution of ADN and a solution of the sulfate salt of guanylurea with 81% yield. [229]. It has a density of 1.755 $g\,cm^{-3}$ and is very insensitive (to impact as well as friction) compared with RDX. GUDN is a dinitramide with excellent thermal stability, low water solubility and no hygroscopicity. It is an excellent ingredient for gas-generating propellant compositions and finds applications in automotive safety also. GUDN could be a main component in insensitive warhead fillings with calculated performance between TNT and RDX.



Structure (2.58): *N*-Guanylurea dinitramide (GUDN/FOX-12)

These properties of FOX-7 and FOX-12 suggest that they are very promising candidates for IM and are likely replacement of RDX as warhead fillings. These explosives are also potential candidates for low-vulnerability ammunition (LOVA) propellants. It has been reported that FOX-12-based propellants are highly resistant to shaped charge attack.

2.2.26.4 **American Formulations**

Picatinny Arsenal, in association with ATK Thiokol and others, are in the process of developing PAX Series of explosive formulations and also a series of IM melt-cast explosives. They claim that the 'IM-ness' is accomplished by dispensing with TNT completely and using dinitroanisole (2,4-dinitroanisole, DNAN) which is a yellow crystalline substance at room temperature [218, 230] and has a m.p. of 94.5 °C. The formulation, PAX-35, is less sensitive but of comparable performance to Composition B (TNT-based melt-cast explosive formulation). Also under development are pressed and cast-cured IM PBXs and important example is PAX-3. BAE Holstan Army Ammunition Plant (HAAP), USA has developed PAX-34 which has the following ingredients

- 2,4-dinitroanisole (DNAN) as a TNT replacement;
- nitrotriazolone (NTO) (explosive output less than that of RDX but more insensitive than RDX);

- triaminotrinitrobenzene (TATB) (explosive output less than that of RDX but very insensitive);
- HMX.

PAX-34 has been chosen as a possible replacement for the Composition B filling as it meets the IM requirements and also can be implemented on standard melt-pour equipment.

A new insensitive, cast-cured PBX called PBXIH-135, has been developed in order to meet the requirements of US Navy's Insensitive Munitions Advanced Development Program for High Explosives (IMAD/HE). PBXIH-135 has enhanced internal blast performance, improved non-vulnerability and penetration survivability characteristics compared with PBXN-109. Thermobaric explosives are required to defeat hard and deeply buried structures. PBXIH-135 thermobaric explosive which not only offers effective blast and thermal effects, but is also extremely insensitive to factors responsible for accidental detonation during transit or storage, may also be used for this purpose.

SNPE, France, produced reduced sensitivity RDX (RS-RDX) by the Woolwich synthesis by employing a proprietary recrystallization process. This RS-RDX displayed reduced sensitivity to shock initiation. Subsequently, some other manufacturers also claimed to produce some form of RDX that exhibits reduced sensitivity to shock compared with the conventional RDX produced by the Bachmann process. EURENCO has also developed a process to mass-manufacture a variety of low sensitive Hexogen (RDX), called I-RDX.

2.2.27
Basic Lead Azide

Lead azide has been used as a detonant for many years even though it has several limitations such as high friction sensitivity, poor stability in humid atmosphere in the presence of carbon dioxide, poor flash pick-up and incompatibility with copper, brass and some plastics used in ammunition. It is also susceptible to spontaneous detonation during manufacture under certain unfavorable conditions causing damage to machinery or plant and personnel. As discussed earlier, several modifications to the method of preparation of lead azide have been investigated using colloids. Use of a nucleation technique has also been tried to modify crystals of lead azide. The main aim of these investigations has been to precipitate lead azide in a less sensitive form. However, the potential hazards of lead azide could not be eliminated. Due to non-availability of an ideal safe detonant, lead azide has been used as a detonant by enforcing strict safety measures during its manufacture, handling, filling and storage. In spite of this, accidents do take place during the use of lead azide and it must be replaced by a safe and powerful detonant which will have better thermal and hydrolytic stability in addition to other desirable characteristics. A number of researchers have attempted research on the synthesis and evaluation of new initiatory compounds to replace lead azide. Most of these pertain to metal salts of nitrophenols [231], tetrazoles [232], substituted tetrazoles and their double salts [233–236]. However, these attempts have only resulted in limited success.

The erstwhile Explosives Research and Development Laboratory (ERDL), now High Energy Materials Research Laboratory (HEMRL), Pune, had undertaken a study on primary explosives with a view to synthesizing a series of new explosives, which are safer, powerful and free from the drawbacks of lead azide and MF. As a result of these sustained efforts, HEMRL has successfully synthesized and developed a new and safer initiatory explosive called basic lead azide (BLA).

Basic lead azide is prepared by reacting aqueous solution of lead acetate containing Cepol DV and glycerine with a mixed aqueous solution of sodium hydroxide and sodium azide containing trinitrophloroglucinol (TNPG) at a suitable temperature and rate of stirring. The process of preparation of BLA has been reported in the literature [237] and has been successfully established on a pilot plant scale (2.5 kg/batch). Based on lead metal content, lead azide content and IR, BLA has been assigned the empirical formula [$3Pb(N_3)_2.2PbO$]. BLA is a crystalline, free flowing, non-hygroscopic and non-sticking material. It has a bulk density of $2.0 \pm 0.2\,g\,cm^{-3}$ and detonates high explosives efficiently. It also has a better thermal and hydrolytic stability. Its compatibility with copper is better than Service lead azide (SLA) and it has initiating value of 70 mg. A comparative account of the properties of BLA with SLA is given in Table 2.12.

It is evident that BLA is less sensitive to impact and friction than SLA. Its F of I is 65–72 which is the range for secondary high explosives and is considered safe during operations like manufacture, drying, sieving, filling, handling, transportation and storage. It has been made sensitive to flash pick-up by the addition of TNPG during manufacture and therefore, requires a smaller quantity of LS in a detonating composition which was subsequently developed to replace the composition containing SLA. Besides, BLA is in the form of round crystals and has better flow property which offers advantage during filling operations. Thus, BLA is an

Table 2.12 Comparative properties of SLA and BLA.

Sr No	Property	SLA	BLA
1	Lead azide content, % Min	95.66	66.0
2	Impact sensitivity (F of I)	9–10	65–72
3	Friction sensitivity on Julius Peters apparatus	Highly sensitive (exploded at 50 g load)	Less sensitive (did not explode even at 200 g load)
4	Explosion temperature/°C	325.0	350.0
5	Bulk density/$g\,cm^{-3}$	1.75–1.85	2 ± 0.2
6	Initiating value/mg	40–50	70.0
7	Sensitivity to flash	Poor	Good
8	Compatibility with copper and brass	Not compatible	Better compatibility

ideal detonant having less sensitivity and better thermal and hydrolytic stability. The technology for the manufacture of BLA on a pilot plant scale (2.5 kg/batch) has been successfully transferred to ordnance factories. Based on HEMRL technology, these factories are manufacturing BLA regularly on out-turn basis for the production of various detonators. Several hundred tonnes of BLA have been manufactured so far and hundreds of thousands of detonators using BLA have been produced and accepted without any difficulty.

The performance of BLA has been evaluated in both types of detonators, that is, tubular or open detonators (No. 27, 33, 36M and 78) as well as closed/fuse detonators (No. 40 mg, 80 mg, 132 mg, 400 mg, 5 gm, 8.64 gm, and 26 gm). Detonators normally contain ASA composition (LA: LS: Aluminum powder: 65.0:32.5:2.5) pressed above the base charge of high explosives. Based on the characteristics of ASA composition and properties of BLA, a composition using BLA, designated as BLASA, was formulated (BLA: LS: Aluminum powder: 80:19:1) which is used for the manufacture of different detonators. The sensitiveness to impact and friction of ASA and BLASA compositions is given in Table 2.13 which shows that BLASA composition is much less sensitive than ASA composition and therefore its use makes mixing, filling and handling operations safer. Further, BLA requires only 19 parts of LS as against 32.5 parts in ASA composition to get good flash pick-up properties.

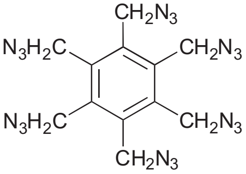
After the standardization of all filling parameters on already available filling plant for LA-based detonators, a new generation of BLA-based detonators was made and tested. The results from various proof tests were found to be satisfactory in the light of the proof schedule for these detonators. Further, a storage stability test ISAT (B) carried out for six months indicates that BLASA-filled detonators and ASA-filled detonators give comparable results and in some cases, BLASA-filled detonators give better results than SLA-filled detonators. Based on these results, a life of more than 10 years has been assigned to BLASA-filled detonators. Thus the use of BLA offers a number of advantages over SLA and also confers safety in every step involved, right from the manufacture, handling, filling, storage and thereby provides a new series of safe detonators for the Services as well as for commercial purposes.

Table 2.13 Sensitivity data for BLASA and ASA compositions.

Sr No	**Test**	**Data**	
		BLASA	**ASA**
1	Figure of Insensitiveness (F of I)	64	15
2	Friction sensitivity by J.P. Apparatus	Does not function at 300 gm but functions at 350 gm	Does not function at 150 gm but functions at 200 gm

2.2.28
Hexakis(azidomethyl) Benzene

Lead styphnate is a less powerful initiator and is used in combination with LA in detonators to increase flame sensitivity or flash pick-up of detonating compositions. It is also used in cap compositions to replace MF. However, tetrazene is required to make compositions percussion sensitive but its stability is poor in hot and humid climates, like MF. Lead styphnate is also prone to electrostatic hazards and efforts are underway to develop a substitute for LS. The US Army Armament Research and Development Command (now ARDEC) has reported synthesis of hexakis(azidomethyl) benzene (HAB) [Structure (2.59)] by the reaction of hexakis(bromomethyl) benzene and sodium azide in DMF. HAB [$C_6(CH_2N_3)_6$] in which all six positions on the benzene ring are substituted by azidomethyl groups, contains 61.8% nitrogen and belongs to the class of 'planar radial' compounds which have compact, symmetrical and disc-like structures. These features result in high m.p., good stability and low solubility in solvents. Based on the physical, thermochemical and explosive properties of HAB, it is observed that it is a thermally and hydrolytically stable material and not highly sensitive to shock, friction or electrostatic charge but is sensitive to some types of impact. Further, it shows preliminary promise for possible use as a substitute for normal LS in less-sensitive bridgewire detonators and as a substitute for tetrazene in percussion detonators, for example, M-42 primer. Its ease of ignition and a high burning rate without detonation suggest its application as an ingredient of igniter formulations also. As HAB is not sufficiently powerful to dent an aluminum witness block, it would not be suitable as a replacement for LA as an intermediate detonator charge [238].

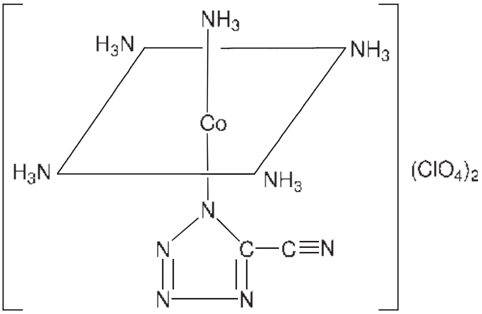


Structure (2.59): Hexakis(azidomethyl) benzene (HAB)

2.2.29
Tetraamine-cis-bis(5-nitro-2H-Tetrazolato-N^2) Cobalt (III) Perchlorate

An intensive search for explosives with the contradictory properties needed for low voltage detonators led to the discovery of a new series of explosives by Sandia Laboratories. The general chemical formula of this group of coordination compounds can be assigned as $[(NH_3)_4CO^{III}XY](ClO_4)_n$ where X and Y represent different ligands and value of n depends on electronic charges on X and Y. An explosive designated as CP, [1-(5-cyanotetrazolato) pentaamine cobalt (III) perchlorate] [Structure (2.60)] was found to be a most promising explosive, possessing a desirable combination of properties for safety and sensitivity in hot wire detonators. CP is a free-flowing gold/yellow-orange powder with loose powder density of

$0.6\,gcm^{-3}$. The explosive is slightly hygroscopic and can be easily pressed and forms a free standing pellet without a binder at densities greater than $1.2\,gcm^{-3}$. It is more thermally stable than RDX but somewhat less thermally stable than HNS with instantaneous auto-ignition temperature of 340 °C.



Structure (2.60): 1-(5-Cyanotetrazolato) pentaamine cobalt (III) perchlorate (CP)

The explosive was exhaustively characterized for thermal behavior, impact sensitivity and electrostatic discharge sensitivity etc. Based on this data, CP has been described as much less sensitive to accidental initiation than primary explosives such as LA but at the same time, initiation grows rapidly to detonation when properly confined. Its performance evaluation in a test detonator or hardware indicates that CP can replace primary explosives in many hot wire detonator applications especially if safety considerations are of prime importance [239].

CP is no longer available for hot wire applications as one of its starting materials (cyanogen) is not available due to its hazardous nature and Environmental Protection Act (EPA) restrictions. Bates [20] of RARDE reported a related compound, tetraamine-cis-bis(5-nitro-2H-tetrazolato-N^2) cobalt (III) perchlorate (BNCP) [Structure (2.61)] for this purpose in 1986. The synthesis of BNCP has been described previously [240–242] and consists of four steps:

1) Preparation of 5-aminotetrazole monohydrate (AT) by treating dicyandiamide with sodium azide in acidic medium at 65 °C.

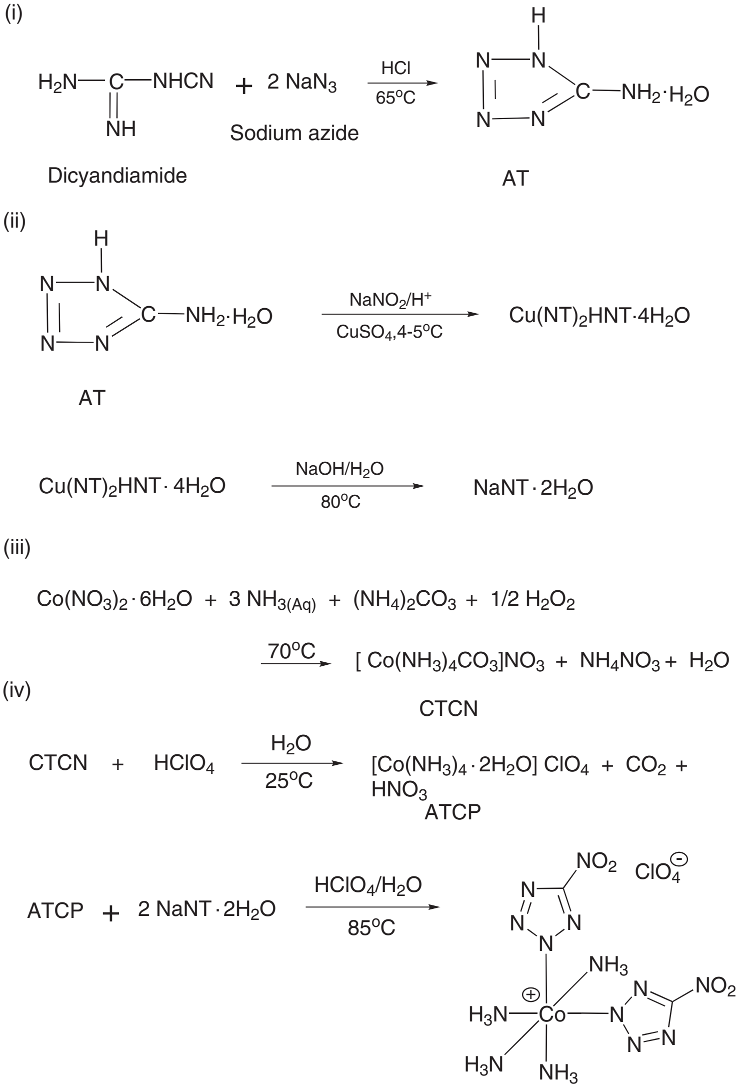
2) Preparation of sodium-5-nitrotetrazole dihydrate: The diazotization of 5-aminotetrazole monohydrate (AT) in the presence of excess of sodium nitrite and copper sulfate gives a complex cupric salt intermediate $[Cu(NT)_2 \cdot HNT \cdot 4H_2O]$ which is then converted to the sodium salt $[NaNT \cdot 2H_2O]$.

3) Synthesis of carbonato tetraamine cobalt (III) nitrate (CTCN) by Schlessinger's method [243].

4) Preparation of BNCP by acidifying CTCN with aqueous perchloric acid (3%) and then adding a solution of sodium-5-nitrotetrazole dihydrate drop by drop.

The reactions involved in the preparation of BNCP are shown in Scheme 2.13.

The crude product thus obtained is recrystallized from slightly acidified distilled water with perchloric acid (~1%). The yield is ≈75% and the product is in the form



Structure (2.61) : BNCP

Scheme 2.13 Synthesis of tetraamine-*cis*-bis(5-nitro-2H-tetrazolato-N^2) cobalt (III) perchlorate (BNCP).

of needle shaped crystals of light orange color. The structure of BNCP was assigned on the basis of elemental analysis, gravimetric analysis, electron spectroscopy for chemical analysis (ESCA) and IR spectroscopy. Some important properties of BNCP are given in Table 2.14. Also BNCP undergoes the DDT process more rapidly and in a shorter distance than CP under steel confinement [244].

Table 2.14 Some important properties of BNCP.

Properties	Observations/Data
Crystal habit	Light orange color needle-shaped crystals
Bulk density/g cm^{-3}	0.3
Volatile matter/%	0.02
Impact sensitivity (50% Height of explosion)/cm	30–34
Friction sensitivity, insensitive up to/kg	3.2
Spark sensitivity/J	5.0
Explosion temperature/°C	260.0
Velocity of detonation (at loading density of 0.6 g cm^{-3})/m s^{-1}	5700
Heat of explosion/cal g^{-1}	1053
Gas volume/cm^3 g^{-1}	739

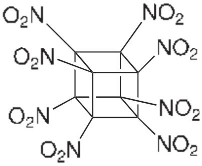
A comparison of properties of BNCP with the reported data of conventional explosives, that is, LA, LS and MF indicates that BNCP is superior to conventional primary explosives in the following respects:

- BNCP has greater explosive output;
- it undergoes DDT with less confinement and also in a shorter distance;
- is environmentally less hazardous;
- is safe in handling.

This makes BNCP safer for handling and transportation and as a result, it is likely to be a potential replacement for conventional DDT explosives. Also, it is compatible with the semi-conductor bridge. As a consequence of all these favorable properties, HEMRL and ARDE, Pune are jointly developing the use of BNCP as a DDT explosive for semi-conductor bridge (SCB)-based safe electro-explosive devices (EEDs) [245, 246].

2.2.30
Octanitrocubane

More powerful and less shock sensitive explosives are continually being sought for both military and commercial use and work on octanitrocubane (ONC) [Structure (2.62)] is a meaningful step in this direction. ONC is a nitro derivative of



Structure (2.62): Octanitrocubane (ONC) cubane (C_8H_8) which has been named appropriately as its skeleton is in the shape of a cube. ONC, the first new nitrocarbon in the last 25 years, is introduced as a potential explosive of great power. Cubane is an exceptionally dense ($1.29\,g\,cm^{-3}$) energetic molecule that has a surprisingly kinetic stability in spite of its tremendous strain energy of $161\,kcal\,mol^{-1}$. This latent strain energy in cubane is useful for increasing the performance of both explosives and solid and liquid propellants [247]. Cubane was first synthesized in 1964 at the University of Chicago [248, 249]. The measured heat of formation ($+144\,kcal\,mol^{-1}$) is remarkably close to the predicted value but this thermodynamic instability is not accompanied by kinetic instability. On the other hand, cubane and most of its derivatives are amazingly stable.

Nitration of aromatics and other unsaturated systems, that is, replacement of a hydrogen by a nitro group is considered as a classical electrophilic substitution. Such nitration is not applicable to the cubane system, which does not have any unsaturated carbons. More usually, nitro groups on saturated systems are introduced instead by functional group transformation. On the way to ONC synthesis, tetranitrocubane [TNC – an extraordinary material: stable, highly crystalline solid and m.p. 270 °C (with decomposition)], pentanitrocubane (PNC, the first polynitrocubane with adjacent nitro groups), hexanitrocubane (HNC) and heptanitrocubane (HpNC) were synthesized and characterized for structural aspects and details of their synthesis are described in the literature [250–252].

Both PNC and HNC are stable and crystalline materials of high density. Heptanitrocubane (HpNC) forms beautiful colorless crystals when its solution in fuming nitric acid is diluted with sulfuric acid. Its calculated density on the basis of single crystal X-ray analysis is $2.028\,g\,cm^{-3}$ at 21 °C (impressively high for a C, H, N, O explosive). HpNC also undergoes oxidative coupling and produces tetradecanitrobicubyl (14 nitro groups) with $1013\,kJ\ mol^{-1}$ and density $1.336\,g\,cm^{-3}$ (higher than cubane:$1.29\,g\,cm^{-3}$). Like cubane, ONC was first thought to be impossible to make and even more impossible to keep. ONC is a C-nitro explosive in which nitro groups are attached to carbon similarly to TNT. That is why ONC tends to be reasonably shock-stable or shock insensitive on the basis of analogy with TNT.

Octanitrocubane (ONC) is a white solid, somewhat soluble in hexane and readily soluble in polar organic solvents. The density of one of the ONC polymorphs is very high ($1.979\,g\,cm^{-3}$) but is still lower than the calculated value (the latest and most sophisticated calculation predicts a density above $2.1\,g\,cm^{-3}$ for the most stable polymorph of ONC) which indicates the existence of a crystal form of ONC much more dense than that synthesized. Kamlet–Jacobs equations predicted that ONC is 15–30% better than HMX [109] (a most powerful currently employed military explosive) and 6% better (perhaps also less shock sensitive) than the recently discovered explosive HNIW [121, 253–258] or CL-20 as shown in Table 2.15. It is interesting to note that both HpNC and ONC have decomposition points well above 200 °C and are not detonated by hammer blows.

NASA Lewis I_{sp} calculations show that the performance of HTPB/AP and HTPB/AP/Al propellants increases on substitution of HTPB polymer by cubane

Table 2.15 Estimated properties of some well-known explosives vis-à-vis ONC.

Compound	Density/g cm^{-3}	Oxygen balance/%	Detonation velocity/m s^{-1}	Detonation pressure/kbar
TNT	1.6	−74	7000	190
RDX	1.8	−22	8800	338
HMX	1.9	−22	9100	390
HNB	2.0	0	9400	406
CL-20	2.0	−11	9400	420
ONC	2.1	0	10100	500

[259, 260]. ONC has a ‘perfect’ oxygen balance and its complete detonation produces eight molecules of carbon dioxide and four of dinitrogen. As ONC has no hydrogen, no water is formed when it burns and therefore, when used in propellants such zero-hydrogen compounds, leaves little or no visible smoke (steam) in the plume behind the rockets or missiles and as a result, it is difficult to track such ‘low-signature’ rockets or missiles. This property of ONC is considered of strategic importance in the present scenario.

At present, HpNC is significantly easier to make than ONC, which is an expensive explosive and also difficult to make. Research is now focused on finding an economical synthetic route and to make it directly by tetramerization of dinitroacetylene (a compound not yet known). By exploiting the property of TNC (of highly acidic nature) and use of interfacial nitration, TNC is converted to PNC [261]. Acetylene (parent hydrocarbon of dinitroacetylene and a cheap starting material available in abundance) is acidic in nature and therefore, it is speculated that acetylene may be converted to dinitroacetylene by following the approach of conversion of TNC to PNC, followed by its tetramerization resulting in the formation of ONC.

2.2.31
Nickel Hydrazine Nitrate

The detonator is considered as the first fire-device of key importance in any explosive train and contains a small quantity of a very sensitive explosive as a means of initiation of inorganic salts of weak acids, that is, MF, LA and LS. However, they all suffer from some shortcoming and are not eco-friendly. In order to overcome these shortcomings of the existing initiatories, use of nickel hydrazine nitrate (NHN) [$\{Ni(N_2H_4)_3\}$ $(NO_3)_2$], which has better storage stability and is also eco-friendly, has been reported in the literature [262, 263].

Pai Vernekar and Patil [264] and Shanguan *et al.* [265] reported synthesis and characterization of NHN. Its important attributes are: (i) easily prepared from cheap and readily available raw materials; (ii) hydrolytically and thermally stable; (iii) less sensitive to impact ($h_{50\%}$: 84 cm), friction (insensitive up to 10 N) and electrostatic discharge but at the same time, sensitive to flash, flame and hot wire;

(iv) undergoes detonation in open conditions; (v) yields large volume of high pressure gas; and (vi) its explosivity (VOD: 7000 ms^{-1}) lies between those of primary and secondary explosives. In a nutshell, all these characteristics qualify NHN for use as a primary explosive in detonators and it can be used in place of LA without compromising on performance [244, 266, 267]. Two groups of scientists are vigorously pursuing research on NHN-based detonators in India: the Vikram Sarabhai Space Centre (VSSC): 1A/1W rating detonators with simple design and construction; and the Defence Research and Development Organization (DRDO): tubular detonators No. 27 and 33. It is expected that NHN-based detonators will be available in near future for bulk use in place of LA/SLA/BLA-based detonators [268–270]. As a consequence, it will enhance safety during handling (manufacturing and processing), transportation and storage.

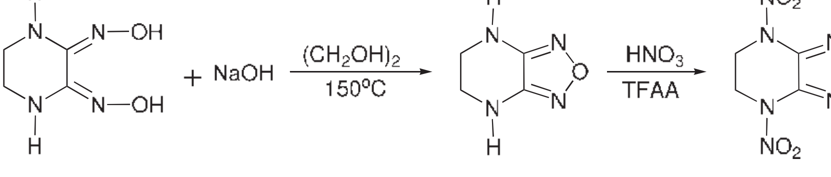
2.2.32
Furazan-, Furoxan- and Tetrazine-Based Explosives

A new area of research and activity in recent years is the development of new explosives based on furazans, furoxans and tetrazines in order to achieve an increase in density, stability, insensitivity and velocity of detonation. As a result, a number of prospective HEMs which are potential ingredients of explosive, propellant and pyrotechnic formulations have been synthesized.

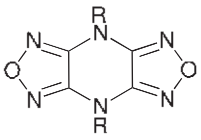
The explosive, 1,4-dinitrofurazano [3,4b] piperazine has been prepared from the piperazine dionedioxime by dehydration to the furazan followed by nitration (Scheme 2.14) [271].

The compound has density, VOD, detonation pressure and specific impulse similar to RDX. The insensitiveness of the compound [impact sensitivity: 162 cm (12.5 kg. wt.)] coupled with high I_{sp} renders it excellent for propellants.

Subsequently, Tselinskii *et al.* found the dianion of Compound 2a to be stable and reacted it with a variety of electrophiles including picryl chloride, acetic anhydride, methyl iodide and vinyl ketone. They synthesized its dinitro derivative, dinitrodifurazano piperazine (2b) (DNDFP) [Structure (2.63)] by reacting the dianion (2a) with nitrogen oxide in CH_3CN. The dinitro derivative which is quite reactive, was isolated by column chromatography and confirmed by mass spectroscopy [272].



Scheme 2.14 Synthesis of 1,4-dinitrofurazano [3,4b] piperazine.

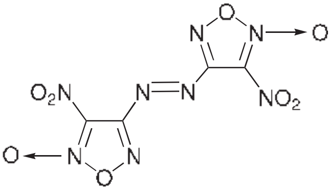


2a : R=H; 2b : R= NO$_2$

Structure (2.63): Dinitrodifurazano piperazine (DNDFP)

The predicted properties of Compound 2b are density 2.00 g cm^{-3}, VOD 9700 ms^{-1}, detonation pressure 450 kbar and specific impulse 266 s (HMX 263 s) [273].

The introduction of explosophoric groups into furazan and furoxan rings allows higher density and energetics. One very interesting furoxan-based HEM is 4,4′-dinitro-3,3′-diazenofuroxan (DNAF/DDF) [Structure (2.64)] which was obtained by using step-wise transformation of functional groups in 4-amino-3-azido carbonyl furoxan at the Zelinsky Institute of Organic Chemistry (ZIOC) [274]. The VOD determined experimentally by extrapolation of data on pressed samples was reported to be ≈10 000 ms^{-1} for a single crystal density of 2.00 gcm^{-3}. The high density value is caused by both the high molecular packing rearrangement and the high packing coefficient of this compound. However, the value of DDF/DNAF compared with CL-20 and ONC needs to be verified in view of its low decomposition temperature (127–128 °C) and particularly high impact sensitivity.



Structure (2.64): 4,4′-Dinitro-3,3′-diazenofuroxan (DNAF/DDF)

Chavez and Hiskey continued their research on 1,2,4,5-tetrazine-based explosives and synthesized a number of derivatives which are considered interesting as propellant or smoke-free pyrotechnic ingredients because of their low carbon content, high heat of formation and a density of ≈1.61 g cm^{-3}. One such compound is 3,6-dihydrazino-1,2,4,5-tetrazine which appears to be an important energetic fuel [275, 276].

2.2.33
High Nitrogen Content-High Energy Materials

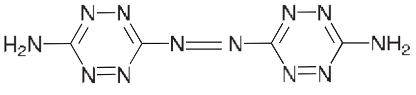
High nitrogen content–high energy materials (HNC–HEMs) are becoming a focal point of research in the area of advanced HEMs aimed at future defense and space applications [277–279]. The high energy content of HEMs stems from the presence of adjacent nitrogen atoms poised to liberate nitrogen gas. Such transformations are accompanied by the enormous energy release due to the large difference in the average energies of N–N (160 kJmol^{-1}) and N=N (418 kJmol^{-1}) bonds compared with the average energy of the triple N≡N bond (954 kJmol^{-1}). As a consequence of their chemical structures, HNC–HEMs also generate a large volume of nitrogen gas (N_2) per gram of HEM projecting them as a possible material for clean gas generators.

The research in this direction commenced with the studies on materials from the class of azotetrazolates and tetrazines that can be relatively easily isolated [280–284]. The high potential of some nitrogen-rich compounds such as diamino azobistetrazine (DAATz) [Structure (2.65)] [280], 1,4-dihydrazino tetrazine (DHTz) [Structure (2.66)] [281] and azotetrazolate salts [Structure (2.67)] [282–284] has been reported in the literature. The structures of these compounds are shown in Figure 2.4.

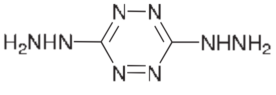
DAATz, having a high positive heat of formation (1032 kJ mol^{-1}), is considered a potential HEM to be used in rocket propellant and IHE formulations. On the other hand, DHTz may find application as an eco-friendly smoke ingredient in pyrotechnic formulations for special applications. As regards tetrazolates, the triaminoguanidinium salt having a heat of formation equal to 560 kJmol^{-1} and reasonable sensitivity characteristics, these salts compete with DAATz.

Los Alamos National Laboratory, USA also prepared three unique high nitrogen content-HEMs (a new and relatively unexplored class of energetic materials): ammonium azotetrazolate (AAT) [Structure (2.68)], guanidinium azotetrazolate (GAT) [Structure (2.69)] and triaminoguanidinium azotetrazolate (TAGAT) [Structure (2.70)] [282]. The structures of these compounds are given in Figure 2.5.

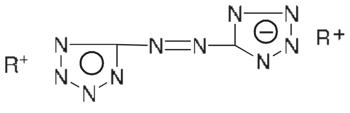
A comparative account of the properties of AAT, GAT and TAGAT is given in Table 2.16. The unique properties of these materials allow their use as ingredients in gas generants, low signature propellants and pyrotechnics. Ammonium and triaminoguanidinium salts appear to be suitable for use in propellants. The composite propellants based on these HEMs are expected to give comparable performance on replacement for HMX. At the same time, the combustion products consist of cooler, less reactive and less visible gases. On the other hand, the



Structure (2.65) : DAATz



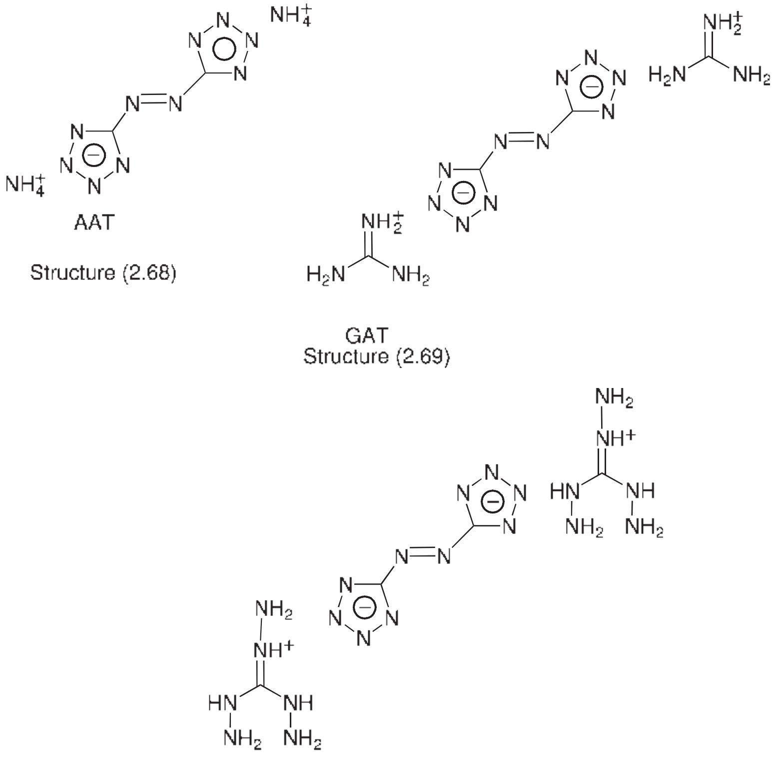
Structure (2.66) : DHTz



Azotetrazolate salts
Structure (2.67)

R$^+$: Na$^+$,NH$_4^+$,Guanidinium
Triaminoguanidinium,Hydrazinium

Figure 2.4 Some high nitrogen content–high energy materials (HNC-HEMs).



AAT

Structure (2.68)

GAT

Structure (2.69)

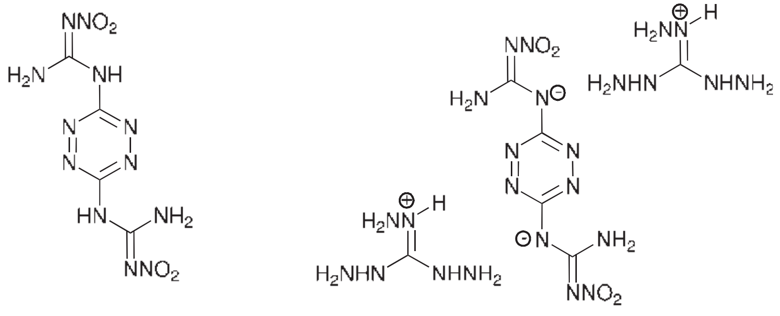
TAGAT

Structure (2.70)

Figure 2.5 Structures of AAT, GAT and TAGAT.

Table 2.16 Various properties of AAT, TAGAT and GAT.

Properties	**AAT**	**TAGAT**	**GAT**
Density/g cm^{-3}	1.53	1.602	1.538
Heat of formation/kcal mol^{-1}	+106.1	+257.0	+98.0
Spark sensitivity/J	0.18	–	–
Impact sensitivity, Cm (Type 12) (HMX = 25)	21.4	25.0	>320.0
Vacuum stability/ml g^{-1} (for 48 h at 100 °C)	0.54	0.25	0.21
Friction sensitivity (BAM)/kg	4.4	8.4	Not sensitive up to 36 kg
DTA exotherm/°C	190	195	240
Calc. detonation velocity/m s^{-1}	7600	9050	7100
Calc. detonation pressure/GPa	187	292	155



Structure (2.71) Structure (2.72)

Figure 2.6 Structures of some nitroguanyl tetrazines.

guanidium salt has been explored as a replacement of sodium azide in safety equipment without any problems associated with the use of sodium azide (toxicity and formation of sodium hydroxide).

At Los Alamos National Laboratory, USA, Chavez *et al.* still continue their work on the development and discovery of new high nitrogen content-HEMs for various applications [281, 285–287] and recently reported the preparation of several novel nitroguanyl-substituted tetrazines including 3,6-bis(nitroguanyl)-1,2,4,5-tetrazine [Structure (2.71)] and bis (triaminoguanidinium) salt [Structure (2.72)] as shown in Figure 2.6.

These compounds exhibit very low pressure-dependence during combustion and the compound [3,6-bis(nitroguanyl)-1,2,4,5-tetrazine] in particular, shows the lowest pressure exponent known in the literature for a neat material. Further, the interesting combustion behavior of these explosives make them suitable for gas-generating and propellant applications [288].

2.2.34
Fuel-Air Explosives

The first recorded dust explosion occurred when a bakery storeroom exploded in a small city called Turin (Italy) way back in 1785. Such an explosion is also labeled as ‘thermobaric’, a chemical reaction that produces extremely high pressure and heat very rapidly. In the early 1960s, scientists began experimenting with this concept to produce a weapon that uses the same principle, but employs volatile gases and finely powered explosives.

Molecular high explosives which have been in use for a long time, generate fast decaying blast waves of high peak pressure with very short duration. Efforts to develop new explosives for generating higher impulse blast led to the development of metalized explosives like Tritonal, Torpex etc. Further advancement in this field is the development of fuel-air explosives (FAEs), which are explosive mixtures of fuel dispersed in air, which can be detonated. Since most of the oxygen needed for combustion comes from the air, it is sufficient for FAE weapons to carry only fuel. Therefore, higher destructive efficiency is achieved compared with that of conventional high explosives. According to Smith *et al.* [289, 290], a typical ethylene oxide (EO)-based FAE has a TNT equivalent 2.7–5.0, that is, one kg of EO is equivalent to the blast effect of 2.7–5.0 kg of TNT. FAEs are fuel aerosols formed in air by the dispersion of certain hydrocarbons and hydrocarbon oxides like hexane, heptane, EO and propylene oxide (PO) etc. The aerosols can be detonated over a wide range of fuel concentrations in air and yield very high impulse blasts compared with that of conventional HEs of the same weight. This is due to higher 'heat of combustion' and greater specific volume of FAE (heat of combustion and specific volume of EO are 6 and 800 times respectively greater than that of TNT). As an FAE is in aerosol form, its effect is not restricted by land contour or protective structures and as a result, covers a larger area They are also weight efficient as they take oxygen from atmosphere for detonation, unlike high explosives which carry their own oxygen. These advantages led to the development of several FAE-based weapons for military applications by various countries. Oxygen/air mixtures of a number of hydrocarbons and their oxides have been studied by many investigators. However, only methane, EO, PO and a mixture of methylacetylene, propadiene and propane (MAPP) found use in military applications.

The concept of FAEs is very simple. The two-part warhead first detonates forming an aerosol cloud which is then detonated and consumes oxygen from the surrounding area. This lack of oxygen creates an enormous overpressure, which is primarily responsible for destroying residential structures targeted by this weapon. Russians describe FAEs as 'vacuum bombs'. FAEs can have the effect of a tactical nuclear weapon without the residual radiation [291]. Bunkers, buildings and other fortifications that are not hermetically sealed are also subjected to the lethal force of FAEs as the fuel-air mixture flows easily into these cavities and when detonated, amplifies destruction of the load-bearing components of the structures. This type of blast can also be used to clear minefields, prepare and clear landing zones for helicopters and as a herbicide, destroying crops and vegetation.

America used FAEs in Vietnam to clear jungle foliage, destroy Viet Cong tunnels, and to clear heavily-wooded sites for helicopter landing zones. The Russians first used FAE weapons in early 1980s during the Soviet–Afghan War and then in the war with Chechnya. These weapons were also used by Americans during 'Desert Storm' operations in the Middle East [292].

Ethylene oxide is an important fuel for FAEs and has proved its potential as one of the best fuels for them. It has wide explosive limits and low boiling point (10.5 °C) which facilitates its vaporization faster at room temperature and results in the formation of a cloud with air which is detonated. However, EO has a tendency to polymerize during storage thereby decreasing its shelf-life as well as the performance of EO-based weapons. The phenomenon of polymerization of EO, effect of temperature and materials of construction of weapons on polymerization and retardation of EO polymerization by the addition of well-known anti-oxidants have been studied by Agrawal *et al.* [293]. The addition of anti-oxidants retards EO polymerization and enhances the shelf-life of EO but does not meet the requirements of the Services, stipulating a shelf-life of minimum 10 years for weapons. The USA has developed weapons based on FAEs where EO is used as a fuel. The Gulf War also witnessed the use of FAEs on a large scale [294].

Present day missions need explosives which are more powerful than well-proven nitramines, that is, RDX/HMX but at the same time, they should be safe to handle, compatible with materials of construction of weapons and insensitive to impact, friction and shock. Fuel-air explosives meet these criteria. They are highly effective against soft targets like light vehicles, tanks, trenches, bunkers and anti-tank mines. Selection of fuel for FAE munitions mainly depends on the requirements. In general, the fuel must have a wide range of explosive limits in air, high sensitivity to detonation, sufficient damage potential and good storage stability. Ethylene oxide which was initially used in FAE warheads in the USA, has been subsequently replaced by PO to overcome the storage-related problems. Heptane with 20% normal propyl nitrate forms detonatable mixtures with air in a wide range of concentrations and covers a larger area compared with propylene oxide. This mixture has a higher 'heat of combustion' and produces higher blast effectiveness. This combination is considered to be a fuel for future FAE munitions [295].

Fuel-air explosion is presently a two-event process viz. dispersion of fuel in air resulting in the formation of a fuel-air cloud, followed by its detonation. The current emphasis is to make it a single event process with the elimination of second event. In a single event process, fuel and an initiating chemical (catalyst) are dispersed simultaneously to form a vapor cloud. The catalyst reacting with either fuel or oxygen in air produces free radicals to initiate the explosive mixture. Several investigators [296, 297] have achieved success with the concept of single event FAEs. Injection of a gaseous pyrophoric fuel (dimethyl zinc etc.) in an equimolar oxy-acetylene mixture has been reported to initiate detonation in the mixture. Current efforts are under way to achieve more detailed qualitative/quantitative data of this phenomenon.

The USA has been working in this field since 1960 and has developed a number of FAE-based weapons such as 500 lb CBU-55 B Cluster Bomb and SLUFAE rocket system for mine breaching. Their work included studies at simulated high altitudes and under water for application in anti-ballistic missiles, anti-ship missiles etc. and also for replacement of nuclear warheads. FAE has also been used as a blast simulator for small yield nuclear weapons. Though USSR has been reported to have a large arsenal of FAE weapons, little information is available in the open literature. Some reports suggest that the Russians are now working on their third generation of thermobaric weapons after developing over 14 weapons to deliver these munitions.

The US Navy began development of thermobaric explosives in the late 1980s responding to the need for internal blast explosives to defeat hard and deeply buried structures as evidenced during operation 'Desert Storm' and developed PBXIH-135 thermobaric explosive which not only offers effective blast and thermal effects but is also extremely insensitive to factors that may cause accidental detonation during transit or storage. The secret of PBXIH-135 is the addition of a precise mixture of aluminum powder which burns in the hot gases and as a result, burning aluminum sends heat and pressure bounding through corridors.

2.3
Future Scope for Research

High explosives are chosen for intended applications in the light of their special properties. The problem of development of an explosive meeting contradictory requirements – high performance and high insensitivity, is very difficult and is still open for further research in order to find an ideal explosive combining contradictory properties. Research in this field has a tremendous scope and is being pursued all over the world. The explosives and propellants are likely to enjoy continued incremental improvements in compatibility, stability, energy and density to the extent where these materials are safer and superior. The future of research in propulsion and ordnance technology holds many possibilities and further research is likely to be on the following lines.

2.3.1
High Performance, Thermally Stable and Insensitive Explosives

The main objective for high performance applications is to pack as much energy as possible into a minimum space. Based on computer simulations, high energy, and at the same time, high density target explosives have been defined. High densities can be achieved if the molecular structure contains fused ring systems. Energy can be brought into the system by strained rings and nitro or nitramine groups are responsible for an appropriate oxygen balance and nitrogen content. Keeping in view these facts, target molecules such as HNIW or CL-20, now available on a pilot plant scale and ONC available on a laboratory scale, will be manufactured in large quantities to replace HMX in the next generation of munitions. Once researchers are able to bring down the cost of CL-20 either with the use of cheap starting materials or alternate production processes, HMX will be replaced by CL-20. Similarly, an alternate route for ONC (Acetylene → dinitroacetylene → ONC by tetramerization) is being explored and once it is successful, ONC is likely to be available for bulk use. Based on computer calculations, octaazacubane (OAC) has been predicted to have a density of $2.69\,\mathrm{g\,cm^{-3}}$ and VOD of about $15\,000\,\mathrm{ms^{-1}}$, far more than the most powerful high explosive known today, that is, CL-20. Similarly for thermally stable and impact insensitive explosives, TATB is a benchmark explosive and any explosive better than TATB may bring technological revolution in the field of thermally stable explosives and allied devices. BTDAONAB which has been recently reported, does not melt up to 550 °C and appears to be promising but needs scaling-up, detailed characterization and evaluation. Similarly, impact, friction and shock insensitive explosives hold great potential for IMs.

As discussed earlier, nitro explosives with an SF_5 group possess improved properties – increased density, greatly reduced impact sensitivity and good thermal stability with respect to similar explosives without SF_5 groups. Some work commenced in this field in the USA in the late 1980s and early 1990s but subsequently, there have been no efforts in this direction. However, there is a lot of scope in this area and it needs further exploration.

2.3.2
Melt-Castable Explosives

Russians have recently reported that the introduction of a nitrofurazanyl (Nif) moiety in explosives results in better performance in terms of density, VOD and detonation pressure. In addition, it brings down the melting point of explosives. By following this approach, preparation of melt-castable explosives may also be explored. Similarly, introduction of pentafluorosulfonyl (SF_5) group or groups in nitro explosives which results in explosives with improved properties and lower melting points as reported by Americans in early 1990s also needs further investigation.

2.3.3
Energetic Binders and Plasticizers

A number of new binders such as GAP, NHTPB, poly(NiMMO), poly(GlyN) etc. and energetic plasticizers such as butyl-NENA, BDNP A/F, BTTN, TEGDN, MTN/TMETN, K-10 etc. have been developed and used as experimental materials. HEMs community has reached a saturation level in terms of performance of explosive and propellant formulations with the use of conventional binders and plasticizers. As a consequence, use of such energetic binders and plasticizers needs promotion after resolving problems associated with materials synthesis, production and processing techniques. Fluoropolymers as binders and plasticizers with fluoroamino groups have great potential in the explosive and propellant industry as they also release energy due to the formation of HF during the detonation/combustion of fluorobinders or fluoroplasticizers. Research should also continue in this area in order to make newer energetic binders and plasticizers available for this purpose.

2.3.4
Particle Size of Explosives

Apart from the viscosity of binders, solids loading (explosive and metal powder) in a binder for making grains by casting technique also depends on their particle size and shape. As a rule of thumb, solids loading is high with coarse explosives whereas it is low with fine explosives. In order to achieve maximum solids loading, particle size is carefully controlled and bi- and tri-modal mixtures of different particle sizes are used. In this way, maximum packing density is achieved with smaller particles packing the interstices between larger ones. As regards the shape of explosive particles, introduction of spheroidized explosive/oxidizer into the formulations reduces their viscosity, resulting in a higher solids loading.

Experience with explosives such as DATB, TATB, PYX, etc. suggests that the synthesis of explosives with coarse particles may prove to be a real bottleneck and no ready-made solution to this problem is available as there are no standard methods to increase particle size. The parameters reported to affect particle size are: (i) concentration of precipitating solutions; (ii) temperature of precipitating solutions; (iii) rate of cooling of solutions; (iv) material of construction of stirrer; and (v) rotation rate of stirrer [298]. By varying one parameter at a time, the effect of each of them on particle size can be determined and thus parameters may be established to increase the particle size of an explosive. However, this requires an in-depth study by a team of synthetic chemists and chemical engineers. Further, with the advent of science and technology of nanomaterials, some HEMs researchers have already directed their capabilities to develop nano-sized explosives, metallic fuels and metallic oxides etc. The available data in this regard indicate that explosive and propellant formulations with the use of nano-sized explosives or oxidizers and metal powders have manifold improved performance compared with conventional materials. The aspects such as size enlargement, size reduction (including nanoparticles) and crystallization etc. have recently been discussed in a comprehensive manner and reported in the literature [299].

2.3.5
Eco-Friendly Production Processes and Explosives

Lead is present in most of the primary explosives and thus use of such primary explosives results in corresponding adverse environmental impact. Therefore, development of lead-free primary explosives is an important area of research. Several new explosives such as 1,3,5-triazido-2,4,6-trinitrobenzene (TATNB) and 1,4-diformal-2,3,5,6-tetranitratopiperazine (a new primary explosive based on glyoxal) [300] have been developed for use in lead-free primary compositions. But they have their own limitations. For example, TATNB undergoes decomposition reactions over a period of time which results in loss of its initiating power. One such molecule which has succeeded in all preliminary trials is nickel hydrazine nitrate (NHN) which holds a tremendous potential in future. However, life assessment trials are considered essential before it is accepted for regular use. Another approach to obtain lead-free primers is to substitute lead by other less toxic metals. Silver azide or silver fulminate have good initiation capability but their sensitivity and cost make their commercial use impossible. In spite of all these efforts to substitute lead in primary explosive compositions, a real breakthrough has not been achieved as yet.

The manufacture of explosives with the use of conventional nitrating agents is not considered eco-friendly as a large amount of spent acid is generated in the end. The N_2O_5 methodology of nitration invented and perfected by the UK scientists, appears to be a good option as explosives with $-ONO_2$, $-N-NO_2$ and $-C-NO_2$ linkages are synthesized in higher yields and better purity in addition to eco-friendliness of the process. Therefore, there is a need to discard old nitrating agents in favor of N_2O_5 in order to derive the fruits of this new technology.

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3
Processing and Assessment Techniques for Explosives

A large number of explosives are already available for use. However, selection of an explosive is made in the light of its stability, reliability, safety, application and mission requirements. At the time of development of a new explosive, it is essential to keep in mind factors such as indigenous availability of starting materials, ease of method of preparation, purity of explosive and its cost, in addition to its impact on the environment and potential for demilitarization. In this Chapter the following aspects of explosives will be discussed:

- processing techniques for explosives;
- formulation of explosives;
- experimental assessment of explosives.

3.1
Processing Techniques for Explosives

The technique used to fill an explosive formulation into its casing usually depends on the physical properties of the formulation, and therefore no single technique is suitable for all types of formulations [1, 2]. Filling is generally performed through casting, extruding or pressing. The filling process and final integrity of the charge is often critical for the vulnerability of the resulting charge to accidental stimuli. Cracks, micropores and de-bonding from the casing each increases its sensitivity and also affects its performance. Melt-cast formulations and some thermoplastic-based formulations can be recast if the quality of filling is unsatisfactory, but cured plastic bonded explosives (PBXs) cannot be reprocessed.

The density of explosive fillings contained in munitions should be as close as possible to the theoretical maximum density (TMD) of formulations, which is calculated from the crystal densities of ingredients of an explosive formulation, taking into account their relative proportions. The density of a formulation directly affects its performance as is shown by an empirical relationship (Equation 3.1):

$$P_{CJ} = 1/4\,.\,\rho D^2 \tag{3.1}$$

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where P_{CJ} = detonation pressure
ρ = density of formulation
D = velocity of detonation.

Processing of an explosive is performed by one of the following techniques depending upon the caliber of weapon, particle size of the explosive and quantity involved. The general outlines of the processing techniques are given here.

3.1.1
Casting

Processing of explosives through casting techniques is done in the following manner.

3.1.1.1 Melt-casting

RDX/TNT formulations are melt-cast although the process is not as simple as it sounds. Pure TNT melts at 80.4 °C, much lower than its decomposition temperature, 300 °C, and therefore it can be safely melted using steam heating. RDX or HMX is first incorporated into the molten TNT. Viscosity considerations limit the solids content of TNT slurries to about 75% which can be increased by casting under vacuum. TNT contracts by about 11–12% on cooling and results in cracking and de-bonding. In order to prevent cracking and de-bonding, controlled cooling processes as in the case of the 'Meissner Process' are employed. The explosive cools from the casing inwards and from the base upwards, aided by a steam-heated pipe which is gradually withdrawn [3]. As solidification occurs, more molten RDX/TNT is added from a header. Sometimes, alkylated polyvinyl pyrrolidones are also used as emulsifying agents in order to improve the quality of castings [4]. For some fillings, a small amount of hexanitrostilbene (HNS) is also added to the TNT in order to provide nucleation sites to TNT. This is very effective in improving the physical integrity and strength of the charge. In order to ensure that RDX/TNT fillings do not contain serious flaws, they are X-rayed as a part of quality control and quality assurance. Once these are fully solidified and dimensionally stable, they are machined if required.

So far TNT has been the only explosive that can be converted into liquid at a low temperature (80.4 °C) and is stable in the molten condition for relatively long periods. Further, it is not affected by the surrounding temperatures and as a result, TNT is preferred as a casting medium. But, at the same time, the disadvantage with TNT is that it shrinks to the extent of 11–12% (by volume) on solidification, giving rise to a wide range of defects. With the advent of a number of new high energy materials (HEMs) in the recent past [5], a new class of explosives known as 'melt-castable explosives' has taken shape and important members of this class are Tris-X and Methyl Tris-X [6], 1,3,3-trinitroazetidine (TNAZ) [7–10] and 4,4′-dinitro-3,3′-bifurazan (DNBF) [11].The data on various properties of TNAZ and preliminary evaluation trials suggest that it has a high potential to replace TNT in view of its better performance [12].

3.1.1.2 **Normal Casting**

To overcome the shortcomings of RDX/TNT formulations, PBXs have been developed which will replace melt-cast explosive formulations in the near future and also provide greater performance together with reduced sensitivity. PBXs generally contain a high percentage (>80%) of particulate high explosive, usually nitramines RDX and HMX. The explosive content is limited by the viscosity of formulation during processing and filling. In order to achieve the highest possible percentage of explosive (by weight) in the formulation, the particle size of explosive is carefully controlled and bi- and tri-modal mixtures of different particle sizes are used. In this way, the highest packing density is achieved with smaller particles packing the interstices between larger ones. Research on the morphology of crystals indicates that spheroid crystals flow better than angular normal crystals and as a result, the viscosity of the mixture during processing is reduced and correspondingly, the percentage of nitramine increased.

Liquid polymers such as HTPB, GAP, poly(NiMMO) and poly(GlyN) etc. are used as binders while explosives such as RDX, HMX and CL-20 etc. are used as fillers for PBXs. The explosive is mixed with a binder (for example hydroxy-terminated polybutadiene, HTPB) which may be crosslinked with a diisocyanate to provide a cured and dimensionally stable matrix. Casting is often performed under vacuum, and filling can also be agitated by vibration in order to remove any gas bubbles trapped in the mix. The curing times are shortened by the addition of a small amount of a catalyst or by curing the PBXs at a slightly elevated temperature. Curing time is, however, tailored to be sufficiently long in order to allow processing and filling to be completed before curing starts. Also, plasticizers such as dioctyl phthalate (DOP) are added to increase the flexibility of formulations and prevent cracking. Further, this reduces the viscosity of uncured formulations which facilitates processing and filling. However, this is likely to result in its exudation at high temperatures and during storage.

The limitations associated with the normal casting method are:

- Porosity and low density because of the presence of air pockets or cavities due to occluded air.
- Formation of axial longitudinal cavities due to volume contraction during solidification.
- Non-uniformity/non-homogeneity in the formulation.
- Segregation or separation due to the difference in densities of ingredients such as TNT, RDX, HMX and Al powder.
- Uneven crystal sizes due to non-uniform cooling rates.
- Poor mechanical strength of the charge due to the presence of residual stresses in it.
- It is not possible to load more than 70–72% of energetic solid ingredients (RDX/HMX/Al).

Some of the limitations and defects can be minimized by adopting methods like using a header or dolly, preheating the mold or casing, hot probing, imparting vibrations, controlled cooling and adding solid biscuits of the same formulation.

This type of casting is generally adopted for large caliber blast or fragmentation type of warheads. The quality of casting is improved by introducing vibration or pressure and accordingly, normal casting is termed vibration or sedimentation casting or squeeze or pressure casting.

3.1.1.3 Vibration or Sedimentation Casting

This is suitable for the formulations in which the percentage of solid ingredients, suspended in liquid is to be increased. The advantage of density difference between the molten medium and suspended particles is used in this process. The concentration of heavier particles is increased in the lower part of the casing either by natural sedimentation or by forced sedimentation caused by vibrating the whole casting assembly. The sedimentation process is controlled by a number of parameters such as particle size of solid suspension, temperature of melt, period of sedimentation, viscosity of melt, concentration of solid ingredients and column of melt etc.

3.1.1.4 Squeeze or Pressure Casting

This is adopted where the percentage of energetic ingredients RDX/HMX is required in the range of 80–90%. In pressure casting, a pourable formulation in the ratio of 60/40 RDX/TNT or HMX/TNT is poured into a mold and pressed by a permeable piston or plunger to squeeze out molten TNT from the formulation. As a result, the pressed portion becomes rich in solid content. During this type of casting, there is uniformity in the percentage of RDX/TNT or HMX/TNT in radial direction. However, a gradation exists in the axial direction.

3.1.2
Extrusion

Not all PBXs that are extrudable can be produced by extrusion, as some extrude too slowly to be economical. In this process, the formulation is mixed and passed directly into an extruder where it is forced through a die of required size under pressure. This has the obvious advantage of allowing the process to be continuous rather than a batch process. PBXs that eventually cure should have a sufficiently long curing time in order to prevent their curing during the processing stage itself.

3.1.3
Pressing

A pressing technique is used for small caliber stores while large caliber ammunition are filled preferably by a casting technique. The advantages of pressing are greater economy, superior quality, high production rate and better dimensional control. PBXs may also be pressed, usually for higher explosive content formulations. Pressing is performed by a variety of methods: directly or incrementally with pressure applied from all directions, hydrostatically or isostatically.

3.1.3.1 **Unidirectional Pressing**

In this technique, a charge is fabricated with the application of pressure in one direction for a certain dwell time. Vacuum is applied to prevent air from being trapped in the formulation during pressing and densities approaching ≈98–99% TMD may be achieved. The pressure is released and the pellet is extracted by the movement of a ram in the same direction. Direct pressing does, however, lead to a pressing gradient in the formulation caused by its friction with the die wall. This adversely affects the performance and sensitivity of the formulation. The L/D ratio is generally limited to one in this case.

3.1.3.2 **Double Action Pressing**

This technique overcomes the drawbacks of unidirectional pressing and produces a charge of uniform density and homogeneity. In this method, the explosive formulation in the mold is compressed into position in two modes. In the first mode, pressure acts from top by the downward movement of the ram. In the second stage of pressing, the spacer is removed and the base plate moves upwards on application of pressure. Thus the formulation experiences equal pressure throughout the length. The L/D ratio is two in this case.

3.1.3.3 **Incremental Pressing**

This technique was developed to overcome the problems associated with direct pressing. In this method, the entire quantity of explosive is not pressed at one time but explosive is added and compacted incrementally until all explosive material has been pressed to the required density (Figure 3.1)

The increments should be less than the diameter of the charge each time to maximize the effect of this method. Although pressure and density gradients are reduced, they are not completely eliminated in this method and are proportional to the number and size of increments used. However, interfaces between the increments have been found to cause initiation problems in some cases.

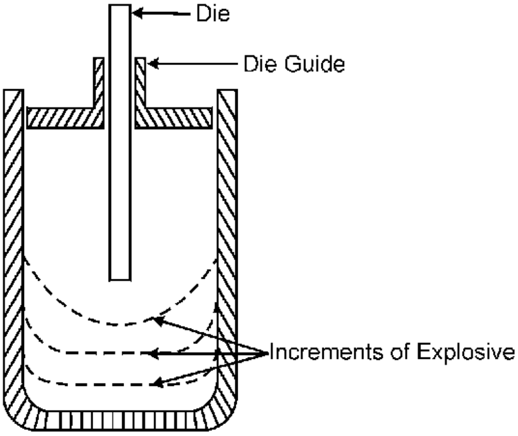


Figure 3.1 Incremental pressing technique. Based on Reference [3].

3.1.3.4 Hydrostatic Pressing

This technique is used where charge density as well as uniformity are critical and are of paramount importance. The formulation is contained in a rubber bag which is evacuated before the application of pressure to it by means of an incompressible oil (Figure 3.2) Although wall friction is eliminated, some residual pressure gradients do occur because the bag rests on the surface at one end.

3.1.3.5 Isostatic Pressing

This technique eliminates almost all pressure gradient effects found in the other techniques. This is achieved by suspending the rubber bag (containing explosive to be pressed) in the fluid so that it is not in contact with any surface while it is being compressed (Figure 3.3). Isostatic pressing is used for high-performance

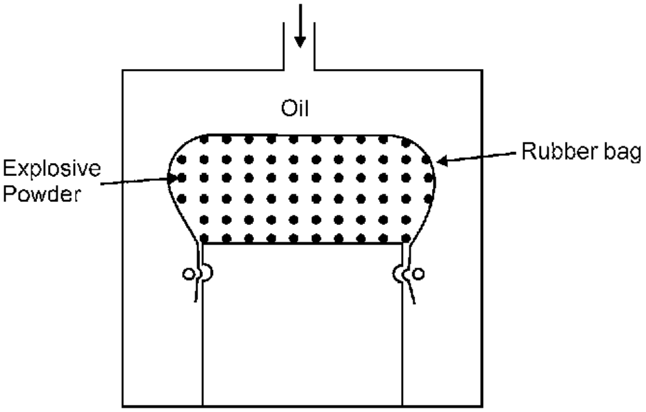


Figure 3.2 Hydrostatic pressing technique. Based on Reference [3].

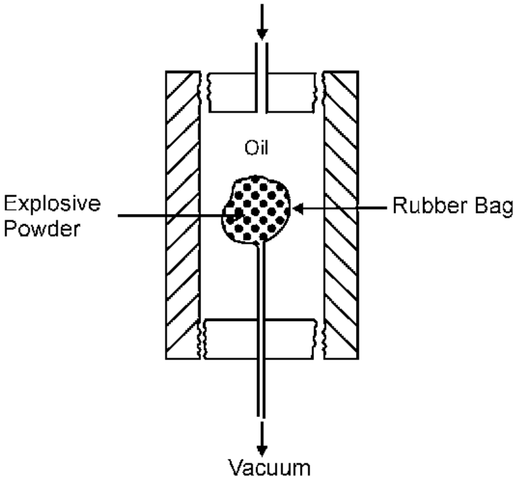


Figure 3.3 Isostatic pressing technique. Based on Reference [3].

fillings where densities greater than 99% TMD are required. It is however, relatively slow and expensive compared with other techniques and has been developed only recently for wider use in the production of PBXs.

The casting, extrusion and pressing of explosives is always done behind a shield. In production facilities, the air or hydraulic supply to the press is cut off when the shield (door) is in the open position. In some facilities, removable shields are also used. The operators work behind the shields which are placed in front of the facility.

The pressed and cast formulations can also be machined afterward if required but this is carried out remotely because of the hazards involved during the machining process. Also, the tools which are used for machining purpose should be of non-sparking type viz. made of brass or beryllium–copper alloy.

Explosives such as PETN, RDX, HMX cannot be used as such for pressing because of their sensitivity and granular nature. The sensitivity is reduced considerably to safer limits by coating them with waxes or polymers. This process is called phlegmatization. In some cases, zinc stearate, barium stearate, graphite etc. (up to 1%) are added to decrease sensitivity and at the same time, increase packing density and compression strength. The addition of graphite makes the formulations more conductive. The general method for the coating of explosives by wax or polymer is the slurry process in water or a solvent. The factors affecting the quality of the charge are: particle size of explosive, loading pressure, L/D ratio, and dwell time. Different types of warheads filled with explosive formulations and processed by different techniques are listed in Table 3.1.

Table 3.1 Various processing techniques for filling of warheads.

Type of warhead	Formulation	Processing
Natural fragmentation	Torpex RDX/TNT/Al (45/37/18)	Normal Casting
Controlled fragmentation	RDX/TNT (60/40)	Normal Casting
Pre-fragmented	HMX/TNT (70/30)	Vibration Casting
Blast-cum-fragmentation	Dentex RDX/TNT/Al (48.5/33.5/18.0)	Vibration Casting
Shaped charge	HMX/TNT (85/15)	Pressure Casting
Shaped charge	RDX/Wax (95/5)	Pressing (single action)
Shaped charge	HMX/Wax (95/5)	Pressing (double action)

Any explosive consisting of fine particles will not have a uniform coating of binder. Furthermore, if it is processed by the casting technique, explosive loading is poor, resulting in poor performance. High explosive loading is possible with an explosive consisting of a multimodal particle size distribution. Crystal size of an explosive and crystal perfection are likely to affect many factors such as decomposition, deflagration, deflagration-to-detonation transition (DDT), strength, sensitivity, etc. Research on crystal size, shape, morphology, perfection, defects etc. are regarded as the key factors in the optimization of loading of solids or explosives while processing them.

3.2
Formulation Fundamentals

The formulation of explosive compositions is governed by a number of considerations including performance, safety, physical and chemical properties, ease of processing and cost. Performance is considered to be critical and should be close to the maximum currently available for that type of munition. Since the hazard response of a formulation to accidental stimuli is also of paramount importance; there is no point in having a most advanced munition in terms of performance if it is too sensitive to be safely deployed. The physical and chemical properties should be sufficient to maintain dimensional and chemical stability of a formulation over a relatively long period of time. Processing should be as simple, safe and cheap as possible and lastly, though by no means of lesser importance, the cost of formulation has to be considered, especially for an explosive that may be produced in large quantities.

3.2.1
Current Formulations

In the earlier part of the twentieth century, a high explosive such as picric acid was used as the main charge filling on its own. This filling was subsequently discarded because of its unacceptable risk through its tendency to form impact-sensitive metal salts (metal picrates) after its contact with shell walls. The nitramines and nitrate esters are certainly too sensitive to be used on their own and require desensitization by means of some binder (non-energetic such as some polymers or energetic one such as TNT) capable of absorbing energy applied accidentally.

Most of the current in-service munitions have melt-cast, TNT-based explosive fillings which, while offering reasonable performance, have a number of drawbacks and as a result are becoming increasingly unacceptable. RDX/TNT or HMX/TNT fillings require careful processing techniques; the formulation cannot just be melted and cast as the name suggests. The temperature of the process is carefully controlled to prevent contraction and crack formation. These types of fillings that are in use are susceptible to rough handling and exhibit a relatively high sensitivity

Table 3.2 Some typical HE formulations and their performance parameters.

Explosive	Formulation	Density/g cm^{-3}	VOD/m s^{-1}	Detonation pressure/kbar
Composition B	RDX/TNT/WAX (59.5/39.5/1)	1.73	7920	292
Composition B–3	RDX/TNT (60/40)	1.72	7900	287
Composition A–3	RDX/Wax (91/9)	1.63	8180	300
Octol	HMX/TNT (76/24)	1.81	8480	343

to accidental impact. The low-temperature sensitivity of the fillings is also poor due to low modulus of elasticity. In addition, maximum performance of these fillings has already been achieved since they consist of 100% high explosives, that is, RDX/HMX and TNT. However, every percent of TNT decreases the performance of filling with respect to a total nitramine content and thus alternatives to these formulations have to be developed as increased performance is always required. Some typical HE formulations along with their performance are listed in Table 3.2.

3.2.2
Aluminized Explosive Formulations

It is desirable to increase blast effect in the case of high capacity, light cased explosive weapons such as torpedoes, mines and high capacity aircraft bombs. It has been established beyond doubt that this is possible by the use of aluminized explosives which contain aluminum powder as an ingredient.

A mixture of ammonium nitrate/TNT/aluminum powder/charcoal (65/15/17/3) called Ammonal had been used in World War I for mining, demolition and in bombs and grenades. However, in World War II, shortage of aluminum powder restricted its use for such HE formulations. The effect of addition of aluminum powder to high explosive fillings of bombs and shells had been found to be of advantage which is evident from the data given in Table 3.3.

3.2.3
Sheet Explosives

High explosives like RDX, HMX or PETN with a polymeric binder form a flexible explosive material that can be rolled into sheet form which can be cut and applied to any contour. They have a variety of applications from metal cutting to demolition and blasting to armor protection. Some important characteristics of sheet explosives are – flexibility, moldability, waterproofness and safety in handling. Also, sheet explosives can easily be cut and initiated.

In India, flexible sheet explosives are generally made from indigenously available unsaturated polyester resins, epoxy resins and natural rubber etc. and common

Table 3.3 Some aluminized explosive formulations and their density and 'velocity of detonation'.

Explosive	Formulation	Density/g cm^{-3}	VOD/m s^{-1}
Tritonal	TNT/Al 80/20	1.72	6700
Minol 1	AN/TNT/Al 48/42/10	1.75	5080
Minol 2	AN/TNT/Al 40/40/20	1.82	5900
Torpex 1	RDX/TNT/Al 45/37/18	1.78	7440
Torpex 2	RDX/TNT/Al 42/40/18	1.85	7360
Torpex 2B	RDX/TNT/Al 42/40/18 +5.5% Desensitizer	1.77	–
Torpex 5	RDX/TNT/Al 30/50/20 +2% C black	1.78	6990
RDX/Wax/Al	RDX/Wax/Al 70/20/10	1.78	7750
Dentex	RDX/TNT/Al 48.5/33.5/18 +0.5% P.wax	1.75	7780
HTA – 3	HMX/TNT/Al 49/29/22	1.81	7600
Max blast	RDX/TNT/Al 45/30/25 +1.0% P.wax	1.80	7700
EDC-1	HMX/RDX/TNT/Wax 70/4/25/1	1.84	8330

explosives. Around 60–70% loading of explosives is generally achieved in the sheet. The explosives used in the binder matrix are either fine or coarse PETN/RDX. These sheets generally possess better mechanical and explosive properties than sheets prepared from natural rubber as a binder, and they have better storage life.

Among various rubbery polymeric materials, a special polyester resin has been developed as a binder in view of its curing at ambient temperature, low viscosity (as a result of addition of vinyl monomers) without appreciable sedimentation of explosives. In addition, polyester resin has the greatest advantage of having an oxygen moiety in the skeleton which increases oxygen balance of the final sheet, thereby increasing its performance. The study conducted by Agrawal *et al*. on PBXs using explosives: RDX and HMX, and polymers: epoxy resin and polyurethane, suggests that epoxy resin-based PBXs have higher loading density, higher mechanical strength and higher VOD compared with polyurethane-based PBXs [13]. These sheet explosives have applications for civil and military purposes and are used for field demolition, metal cutting, cladding, blasting and armor protection.

3.2.4
Plastic Bonded Explosives

The next class of explosives is plastic bonded explosives (abbreviated as PBXs) which are considered better than normal explosives due to high loading density, better mechanical strength, better thermal stability, and better performance than normal explosive formulations. Also processing and handling of PBXs is safer than normal explosive formulations.

The purpose of using a binder in PBXs is to encapsulate each explosive crystal in its own layer so that during accidental stimuli such as impact, none of the explosive crystals are in contact with one another, thus preventing hot spot ignition by frictional heating and/or shear. The binder with a relatively high modulus of elasticity, provides a cushion to explosive particles from impact and shock compression. The ideal situation under crack formation in the material is that the crack runs through the binder rather than through an explosive crystal, which might result in ignition through friction of explosive surfaces and shear banding. Unfortunately, cracks can also occur between the explosive crystal and the binder after impact or thermal stimuli (explosive and binder have different coefficients of expansion) which is likely to lead to the explosive crystal de-bonding from the cushioning matrix and if this process is widespread, sensitivity of the formulation is likely to increase. PBXs do however show a much reduced sensitivity to accidental stimuli than the RDX/TNT formulations and the high percentage of nitramine also results in increased performance. The introduction of spheroidized explosives into the formulations reduces the viscosity of mixtures and possibly reduces the sensitivity of the explosive formulations, as less angular crystals should bind into the matrix better. As covering the surface area of a sphere requires less binder than any other crystal shape, for a PBX where binder forms less than 10% of the formulation, reducing the overall surface area of the solid component in the mixture should allow the thickness of covering for each crystal to be marginally better. However, spheroidized crystals do show an increased tendency to de-bond from the binder matrix.

In most formulations, the binder is not all rubbery polymer as there is also a small amount of stabilizer which prevents oxidation of rubbery polymer and corresponding degradation of physical properties of formulations.

The cured systems have a disadvantage, that is, once filled into a munition, they cannot be removed and munition re-filled, if the quality of the filling is found to be unsatisfactory. Munitions are sometimes re-filled with melt-cast formulations if the original filling is not of the required standard, but it depends on the cost of the metal casing, whether it is economically viable. The explosive is however, not re-used in most cases.

The introduction of binders for explosives resulted in better safety, allowed more sensitive explosives to be used with a corresponding increase in performance and facilitated the processing of crystalline explosives. The binders have, until recently, been inert and made no contribution in terms of performance of the formulation. The use of energetic plasticizers such as K-10 and BDNPA/F has also been advocated to reduce the inert content of the binder, but there can be a degree of physical incompatibility with these plasticizers, which cause exudation at high temperatures and during ageing, with a corresponding degradation in physical properties of the explosive formulations. Current research efforts are being directed at energetic binders and plasticizers so that their dead weight can be usefully exploited. The use of energetic binders and plasticizers could also allow the explosive content of the formulation to be reduced (with a corresponding decrease in sensitivity) but should allow the energy output of the formulation to remain the same. The formulations with energetic binders and decreased explosive content may well conform better to the insensitive munitions (IM) requirements.

A number of energetic binders: glycidyl azide polymer (GAP), nitrated hydroxy-terminated polybutadiene (NHTPB), poly(3-nitratomethyl-3-methyloxetane) [poly (NiMMO)], poly(glycidyl nitrate) [poly(GlyN)] and nitrated cyclodextrin polymers, poly(CDN) etc. and energetic plasticizers: bis(dinitropropyl) formal (BDNPF), bis(dinitropropyl) acetal (BDNPA)] and their 1 : 1 mixture, low molecular weight GAP/poly(NiMMO)/poly(GlyN) etc. which had originally been developed as propellants, have also been used for PBX formulations and have resulted in enhanced performance.

PBXs also include some pressed compositions where the level of nitramine is in excess of 94% (by weight). The explosives are only encapsulated by a minimum amount of binder such as Viton or Estane. The physical properties and safety characteristics of these formulations are not as good as those of castable PBXs but the performance is increased.

When introducing binders or plasticizers into intimate contact with explosives, it is critical that there is no chemical incompatibility either initially or later on, as munitions are expected to have in-service life-spans of up to 30 years. Nitramines for example, have been found to be chemically incompatible with amines which are used for fast-curing epoxy resins. Therefore, all materials that might be used as part of an explosive formulation are carefully tested for their chemical compatibility with each other and also with the explosive, prior to their use for explosive formulations.

Physical compatibility is also important, as components of explosive formulations are required to mix intimately to produce desirable physical properties. There should be no separation of the components over a period of time nor exudation of any component. The physical properties of an explosive formulation determine firstly the response of ingredients to changes in temperature, which may also include thermal cycling (exposure to hot and cold temperatures in succession over a short period of time) and secondly, they determine the resistance of the

Table 3.4 Some PBX formulations and their important properties.

Composition	Density/g cm^{-3}	VOD/m s^{-1}	Compression strength/kg cm^{-2}
RDX/Viton (95/5)	1.73	8488	>113
RDX/Viton (90/10)	1.66	7920	>113
HMX/Viton (95/5)	1.75	8820	>113
HMX/HIP (90/10)	1.63	7404	>88
RDX/HIP (90/10)	1.59	7328	>113
RDX/PPG (90/10)	1.50	7692	–
HMX/PPG (90/10)	1.70	8300	–
RDX/Estane (95/5)	1.72	8400	>130
RDX/Estane (90/10)	1.69	8200	>130
HMX/Estane (95/5)	1.86	8600	>130
HMX/Estane (90/10)	1.84	8400	>130
HNS/Viton (90/10)	1.66	6850	>113
HNS/Teflon (90/10)	1.64	6345	>110
TATB/Teflon (90/10)	1.65	7200	–

end-product to damage through impact, whether at high velocity from a bullet or fragment or at low velocity such as munition being dropped.

Some PBX formulations along with their density, VOD and compression strength are given in Table 3.4. Some important PBX formulations based on high explosives such as TATB, NTO and CL-20 which are used for specialized applications have already been described in Chapter 2.

In conclusion, it is obvious that formulation research is of great importance and it will continue as long as improvements in performance, safety and cost are desired.

3.3
Assessment of Explosives

An overview of the important characteristics of explosives is given in Chapter 1. With the advent of various modeling techniques, much information concerning any given explosive can be obtained by theoretically calculating its properties. This information is valuable but indicative as calculations predict performance, which an explosive may have under ideal conditions. In practise, such perfection is never achieved and it is a matter of practical importance to assess their properties experimentally under conditions more appropriate to their use. Such an assessment is usually made by a series of tests chosen to determine the performance of explosives under various conditions. While these tests are of considerable value, it must be remembered that no laboratory test or series of tests can predict precisely the performance of explosives which may be used for widely varying purposes. The ultimate test for all explosives is their performance in the field.

The experimental assessment of the following properties, which are considered to be of utmost importance from the point of view of their application, are given in the following paragraphs.

1) Compatibility and stability.
2) Sensitivity to heat, impact, friction, spark and shock.
3) Velocity of detonation.
4) Detonation pressure.
5) Explosive power or strength.

3.3.1
Determination of Compatibility and Stability of Explosives

Weapon systems are frequently required to be stored under field conditions for a long time. Therefore, issues related to compatibility and stability are given special consideration while designing, developing, manufacturing and storing these weapon systems containing explosives and propellants. Weapons must be ready for use at a short notice and must operate reliably as originally designed after prolonged storage. The consequence of incompatibility and instability could be catastrophic even to the extent of detonation of a stockpile or ship's magazine of weapons. Therefore, high standards for compatibility and stability are set and accordingly, test methods have been designed and developed.

A detailed account of the compatibility and stability of explosives – definition, implications and effect of various parameters such as temperature of storage, chemical constitution of explosive vis-à-vis other ingredients, sunlight and electrostatic discharge etc has already been given in Chapter 1 (Section 1.4.1). In this section, the test methods used to determine compatibility and stability are discussed.

Compatibility: When an explosive is in direct contact with a polymer or contact material, it is possible that: (i) one or more properties of an explosive are affected; (ii) one or more properties of a polymer or contact material are affected; (iii) none of the properties of the explosive nor of the polymer or contact material are adversely affected.

The explosive – polymer or contact material – combination is considered incompatible under situations (i) and (ii) whereas combination is considered compatible under situation (iii). To some extent, the effect of polymer or contact material on the explosive or vice-versa may be qualitatively predicted on the basis of their chemistry and structures. However, it should be verified through a set of experiments as given below.

Stability: Before use, all explosives are normally kept in magazines for periods ranging up to several years. These magazines do not usually have heating or cooling systems and therefore, temperature varies widely depending on the location of the magazine. It is important from the point of view of safety and use that the explosive in question remains safe and also retains its physical, chemical and explosive properties throughout its storage in magazines.

The vacuum stability test and heat test are the most common tests used to determine the compatibility and stability of explosives with polymers or contact materials. However, an impact sensitivity test is sometimes used in order to derive additional information.

3.3.1.1 Vacuum Stability Test

This test is used most frequently; it is an accelerated test designed to determine the stability of an explosive and also the compatibility of an explosive with a polymer or contact material.. The assembly of the set-up and method of its determination are described in detail in the literature [14]. A dried and accurately weighed sample of a secondary explosive (5.0 ± 0.01 g) or of a primary explosive (1.0 ± 0.01 g) is placed in the heating tube followed by its assembly and evacuation. The heating tube is immersed in a constant temperature bath (100 °C or 120 °C) for a period of 40 h and the volume of evolved gases is recorded. Most explosives or explosive formulations yield less than 1 cm^3 of gas per gram of an explosive during 40 h at 120 °C.

In the compatibility test, 5.0 ± 0.05 g of an explosive is thoroughly mixed with 0.5 ± 0.05 g of finely ground polymer or contact material and the mixture is subjected to vacuum stability test. This experiment is also repeated with explosive and polymer or contact material separately. Most of the time, a temperature of 120 °C is used for high explosives and period of heating is limited to 40 h. The volume of gas (V, cm^3) evolved by the mixture in excess of the volume of gas evolved by individual materials is calculated by Equation 3.2:

$$V = C - (A + B) \tag{3.2}$$

where C = Volume of gas evolved by mixture
A = Volume of gas evolved by explosive
B = Volume of gas evolved by polymer or contact material.

An additional 1 cm^3 gas evolution arising from the mixture of explosive and polymer or contact material is allowed when polymer is intended to be mixed with explosive, and 5 cm^3 gas evolution when only contact of polymer or contact material with an explosive is required. Some investigators are of the opinion that if this difference is between 3 and 5 cm^3, compatibility is uncertain but if this difference is above 5 cm^3, the two materials are definitely incompatible [15].

The compatibility of explosives with a variety of polymers has been the subject of research by a number of investigators and a summary of important conclusions as reported in the literature follows [16–19].

1) **Epoxy resins:** The compatibility of epoxy resins with explosives and propellants is largely decided by the curing agent or hardener. Some curing agents promote cure by catalytic action whereas some participate directly in the reaction and become a part of three-dimensional networks.

   - As a rule of thumb, epoxies cured with aliphatic amines, cause a majority of explosives and propellants to be excessively reactive. Epoxies cured with polyamides (of low molecular weight such as versamide) also cause some explosives to be excessively reactive.

   - On the other hand, epoxies cured with acid anhydrides and phenolic resins exhibit little or no reactivity when stored in direct contact with explosives and propellants.

2) **Polyesters and alkyds:** Polyesters are generally regarded to be compatible with explosives and propellants.

   - Unsaturated polyesters do not, in general, seriously affect the reactivity of a variety of explosives and propellants. Similarly, saturated polyesters do not affect reactivity of explosives and propellants significantly.
   - Rigid unsaturated polyesters generally gain less than 10% weight when stored in contact with explosives and propellants containing NG and TNT whereas flexible unsaturated polyesters gain weight continuously. Therefore, flexible unsaturated polyesters are more susceptible to attack of explosives and propellants containing NG and TNT than rigid unsaturated polyesters.

3) **Polysulfide polymers:** Polysulfide polymers increase the reactivity of some explosives and propellants. They are not compatible with PETN, Pentolite, Composition B, Amatol or Tetryltol. Polysulfide rubbers absorb some NG from DB and triple-base (TB) propellants. However, some propellants show little or no reactivity in the presence of polysulfides.

4) **Polyurethanes:** Polyurethanes appear to be promising and are regarded as compatible with explosives and propellants. However, some research is required to optimize satisfactory cure conditions.

5) **Phenolic resins:** Properly cured phenolic molding materials are substantially unaffected by explosives and propellants. However, rubber modified phenolics, in general, produce greater reactivity than unmodified phenolics.

6) **Lacquers or varnishes:** Many metallic cases and components in contact with explosives are protected by coating of lacquers or varnishes. Some varnishes, even after complete curing, have been found to give high gas rates especially with RDX/TNT. Similarly, the compatibility of lacquers is considerably affected by the use of coloring dyes such as rhodamine red dye.

7) **Acrylates** do not affect the reactivity of explosives and propellants.

8) **Cellulosics** in general do not affect the reactivity of explosives and propellants. However, these are extensively weakened on prolonged contact with propellants containing NG.

9) **Polyethylenes, fluorocarbons (Teflon and Kel-F) and chlorosulfonated polyethylene (Hypalon)** are not affected by contact with explosives and propellants because of their chemical inertness.

10) **Nylon polyamide resins** have little or no appreciable effect on explosives and propellants.

11) **Silicone polymers**, in general, are compatible with explosives and propellants. Such polymers are least affected by explosives and propellants that contain NG.

12) **Straight and modified polystyrenes** have little or no effect on explosives and propellants. However, modified polystyrenes show greater susceptibility than straight polystyrenes to attack by explosives and propellants that contain NG/TNT.

13) **Vinyl polymers**, in general, do not adversely affect the reactivity of explosives and propellants.

The vacuum stability test is convenient and simple but it has certain inherent disadvantages. For example, the volume of gas arising from solvents, foam blowing agents and volatile plasticizers may invalidate the results. An attempt to test a cold curing plastic may result in additional curing reaction during the initial stages of heating and thus convert the plastic to a more compatible plastic. Any contamination which lowers the melting point of an explosive may have quite disproportionate effects in its apparent stability because decomposition and gassing occur much more readily when the substance has a liquid phase.

3.3.1.2 Heat Test

This test is conducted to quickly obtain data indicating deterioration and is used instead of the vacuum stability test when the effect of polymers on the stability of highly sensitive explosives is to be studied. A 0.6 g explosive mixed with 0.6 g polymer and also explosive and polymer separately are heated for two cycles, each of 48-h period at 100 °C. A 5% loss during the two cycles, each of 48-h period, or an explosion within 100 hours indicates excessive deterioration.

3.3.1.3 Impact Sensitivity Test

A small amount of explosive (≈10–20 mg) is subjected to the action of a falling weight (2 kg) and the minimum height at which at least one out of ten trials result in detonation, explosion or exothermic decomposition is recorded, as described in Section 3.3.2.2 on impact sensitivity. The same experiment is also repeated on a mixture of explosive and polymer or contact material. In the case of a considerable fall in the minimum height leading to ignition, explosion or detonation, the combination of explosive and polymer or contact material is termed to be incompatible and hence, is not considered for use.

As described in Section 3.3.2.1 on heat sensitivity, thermoanalytical methods are sufficiently sensitive as an early indication of incipient chemical decomposition or chemical reaction, that is, stability and incompatibility. Some research papers discuss the use of differential thermal analysis (DTA) and differential scanning calorimetry (DSC) for this purpose [20–22].

3.3.2
Sensitivity of Explosives to Heat, Impact, Friction, Spark and Shock

During production, handling, storage, transport, and similar activities, explosives are frequently exposed to various external stimuli such as heat, impact, friction etc. which might result in combustion or detonation. This particular property of explosives is considered a key factor in determining practical applications of a given explosive.

Due to the complex nature of the initiation phenomenon, there is no absolute indicator of their sensitivity in terms of minimum initiation energy. Further, the energy required for initiation of an explosive depends not only on the chemical nature of the explosive and a number of other physical parameters, but also on the kind of initial stimulus and nature of energy transfer to the explosive. Thus, the total amount of initiation energy may vary considerably. It is generally believed that an even distribution of externally applied energy through the whole explosive volume is not suitable for a successful initiation. A high concentration of energy in time and in explosive volume is a necessary precondition for a successful initiation. The energy required for the initiation of decomposition reactions can be applied in the form of thermal impulses (flame, heating, spark etc.), mechanical impulses (impact, friction, projectile impact etc.) and shock waves etc.

3.3.2.1 Determination of Heat Sensitivity

The application of heat for the initiation of explosives can be realized in two ways:

1) By local heating of an explosive by a heat source in the form of a flame, spark, etc. A localized thermal impulse creates a local zone in which reactions start to occur and then propagate through the rest of the explosive due to their self-sustaining character.

2) By homogeneous heating of an explosive throughout its whole mass by means of a heat source but without exposing it to an open flame. In this case, when a critical temperature is reached, decomposition of an explosive follows according to the laws of thermal explosion, that is, initiation occurs after breaking down the heat balance between the energy generated by external heating of the explosive and the heat dissipated into the surroundings.

A comparative evaluation of heat sensitivity of different explosives can be obtained by determining: (a) explosion delay (E_D) or induction period; (b) explosion temperature (E_T); and (c) activation energy (E_a) which are related to each other.

Explosion Delay For any explosive, there is a certain minimum temperature at which it explodes, but it is seen that an explosive takes more time to explode after attaining that temperature. This time lag or induction period which is a characteristic property of the explosive in question, for a particular temperature and under a given set of conditions, is known as explosion delay (E_D). This may vary from hours to microseconds depending on the explosive, temperature and a number of physical parameters such as crystal size, thermal conductivity, etc. Therefore, testing conditions must also be defined while reporting E_D.

Explosion Temperature The explosion temperature is a qualitative term and depends upon several factors, similar to explosion delay. It is measured mainly for a comparative study. In the present work, it is defined as the temperature necessary to cause explosion in exactly 10 or 5 seconds, that is, 10-/5-second time-to-explosion while determining explosion delay with a few milligrams of an explosive.

The determination of explosion delay and explosion temperature is performed in the apparatus shown in Figure 3.4 similar to that employed by Copp *et al.* [23]. A Wood's metal bath is constructed as follows: a solid mild steel block 30 cm long, 10 cm in diameter is selected and three holes are bored on top of the block. The central hole has a diameter of 2.5 cm and depth of 10 cm for filling the Wood's metal. On each side of the central hole, a hole of 0.8 cm dia. and 2.5 cm depth is drilled for inserting a thermometer and a thermocouple probe respectively. The mild steel block is electrically heated by a properly insulated heating coil whose resistance is adjusted in order to impart the desired temperature to the Wood's metal bath. For this purpose, a variable transformer is attached in the circuit of the heating coil. A Beckman thermometer is immersed in one of the side holes containing molten Wood's metal to measure the bath temperature. In the second side hole, a thermocouple probe is placed in the molten Wood's metal to verify the temperature of the bath. Also, a thermostatic arrangement is introduced in the circuit of the thermocouple and heating coil to maintain constant temperature of the bath for a required period. During the course of the experiment, the temperature is not allowed to fluctuate more than ± 0.5 °C. A copper tube (5 cm long, 0.7 cm dia. and open at one end) is taken and a thin mild steel rod (10 cm long and 0.3 cm dia.) is brazed from outside at the open end of the tube. The brazed copper tube is screwed into the mild steel rectangular frame which has sufficient weight to push the copper tube to a definite depth in the molten Wood's metal. This frame

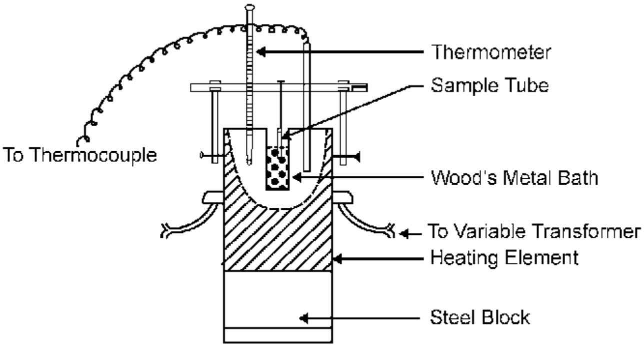


Figure 3.4 Apparatus for determining explosion delay and explosion temperature.

rests on two hooks at a fixed height on the two sides of the mild steel block. The upper end of the rectangular frame is enclosed in a clamp fixed on a retort-stand to stop the frame from being thrown apart at the time of explosion of the sample. This set-up has proved to be very safe for handling of explosives and also provides reproducible results.

The test is performed with 20 mg of a sample, ground and dried. When the temperature of the bath is 300 °C, a test tube with the sample is immersed in the Wood's metal bath and a stopwatch is switched on simultaneously. When explosion of the sample occurs, the time is recorded by the stopwatch, that is, the time interval between the moment of insertion and the moment of explosion is noted. This period is the 'explosion delay' (E_D) or 'induction period' at that temperature. In order to eliminate accidental variations, the mean of three readings is taken in all cases. The bath temperature may be decided depending upon the value of E_D, that is, if value of E_D is too high, the bath temperature may be increased whereas if it is too low, bath temperature may be decreased in order to improve the accuracy of the determination.

Using this apparatus, it is also possible to determine the 10-/5-second time-to-explosion temperature, as follows.

A Beckman thermometer is used to read the temperature of the bath. When the temperature of the Wood's metal bath is ≈300 °C, a test tube with a sample is immersed in it. A stopwatch is used to record the time interval between the moment of immersion of sample in the bath and the moment of its explosion. If the explosion delay (E_D) is more than 10/5 seconds, the temperature of the bath is increased by 10 °C and the experiment is repeated with a fresh sample. This exercise is repeated with incremental temperature changes (higher or lower) until an exact E_D of 10-/5- seconds is obtained. This method is similar to that described by Weber in the literature [24].

Activation Energy It is experimentally seen that the explosion delay (E_D) for the build-up of an explosion decreases with an increase in temperature. Therefore, 'energy of activation' (E_a) can be calculated on the basis of a relationship between the experimentally obtained E_D and the absolute temperature of the Wood's metal bath. This relationship is expressed by an Arrhenius type of equation, that is, (Equation 3.3):

$$E_D = Ae^{Ea/RT} \tag{3.3}$$

where E_D = explosion delay
E_a = energy of activation
R = universal gas constant
T = absolute temperature of the Wood's metal bath
A = frequency factor depending on the explosive.

The logarithmic form of Equation 3.3 is Equation 3.4:

$$\begin{aligned}\text{Log}_{10}E_D &= (E_a/4.57).(1/T) + \log_{10} A\\ &= (E_a/4.57).(1/T) + B\end{aligned} \tag{3.4}$$

A plot of $\log_{10} E_D$ against $(1/T)$ is almost rectilinear. Therefore, E_a may be determined by equating $(E_a/4.57)$ with the slope of the straight line. Equation 3.3 holds good for a number of explosives such as lead azide, cuprous azide, mercury fulminate, lead styphnate, barium styphnate and metal picrates and metal picramates etc. [25–30]. Thus, it appears that the determination of E_a gives a more complete picture concerning the heat sensitivity of explosives than E_D or E_T.

The research papers which originated in the last couple of years in different countries in this field indicate that E_D and E_T are not generally reported and there is an emphasis on the study of comprehensive thermal behavior of explosives as a function of temperature or time by means of different thermal analytical techniques. Most commonly used methods of thermal analysis are differential thermal analysis (DTA), thermogravimetric analysis (TGA) or thermogravimetry and differential scanning calorimetry (DSC).

Thermal Analysis Thermal analysis consists of a group of techniques where a physical property of an explosive is measured as a function of programmed temperature and the most common complementary techniques are listed in Table 3.5.

Differential Thermal Analysis All materials emit or absorb heat when they are heated or cooled and the measurement of how these materials absorb or emit heat or energy with respect to time or temperature is done by thermal analysis.

The construction of DTA apparatus is simple and consists of a furnace, differential thermocouple, temperature thermocouple, specimen holders, temperature programmer and recorder. The schematic of a typical DTA apparatus is shown in Figure 3.5.

Table 3.5 Various thermoanalytical techniques for thermal analysis.

Technique	Parameter measured	Apparatus
TG	Weight change	Thermobalance
Derivative TG	Rate of weight change	Thermobalance or derivative thermobalance
DTA	Temperature difference between sample and reference material	DTA apparatus
Derivative DTA	Derivative of temperature difference between sample and reference material	DTA apparatus
DSC	Amount of heat necessary to establish zero temperature difference between sample and reference material	Differential scanning calorimeter
STA	DTA, TGA, DSC (Cal.) and derivatives of DTA/TGA	Simultaneous thermal analyzer
Evolved gas analysis	Nature and composition of gas liberated during thermal analysis.	Gas analyzer

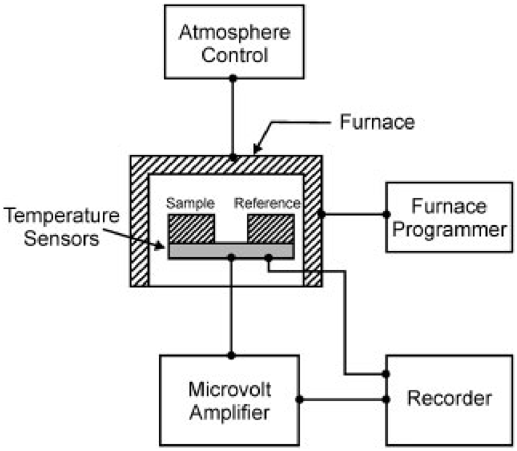


Figure 3.5 Schematic of a DTA apparatus.

The method involves heating of a sample and a thermally inert reference material to elevated temperatures at a constant rate while continuously recording the temperature difference between them as a function of sample or reference temperature. All reactions which can occur in the sample as it is heated are accompanied by energy changes which generally manifest themselves as heat energy. Some produce heat and are called 'exothermic' while some require heat for reaction to proceed and are called 'endothermic'. On a rising temperature basis, endothermic heat effects are caused by vaporization, decomposition, inversion, reduction and fusion whereas exothermic ones are due to oxidation, crystallization and autocatalytic decomposition. The curves (plot of ΔT as ordinate downward for endothermic reactions and upward for exothermic reactions against temperature or time as abscissa, increasing from left to right) obtained by DTA (called thermograms), are then used to characterize the system under study in terms of its thermal reactions, both physical and chemical. A typical DTA thermogram is shown in Figure 3.6.

DTA has been extensively used to study various aspects of explosives and important among them are:

1) Compatibility of explosives with polymers: NC/RDX–polymers [31] and PETN/nitroguanidine–polymers [32]. Similarly, compatibility of explosives such as RDX, PETN and PBXs with various kinds of contact materials is derived from the kinetic parameters obtained from DTA curves [33].
2) Thermal stability of a number of cyclic and acyclic nitramines, amine nitrate salts and guanidine derivatives [34].
3) Thermal decomposition of pure explosives such as primary explosives: lead azide, lead styphnate, mercury fulminate etc. [35], monomethylamine nitrate [36] and explosive mixtures: RDX + HMX mixtures [37].

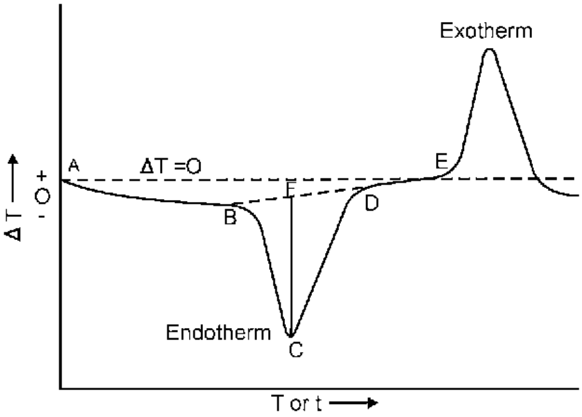


Figure 3.6 A typical DTA curve (thermogram).

4) Kinetics of thermal decomposition of explosives: 3-amino-5-nitro-1,2,4-triazole (ANTA) and its derivatives [38], 1,3-bis(1,2,4-triazol-3-amino)-2,4,6-trinitrobenzene [39] and transition metal salts of NTO [40].

Thermogravimetric Analysis Thermogravimetry is regarded as the science and art of weighing substances while they are being heated. It involves weighing a sample at a constant temperature as a function of time (static method) or recording any change in weight as a function of temperature (dynamic method). Dynamic thermogravimetry is particularly attractive in the early stages of an investigation because it is used to survey rapidly the thermal behavior of many systems. TGA can often be used to supplement information derived from DTA as thermogravimetric curves can be related to chemical and physical changes taking place in a sample as it is heated. Often the rate of weight change is measured by taking the first derivative of weight change with time. This displays more sharply details of the original curve and facilitates calculation of kinetic rates. This technique is called derivative thermogravimetric analysis (DTG).

A TG apparatus consists of a precision balance (thermobalance), a furnace, sample holder assembly, temperature programmer and recorder and its schematic is shown in Figure 3.7.

An idealistic weight loss vs temperature/time curve is shown in the Figure 3.8.

Pai Vernekar *et al.* used simultaneous DTA-TGA to study the changes occurring in lead azide stored under various atmospheres and as a function of time and its storage temperature [41]. It was reported by the researchers that with a sample of constant mass, certain heating rates resulted in the decomposition of lead azide whereas higher heating rates led to its detonation. Also during TGA, the weight loss vs temperature curve shows 28% loss (nitrogen content of lead azide ≈28%). However, when the thermal reaction leads to detonation, TGA shows a 100% weight loss. This is because detonation of lead azide generates a temperature ≈3300 °C which evaporates metallic lead during detonation.

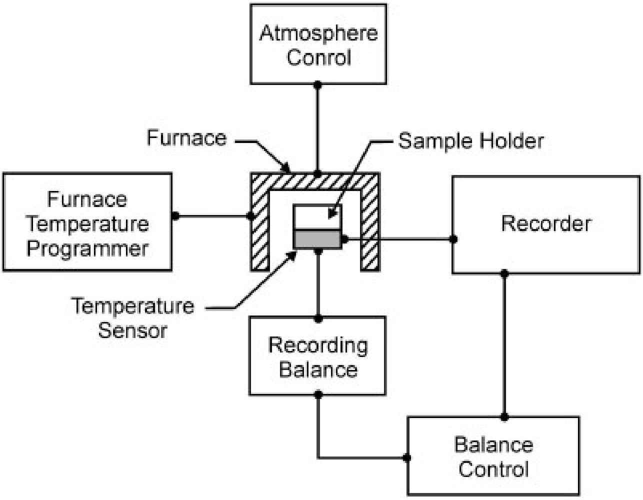
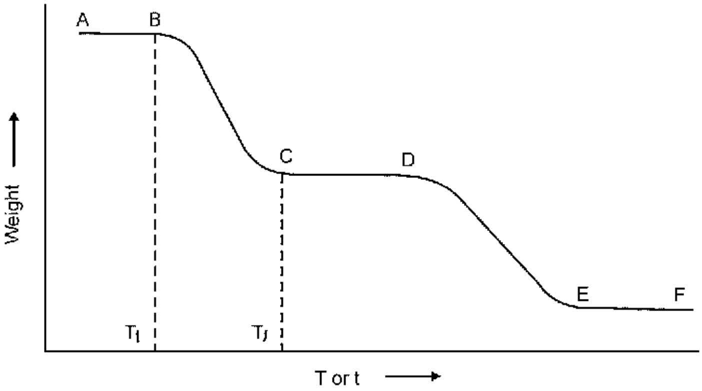


Figure 3.7 Schematic of TG apparatus.



AB, CD and EF : Plateaus; T_i : Initial Temperature, T_f : Final Temperature; $T_f - T_i$: Reaction interval.

Figure 3.8 A typical TG curve.

Differential Scanning Calorimetry In DSC, a sample and reference material are mounted on two separate small heaters. The temperatures of the sample and reference material are monitored and no temperature difference is allowed. The difference in power requirements for the two heaters is measured and recorded as a function of time/temperature. In other words, DSC measures the energy necessary to establish zero temperature difference between the sample and reference material against time/temperature as the two specimens are subjected to a controlled temperature program. The output signal is measured in terms of heat capacity as a function of time/temperature.

A schematic of a DSC sample holder assembly and instrument is shown in Figure 3.9 and a typical DSC curve for indium (standard) is shown in Figure 3.10.

Isothermal DSC was used to determine the kinetic parameters for thermal decomposition of 2,4,6-TNT and it was found that molten TNT shows a temperature-dependent explosion delay prior to its exothermic decomposition. The rate constant of exothermic decomposition and activation energies of explosion delay and exothermic decomposition were also reported [42]. Similarly, House and Zack

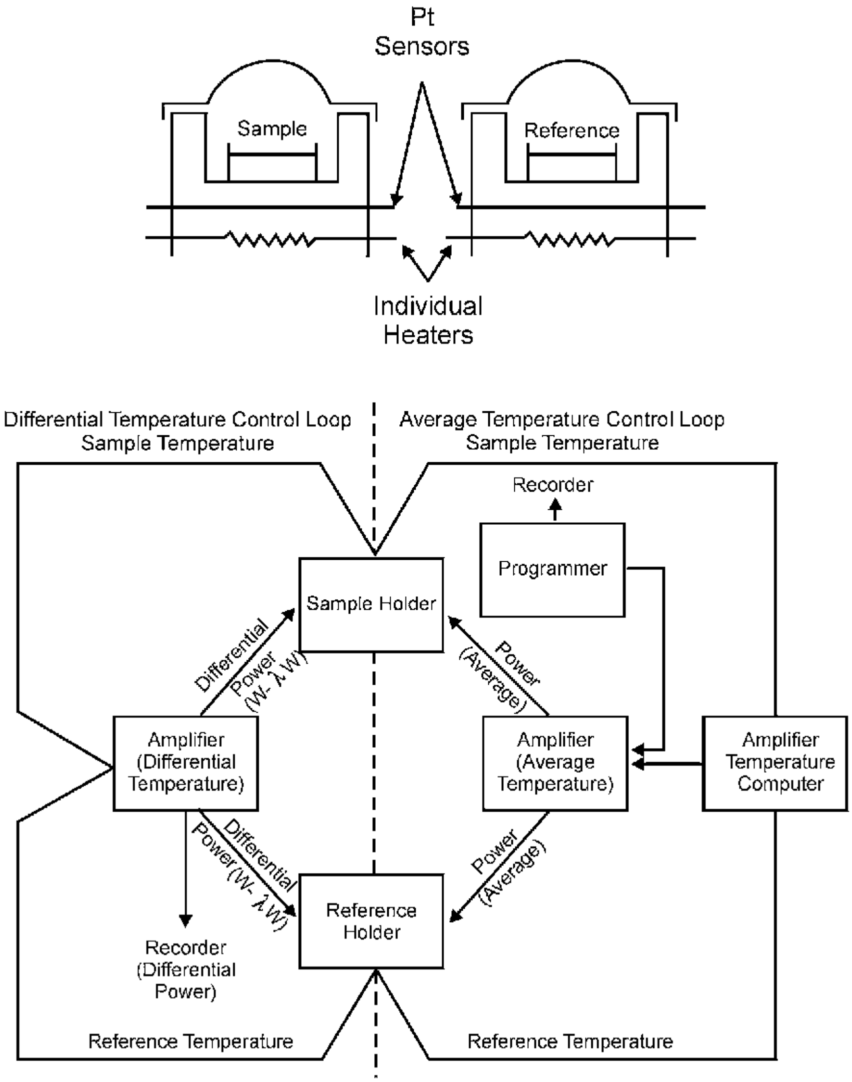


Figure 3.9 Schematic of DSC sample holder assembly and instrument.

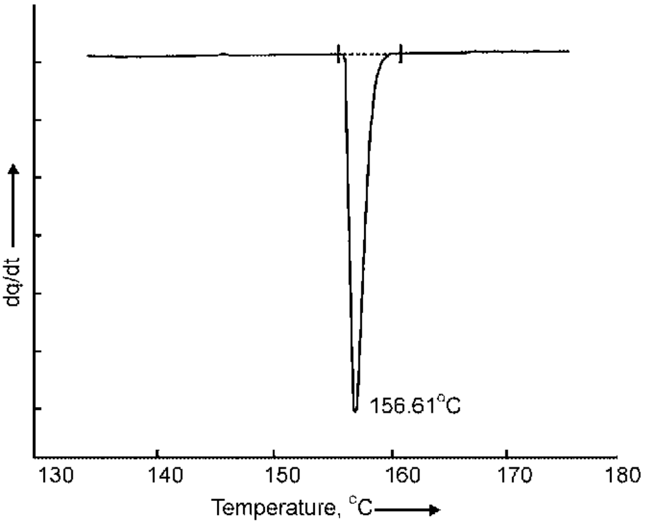


Figure 3.10 DSC curve of indium metal (standard).

used DSC to study the decomposition of NC-based propellants and reported only a single exothermic peak beginning at 185 °C [43].

Simultaneous Thermal Analysis (STA) A technique which combines DTA, TGA, DSC (cal.) and derivatives of DTA/TGA in a single instrument, offers advantages over the performance of each technique as a separate experiment on stand-alone instruments. By examining a single sample, one ensures no variation in sample homogeneity, atmosphere difference and other instrumental parameters. At the same time, there is a provision for detection and analysis of evolved gases (EGA) during thermal decomposition. Also, derivatives of TGA and DTA can be precisely measured (electronically).

Simultaneous TGA and DTA were used by Maycock *et al.* to study the kinetics of the isothermal and adiabatic thermal decomposition of δ-HMX (one of the polymorphs of HMX) under helium atmosphere and reported activation energy [44] ≈63 K cal mol^{-1}. The use of simultaneous DTA/TG has been reported for compatibility testing of TNT with two epoxy-and two alkyd resins paints [21, 45].

In a nutshell, it may be concluded that DTA, DSC and TGA have been used mainly to determine the thermal properties of explosives like melting points, thermal stability, kinetics of thermal decomposition and temperatures of initiation and ignition etc. Further, the properties which can be calculated quantitatively from the experimentally obtained values are reaction rates, activation energies and heats of explosion. DTA data of some explosives are given [46] in Table 3.6.

3.3.2.2 **Determination of Impact Sensitivity**

The literature reports several types of 'impact testing apparatus' also known as 'fall hammer apparatus', for the determination of impact sensitivity of explosives.

Table 3.6 Thermal data of some explosives.[a]

Explosive	Melting point/°C	Ignition temperature/°C	Exotherm temperature/°C	Onset temperature of decomposition (Ti)/°C
2,4,6-TNT	81	295–300	250	–
Ammonium picrate	280 (decomposition)	313	280	–
Tetryl	129	201–212	162	–
RDX	205	229	215	–
β-HMX	275	279–281	260	–
PETN	140	203	160	–
Nitroguanidine	264	210–240	168	–
Ammonium nitrate	169	No ignition up to 360	Endothermic	–
TNAZ	~100	–	253	>240
CL – 20	–	–	225	215
ADN	91.5–93.5	167–174	184	145
HNF	115–124	115–120	–	–

a) Based on Ref. [46].

Basically all apparatuses work on the same principle wherein a sample of the explosive under test is subjected to the action of a drop weight. The mass of the drop weight is fixed, that is, 0.6, 2, 5, or 10 kg and the drop height at which initiation, ignition or explosion of the sample takes place is determined. The main difference between the apparatuses is related to their design and the manner in which the sample is subjected to drop weight impact via different types of plungers.

Different methods are used in different countries to determine the sensitivity to impact of explosives and have been described in the literature at length. The fall hammer test is very popular in the UK [47]. In the USA, several apparatuses developed by different agencies are in vogue to determine impact sensitivity of solid, liquid or gelatinous explosives: The US Bureau of Explosives (BoE) Impact Apparatus, US Bureau of Mines (BoM) Impact Apparatus, Picatinny Arsenal (PA) Impact Apparatus and Explosives Research Laboratory (ERL), Type 12 Apparatus (developed by US Army Armament Research, Development and Engineering Center). On the other hand, the German Bundesanstalt für Materialprüfung (BAM) Impact Apparatus is used for this purpose in Germany and is reported to give reasonably reproducible results.

The description of these apparatuses, sample preparation and method of determination along with the manner of presentation of the results are given in the literature in detail [48] and only an account of the salient features is given here.

1) **Fall hammer test:** The impact sensitivity of an explosive is measured by determining the minimum height from which a specified weight is dropped in order to initiate decomposition, ignition or explosion. Many forms of 'fall hammer' are available and most important point of various designs being the modes used to retain explosive samples in position. In this, the explosive is

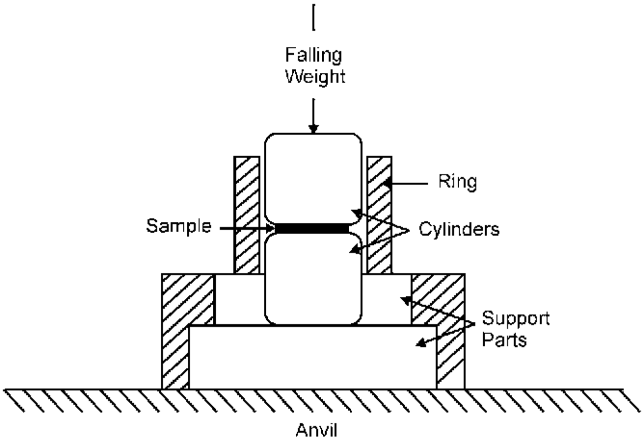


Figure 3.11 BoM impact apparatus. Reprinted from Kohler, J., and Meyer, R. (1993) *Explosives*, 4th edn, © 1993, Wiley-VCH Verlag GmbH, Weinheim, Germany.

positioned between two roller bearings which are placed in a ring of hardened steel resting on a hardened steel base. The falling weight is allowed to impact the upper steel cylinder. The mass of the 'fall hammer' varies from 0.5 to 5 kg.

2) **US BoM impact apparatus:** In this test, a sample of 0.020 g of solid explosive is tested using a fixed 'falling weight', usually 2 kg. The explosive sample is held between two flat, parallel hardened steel cylinders as illustrated in Figure 3.11. The minimum height at which at least one out of ten repeated trials results in explosion or ignition is determined.

   The procedure as used for solid explosives is also applied for liquid explosives. The only difference is that the mass of liquid explosive is ≈0.007 g. The liquid mass is absorbed on a disc of desiccated filter paper which is placed in between the hardened steel cylinders. This is described [48a] in detail in MIL-STD-650.

3) **US BoE impact apparatus:** This method specifies the placement of 10 mg sample in a test cup. The mass of the 'fall hammer' is usually 2 kg.

4) **Picatinny arsenal (PA) impact apparatus:** The sample which is placed in the depression of a small steel die-cup and then capped by a thin brass cover, is used in this test. The value of minimum height at which at least one out of ten trials results in explosion gives impact sensitivity. In the case of liquids, it is filled in a die-cup and tested in a manner similar to solids.

5) **ERL impact apparatus, type 12:** This test was developed by the US Army Armament Research, Development and Engineering Center and is optional for use. The machine (Bruceton Machine) Type 12 consists of a striker pin (made of hardened tool steel, ground and polished) with surface in contact

with explosive, fine flint sandpaper, anvil (made of hardened tool steel) and mass 2.5 kg (hardened steel). The mass of sample used is 35 ± 2 mg and the method of determination is practically similar to the methods for other apparatuses. Twenty trials are done at each height and the candidate explosive passes the test if no ignition or explosion is observed during impact in all 20 consecutive trials.

6) **Bundesanstalt für Materialprüfung (BAM) apparatus:** The 'fall hammer' test was modified by the German BAM in order to get better and reproducable data [49]. The sample is placed in a confinement device which consists of two coaxial cylinders placed one on top of the other and guided by a ring. The device with a sample is positioned on the anvil of the 'fall hammer apparatus' and the weight, guided by two steel rods is allowed to fall by unlocking it. For primary explosives, a small drop weight (about 1 kg) is used whereas a large drop weight (2, 5 or 10 kg) is used for secondary and insensitive explosives. The principle of the method and testing methodology are given in detail in the literature [50, 51].

There are several ways to express impact sensitivity of explosives which are:

1) The experiment is conducted using a drop weight of a fixed mass and by changing the drop height. For each drop height, ten consecutive trials are performed and corresponding percentage of initiation or explosion is calculated. The test results obtained are tabulated or graphically presented, that is, an impact sensitivity curve (relation between percentage of initiation or explosion and height of the drop weight having constant mass for a given explosive) is drawn. The impact sensitivity is expressed as drop height at which 50% initiation or explosion occurs ($h_{50\%}$), minimum drop height at which 100% initiation or explosion occurs ($h_{100\%}$) and maximum drop height at which zero % initiation or explosion is observed ($h_{0\%}$). However, there are some testing methods which consider minimum drop height at which at least one of ten consecutive trials results in ignition or explosion of the sample, as a measure of its impact sensitivity.

2) The results can also be expressed in terms of impact energy (E_I), at which usually 50% initiation or explosion occur [52]. The impact energy is calculated according to Equation 3.5 and expressed in N m (newton meter)

$$E_I = M_W\, H\, g \tag{3.5}$$

where E_I = impact energy
M_W = mass of the drop weight
H = drop height
g = acceleration due to gravity

3) The relative impact sensitivity (O_R) of the sample with respect to the impact sensitivity of a reference explosive, usually trinitrotoluene (TNT), is calculated by Equation 3.6:

$$O_R = \{[E_I(X)]/[E_I(TNT)]\}.100 \tag{3.6}$$

where O_R = relative impact sensitivity
$E_I(X)$ = impact energy of explosive under test
$E_I(TNT)$ = impact energy of TNT

4) Sometimes, impact sensitivity is also expressed as 'Figure of Insensitiveness' (F of I) of the explosive under test as compared with that of standard explosive (Tetryl whose F of I is arbitrarily taken as 70). F of I is proportional to minimum height from which the drop weight falls resulting in explosion or ignition. As this height is not always constant, the height for 50% explosion or ignition (also called median height) is determined and F of I is calculated from Equation 3.7.

$$\text{F of I of explosive} = (A/B).70 \tag{3.7}$$

where A = height for 50% explosion or ignition for the explosive under test
B = height for 50% explosion or ignition for Tetryl

A comparison of the impact sensitivity data of explosives reported by various teams from different laboratories suggests that the results obtained generally vary and it is due to (i) differences in the ways in which the experiments are conducted and (ii) use of different type of impact sensitivity apparatuses. However, when all influencing factors are considered, it appears that there is a similarity between the results obtained by different testing apparatuses.

The following precautionary measures should be taken in order to minimize variation in the impact sensitivity data from laboratory to laboratory and operator to operator.

1) The explosive should not contain lumps or aggregates and therefore, it should be sieved through US 50 and 100 mesh, that is, 50/100 mesh explosive where single explosive is involved and through 50 mesh for mixtures.
2) The explosive under test should be dried.
3) The temperature and humidity of the laboratory (temperature ≈26–27 °C and humidity ≈60–65%) where impact sensitivity test is done, should be maintained.
4) The sample holding assembly should be cleaned every time.
5) The impact sensitivity apparatus should be calibrated periodically by determining impact sensitivity of a standard explosive such as TNT or tetryl or lead styphnate.

In addition, there are a few more impact machines which are more relevant for the study of mechanism of initiation of ignition or explosion of HEMs on impact rather than their impact sensitivity. A lot of research in this direction has been carried out at the Cavendish Laboratory, Cambridge University, UK by Bowden, Yoffe, Field and their coworkers [53–59].

1) **Transparent anvil drop weight apparatus (with high speed camera):** This apparatus was originally devised by Blackwood and Bowden [60]. It has more recently been extensively used by Field *et al.* [61–64]. Typically a 25 mg sample of the explosive is compressed between toughened glass anvils with a 'fall hammer' (mass approx. 5.5 kg). The drop weight which carries the upper anvil is dropped from a height up to 1.5 m and is guided by three rods to ensure a planar impact. Shortly before contact, the mirror within the weight comes into alignment to complete the optical path from the xenon flash light source, through to the high-speed camera. The Atomic Weapons Research Establishment (AWRE) C_4 rotating mirror camera used for this purpose is of continuous access variety so that synchronization is not required. The full length of film (140 frames) is scanned in approx. 1 ms so that the duration of the flash also functions as a shutter and all events right from the formation of 'hot spot' to explosion or detonation are recorded on the film.

2) **Instrumented drop weight apparatus:** This drop weight machine is available with instrumented steel anvils. The system rests on a large blacksmith's anvil which provides an almost-ideal rigid support for the load cell which measures the impact force. The cell is a 12.7 mm × 12.7 mm steel roller of in-house design on which two pairs of strain gauges are mounted. An impact cell is formed by two further rollers stacked on top of the load cell and a sample is placed between this pair. The whole arrangement is impacted by a weight of 2.5 or 4.7 kg. The dynamics of the system have been described in detail earlier [65].

The assemblies of the 'transparent anvil drop weight apparatus' and the 'instrumented drop weight apparatus' are shown in Figures 3.12 and 3.13 respectively.

Based on these studies, it is generally thought that the initiation of an explosive is thermal in origin. Mechanical or electrical energy is envisaged as being converted into heat in localized regions by a variety of mechanisms with the formation of 'hot spots'. Four possible mechanisms as described in the literature in detail are:

1) Adiabatic compression of trapped gas spaces.
2) Viscous heating of explosive rapidly extruded between the impacting surfaces or grains.
3) Friction between the impacting surfaces, explosive crystals, and/or grit particles in the explosive layer.
4) Localized adiabatic shear of the explosive during mechanical failure.

The size, temperature and duration of critical hot spots that can cause ignition are interdependent and should have the following characteristics.

- diameter typically 0.1 to 10 μm;
- duration typically 10^{-5} to 10^{-3} s;
- temperatures typically greater than ca 700 K.

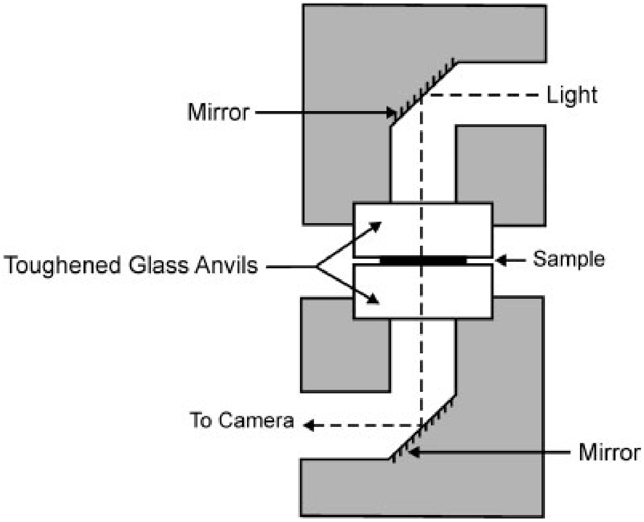


Figure 3.12 Transparent anvil drop weight apparatus. Reprinted with permission from Field, J.E., Swallowe, G.M., Palmer, S.J.P., Pope, P.H., and Sundarajan, R. (1985) Proc. 8th Symp. (Intl) on Detonation; © 1985, Naval Surface Warfare Center, USA.

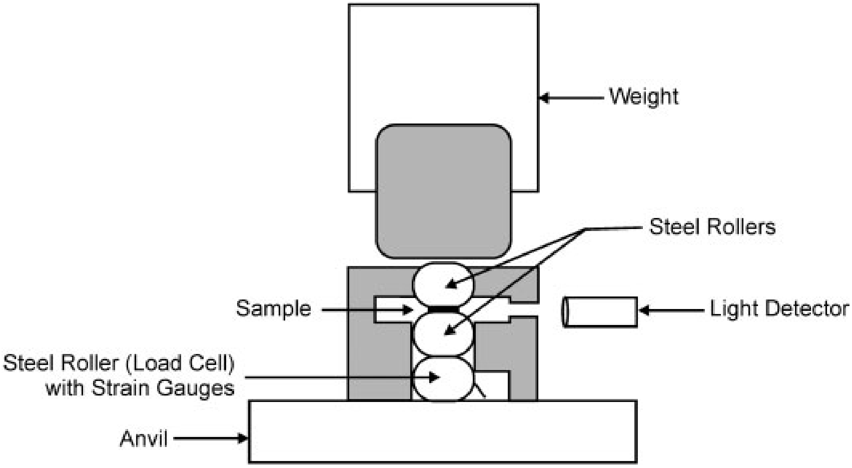


Figure 3.13 Instrumented drop weight apparatus. Reprinted with permission from Field, J.E., Swallowe, G.M., Palmer, S.J.P., Pope, P.H., and Sundarajan, R. (1985) Proc. 8th Symp. (Intl) on Detonation; © 1985, Naval Surface Warfare Center, USA

This has important practical consequences since it means that the processes which produce hot spots of sizes less than 0.1 μm, duration less than 10^{-5} s and temperature less than 700 K would simply cause some decomposition and quench too quickly without producing ignition or explosion.

3.3.2.3 Determination of Friction Sensitivity

During the life cycle of explosives, they are very often subjected to friction either between the explosive particles, or between explosive particles and various types of working surfaces, and this friction is likely to cause initiation of an explosive. Also, a common hazard in the handling of explosives is for them to be subjected to the effects of a blow which is, to some extent, at a glancing angle. This corresponds neither to pure impact nor to pure friction. Also, it is difficult to devise a test which delivers only the friction stimulus without impacting the sample and indirectly heating it by contact with a sliding component in the apparatus.

The determination of friction sensitivity can be carried out using different types of apparatuses discussed at length in the literature which are briefly outlined here.

1) **Pendulum friction apparatus:** This test was developed by the US Bureau of Mines (BoM) and is also used by Picatinny Arsenal [66]. The weight is attached to the lower end of a pendulum which swings down from a height and hits a grooved steel anvil. With no obstruction present, the pendulum can swing freely about 18 times before coming to rest. A small amount of explosive (≈25–30 mg) is spread uniformly over the anvil and the shoe is allowed to hit it from different heights.

   Ten trials are conducted from each height and the number of ignitions are recorded.

   The critical heights where minimum 0/10 and at least 1/10 ignition occurs are recorded and reported.

2) **BAM friction apparatus or Julius Peters friction apparatus:** The BAM method is an improved method and is reported to yield reproducible results. This apparatus is used extensively in Europe [67]. It consists of a rough porcelain plate which is rigidly attached to the sliding carriage of the friction apparatus. A sample (≈10 mg) is uniformly spread on the porcelain plate and a cylindrical shaped porcelain pestle under load rests on top of the sample (Figure 3.14). Loads on the pestle can be varied with the aid of a loading arm. By means of

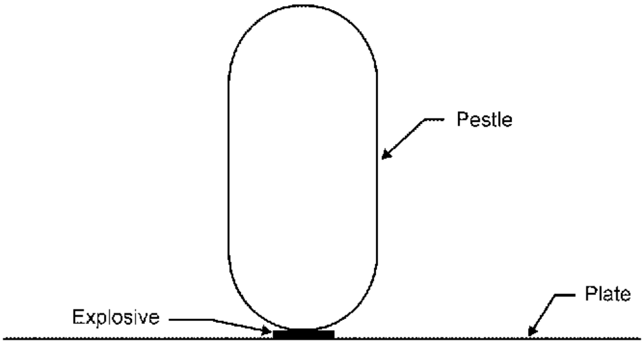


Figure 3.14 Porcelain pestle and plate assembly (BAM friction apparatus).

a motor, the porcelain plate moves forward and backward in arcs of 10 mm, the velocity of rotation being 10 cm s^{-1}. By keeping the load constant on the pestle, the porcelain plate executes a single to and fro motion under the pestle. This is tried with different loads; the smallest load on the pestle under which ignition, deflagration, explosion or crackling is observed, at least once in six consecutive tests, is a measure of friction sensitivity and is expressed in newtons.

3) **Torpedo friction test:** This provides data which is a measure of sensitiveness of explosives to friction and percussion where friction plays a predominating role. The method consists of allowing a torpedo-shaped striker of known weight (≈0.5 to 5.0 kg) made of mild steel to slide down a V-groove set at a selected angle (70° or 80°) on to a weighed quantity of an explosive mounted on a mild steel anvil. Twenty consecutive tests are carried out at each height and the critical heights (minimum and maximum heights where 0/20 and at least 1/20 ignition, decomposition or explosion respectively occurs) are determined [68] which are indicative of friction sensitivity of the explosive.

4) **Friction test for solid and liquid explosives:** The explosive is smeared on a rotating disc on which rests a rod (carrying a known weight) of similar or dissimilar materials. The load employed and also speed of rotation can be varied. The speed of rotation and load are indicative of friction sensitivity. The higher speed (with constant load) and greater load (with constant speed) required for initiation of an explosive in terms of ignition, decomposition or explosion indicate lower friction sensitivity of the explosive. Sometimes, an oscillating plate is also used in the place of a rotating disc.

5) **Friction test by Bowden-Kozlov apparatus:** This was originally devised by Bowden and subsequently modified by Kozlov. A small quantity of explosive

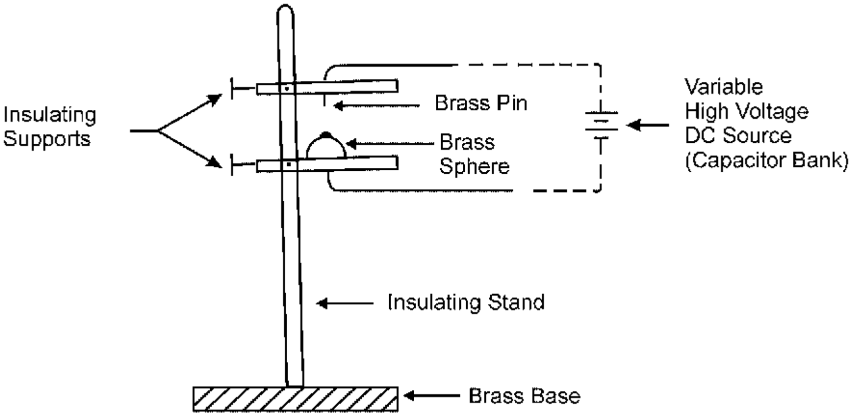


Figure 3.15 Schematic of electrostatic discharge set-up.

is compressed between two rolls by means of a piston actuated by hydraulic press and sliding through a cylinder. The upper roll slides when it is hit by a rod with head, on being struck by a pendulum from a pre-determined height. The pressure on the piston is varied until 50% explosions are observed [69, 70].

3.3.2.4 **Determination of Electric Spark Sensitivity**

The electric spark sensitivity or electrostatic discharge sensitivity of an explosive may be defined as the minimum amount of energy of an electric spark discharge that causes initiation, ignition or explosion of an explosive under test.

There is no standard electrostatic discharge sensitivity test and all apparatuses in current use were designed and fabricated by the laboratories for their own use. However, the basic components of any apparatus include a high voltage supply, an electrical charging circuit, a triggering circuit, an electrode assembly and an electrostatic voltmeter to measure the voltage. Two of the apparatuses commonly used to measure minimum amount of energy are (i) fixed gap method and (ii) approaching electrode method. In the fixed gap method, two electrodes are placed at a fixed distance; the electrodes being either needle-plane, needle-sphere, sphere-plane or parallel-plane. A storage capacitor charged to a desired voltage is discharged between the electrodes. In the approaching electrode apparatus, there is no switch between the electrodes and capacitor. The gap is slowly closed and a discharge takes place at a critical distance. The set-up (Figure 3.15) consists of a capacitor bank of 1150 pF and the DC voltage can be varied using a dimmerstat up to 2 KV. The positive terminal of the capacitor bank is connected to a hemisphere made of brass and the negative terminal to a pin. Approximately 10–15 mg of the sample is placed on the spherical surface and the voltage from the power supply is slowly increased using a dimmerstat. For a fixed distance, sparking occurs at a critical voltage leading to smoke, flame, flash, crackling, decomposition, ignition or explosion. This critical voltage is a measure of electric spark or electrostatic discharge sensitivity of the explosive under test [71–73].

3.3.2.5 **Determination of Shock Sensitivity**

The minimum shock wave pressure that causes complete detonation of the explosive under test is a measure of shock sensitivity of the explosive and is determined with the help of a ‘gap test’. The principle of this test is to subject the explosive under test to the action of a shock wave of known pressure generated by means of a calibrated donor charge and a shock wave pressure attenuator.

The extent of detonation of an explosive, that is, partial detonation or complete detonation is concluded on the basis of mechanical effects: hole cutting in a steel plate, dent depth in a witness steel block or compression of a copper cylinder, produced as a result of detonation of explosive under test. There are several variants of the ‘gap test’ which have been the subject of investigation by several researchers described in the literature [74–77].

3.3.3
Determination of Detonation Velocity

Detonation physics gives an insight into the detonation process. Sometimes, the term ‘detonation’ is confused with ‘explosion’ and gives the impression of a highly disordered process associated with chaos and confusion. However, when studied by high speed instrumentation techniques, detonation appears to be an orderly process, travels with some fixed speed and also follows the laws of physics. Detonation is a process of layer-by-layer propagation of chemical reactions through an explosive and converts the explosive into high pressure and high density products capable of doing work (Figure 3.16). Detonation velocity is defined as the velocity at which the chemical reaction zone propagates through a given explosive and is considered as one of the most important physical detonation parameters.

The determination of detonation velocity is based upon measurement of the time interval needed for the detonation wave to travel a known distance through the explosive under test. The methods used to determine VOD may be classified as mechanical methods (Dautriche method), electrical methods [pin oscillographic technique (POT)], optical methods and radiographic methods. The methods which are generally used for the determination of VOD are:

3.3.3.1 Pin Oscillographic Technique

The POT is a discrete measurement technique using pin type ionization probes as sensors for detecting the arrival time of detonation wave at pre-determined points and measuring propagation time between these points with the help of a high-speed oscilloscope. The schematic of instrumentation set-up is shown in Figure 3.17.

POT essentially consists of the following components.

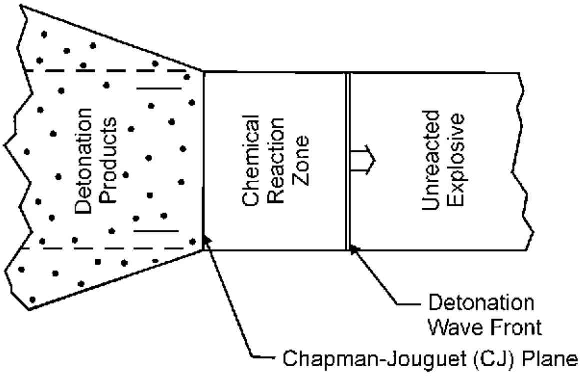


Figure 3.16 Schematic of the detonation process. Reprinted with permission from Suceska, M. (1995) *Test Methods for Explosives*, Ch. 2, © 1995, Springer-Verlag, New York, USA.

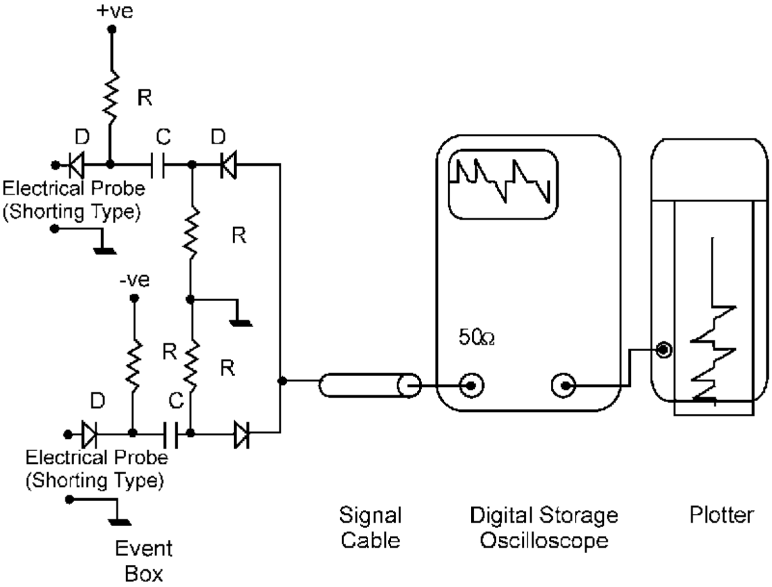
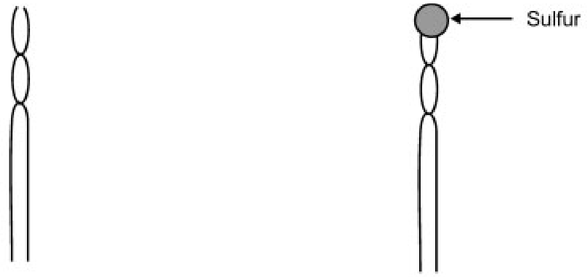


Figure 3.17 Set-up for VOD Determination by pin oscillographic technique (POT).

- probes;
- event box containing resistance capacitance (R-C) network with power supply;
- high speed oscilloscope with plotter.

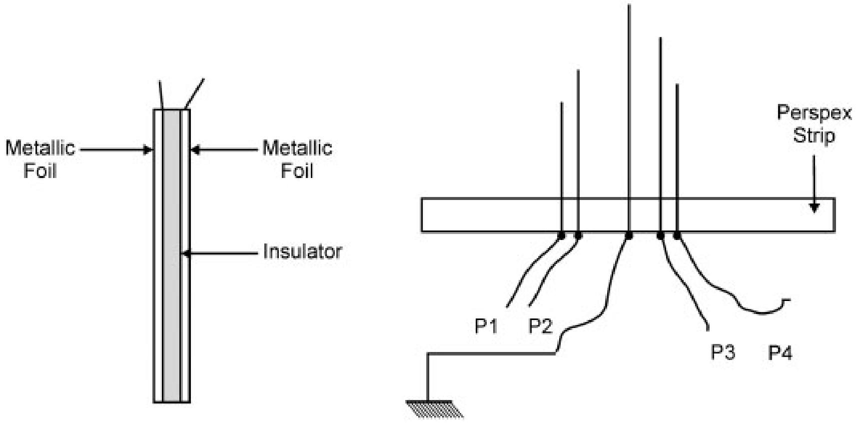
Probes: The probes are of pin type with diameter less than 1 mm which can withstand high pressure and temperature. There are mainly four types of probes which are used depending upon the application (Figure 3.18).

1) **Ionization probes:** These probes are called ionization probes because they get shorted due to the ionization of detonation products. The insulated copper wires of 0.8 mm dia and length 600 mm are taken and twisted together at the center followed by cutting of the twisted ends in the same plane (Figure 3.18a). These are usually inserted and anchored in the test sample to about 2–3 mm depth.
2) **Sulfur probe:** An ionization probe coated with a thin layer of molten sulfur on its conducting tip is used for measurement of shock velocity (Figure 3.18b). This is a special probe which is used in the conducting medium (Sulfur is non-conducting at ambient pressure but becomes conducting at shock pressures as its resistance decreases drastically at such pressures). This property of sulfur allows the R-C network to generate an electrical pulse at the time of arrival of shock wave.
3) **Metallic foil probe:** These probes consist of two thin metallic foils separated by a thin insulator (Figure 3.18c). Aluminum foils are generally used for this



a : Ionization Probe
(VOD Measurement)

b : Sulfur Probe
(Shock Velocity Measurement)



c : Metallic Foil Probe
(Jet Velocity Measurement)

d : Single Wire With Common Earth
(Plate Velocity Measurement)

Figure 3.18 Different types of probes.

purpose. A single aluminum probe is made up of two aluminum foils, each of 0.025 mm thickness and an insulating PVC adhesive tape of 0.075 mm thickness kept in between them. Two such probes are required to measure jet tip velocity.

4) **Single wire probe with common earth**: Such probes are used for the measurement of plate velocity under explosive loading. The configuration of this probe is shown in Figure 3.18d. The pins of suitable heights are fixed on a Perspex carrier in the vertical position. The difference in the heights of pins is measured using dial gauges to an accuracy of 0.01 mm. The tallest one is used as common earth and other pins are connected to the R-C network.

Event Box: It consists of R-C network and a minimum of six sections of such networks are taken in a single event box. The positive power supply is given for three sections of the R-C network whereas negative power supply is given to the remaining three sections of the R-C network. This arrangement facilitates generation of positive and negative pulses. Low noise co-axial signal cable is used to connect these signals to the oscilloscope and properly terminated by a 50 ohm resistance pad to avoid any interference in the signal. A 12-volt power supply or battery is used for this purpose.

High Speed Oscilloscope: Digital storage oscilloscopes having 100/500 MH_z band width and sampling rate of 500 Mega sample per second ($Ms\ s^{-1}$) are being used to capture microsecond detonation events. This has a memory up to 50 Kbytes and the time base can be set from 2 nanosec/div. This has pre-trigger (pre-trigger facility helps in recording the signal without any loss) and post-trigger facilities. The oscilloscopes also have a built-in cursor measurement facility which helps in measuring the period between pulses with accuracy better than 1%. The plotter can be attached to the oscilloscope to have a hard copy record.

The ionization probes are fixed at pre-determined distances in the charge by inserting them 2/3 mm deep and securing with adhesive tape. The other ends of the probes are connected to the event box in such a way that the pulses are generated alternatively in the positive and negative polarities. The distance of the first probe is generally 90 mm from the initiating end to allow the stabilization of the detonation wave. The subsequent probes are fixed along its length at a distance of 30 mm apart. The charge is initiated by an electric detonator through a booster. The probes get shorted on arrival of the detonation wave and the pulses generated by the event box are stored on the high speed oscilloscope. A hard copy can be obtained by using the plotter. A typical oscillogram obtained when detonation velocity is determined using two velocity probes is shown in Figure 3.19. The peaks on the oscillogram correspond to the arrival of the detonation wave at the probes. The time interval needed for the detonation wave to travel the pre-determined distance between two probes is measured using built-in cursors of the oscilloscope. The detonation velocity is then calculated as a quotient of the distance between two probes(*d*) and corresponding time interval (*t*). Similarly the VOD is

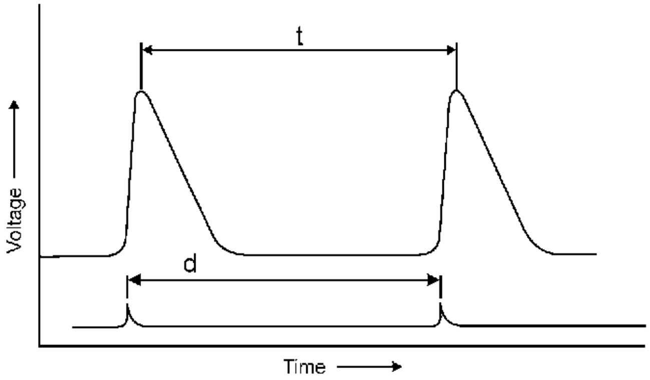


Figure 3.19 A typical oscillogram for determination of detonation velocity.

calculated for each pair of probes and their average is reported as VOD of the sample [78].

Optical methods consist of measurement by different types of high-speed cameras viz. rotating-drum cameras, rotating-mirror or prism framing cameras, rotating-mirror or prism streak cameras and electronic framing or streak cameras. Recently, electronic cameras (with framing and streaking modes) have also been reported for this purpose. In a framing camera, some information is lost in between the frames but the streak camera helps us to reveal that information by continuous writing. The construction details and operating principles of such high-speed cameras which are complex are described in the literature in detail [79] in a lucid manner. The author has given a comprehensive account of all such aspects including methods for VOD determination in that book.

3.3.3.2 **Dautriche Method**

There are some simpler methods which can be applied for the rough estimation of detonation velocity; one such method is known as the 'Dautriche method'. This simple method does not require the use of any special or costly instrument. The determination of detonation velocity is based on the fact that the processes that propagate at different linear velocities travel different distances in the same time. The difference in length of the distance traveled is a simple function of the velocities of these two processes. This method is mainly used for the determination of detonation velocity of commercial explosives. However, the same principle can be applied in order to determine detonation velocities of military explosives. The accuracy of the data obtained by this method is ≈4–5%. The Dautriche method for the determination of VOD of explosives as described by Meyer [80] is illustrated in Figure 3.20.

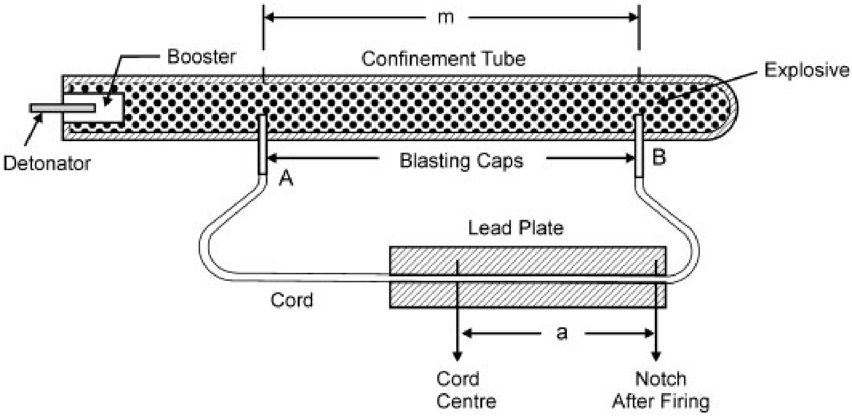


Figure 3.20 Dautriche method for determination of detonation velocity. Reprinted from Kohler, J., and Meyer, R. (1993) *Explosives*, 4th edn, © 1993, Wiley-VCH Verlag GmbH, Weinheim, Germany.

The sample of explosive under test is placed in a confinement tube which may or may not be surrounded by a steel sleeve. The position of two blasting caps along the sample define the part for which the detonation velocity is to be measured. The ends of a piece of detonating cord of known detonation velocity are connected to the blasting caps and the cord is passed across a lead plate as shown in Figure 3.20. The detonation wave in a test sample is initiated by a detonator or booster at the upstream end of the test tube and a steady detonation wave front starts to travel along the confinement tube. As soon as this wave hits the first blasting cap (A), a second detonation wave is instantaneously initiated at the end of the detonating cord connected to that cap. At the same time, the detonation wave in the test sample continues down the confinement tube, and eventually, it reaches the second blasting cap (B) positioned at a distance *m*. This then initiates a third detonation wave at the other end of the detonating cord. Eventually, the two detonation wave fronts in the cord, traveling at equal speeds but in opposite directions, collide and produce a notch in the lead plate at the point of collision. Clearly, the time required for the two opposite detonation waves to travel from the first blasting cap to the collision point at the lead plate is the same [81, 82]. Hence, for the wave going directly into the detonating cord of total length *L*, the time is $[(1/2\,L + a)/D_{\text{cord}}]$ whereas for the other wave, it is $[(m/D_{\text{sample}}) + \{(1/2\,L - a)/D_{\text{cord}}\}]$. By equating these two expressions, we get Equation 3.8

$$\left[\frac{(1/2L+a)}{D_{\text{cord}}}\right]=\left[\frac{m}{D_{\text{sample}}}\right]+\left[\frac{(1/2L-a)}{D_{\text{cord}}}\right] \tag{3.8}$$

$$m/D_{\text{sample}}=2a/D_{\text{cord}} \tag{3.9}$$

or

$$D_{\text{sample}}=D_{\text{cord}}.(m/2a) \tag{3.10}$$

3.3.4
Determination of Detonation Pressure

The VOD is related to the detonation pressure (P_{CJ}) by Equation 3.11:

$$P_{\text{CJ}}=(\rho D^2)/(\gamma+1) \tag{3.11}$$

where ρ = density of the explosive
D = detonation velocity
γ = polytropic exponent of detonation products (≈3 for high explosives)

The VOD may be experimentally determined by any of the methods described in Section 3.3.3 and then approximate P_{CJ} may be calculated using Equation 3.11.

For the accurate determination of detonation pressure (P_{CJ}), a technique of impedance mismatch is applied. The explosive is detonated in contact with water (its ‘equation of state’ is known and is transparent which facilitates record of shock propagation by shadowgraphy technique). Then, after measuring the transmitted shock velocity in water, detonation pressure is calculated by Equation 3.12:

$$P_{CJ} = [P_w(\rho_w U_{sw} + \rho_x D)]/[2\rho_w U_{pw}] \tag{3.12}$$

When water is used as a medium, the Equation 3.12 becomes Equation 3.13:

$$P_w = \rho_w U_{sw} U_{pw} \tag{3.13}$$

where P_w = transmitted shock pressure in water
ρ_w = density of water
U_{sw} = transmitted shock velocity in water
U_{pw} = particle velocity in water
ρ_x = density of the explosive.
D = detonation velocity.

U_{sw} is determined experimentally by the Aquarium Technique and then, U_{pw} is calculated by substituting the values of U_{sw}, a and b in Equation 3.14:

$$U_{sw} = a + bU_{pw} \tag{3.14}$$

where $a = 1.51\,\text{mm}\,\mu\text{s}^{-1}$, $b = 1.85$

Finally, detonation pressure (transmitted shock pressure in water) is calculated by putting the values of U_{sw}, U_{pw} and density of water (which is 1) in the Equation 3.13.

3.3.5
Determination of Strength

The strength of explosives is determined by Trauzl or lead block test. In this test, volume increase produced by the detonation of an explosive under test in the cavity of a soft lead block is measured. This volume increase is a measure of the strength of an explosive. It is a comparative method for determination of strength of an explosive. The principle of this test is illustrated in the Figure 3.21.

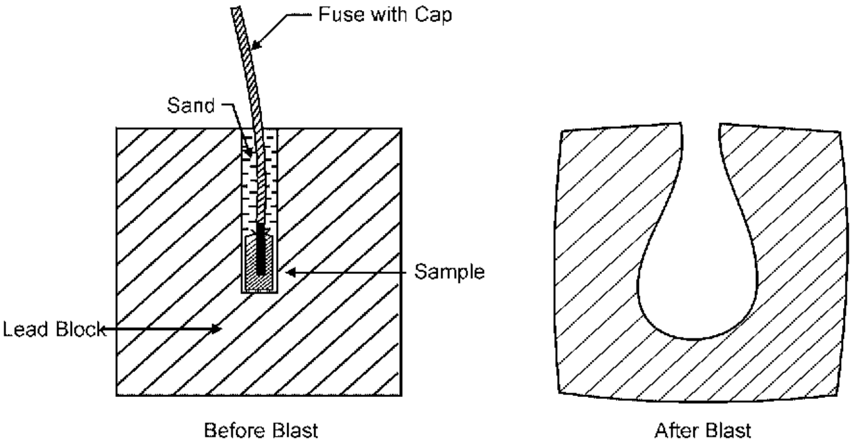


Figure 3.21 Trauzl/lead block test. Reprinted from Meyer, R. *Explosives*, 1987; © 1987, Wiley-VCH Verlag GmbH, Weinheim, Germany.

In this test, a sample of 10 g (wrapped in tin foil) is introduced into a central bore hole (25 mm dia. and 125 mm deep) in a massive cylinder of soft lead block (height and diameter being equal i.e., 200 mm). A blasting cap with a fuse is introduced into the center of the explosive charge (sample) and the remaining free space is filled with dried quartz sand of standard grain size. After explosion, the volume of the resulting bulge is determined by filling it with water. The volume of the original cavity is deducted from the resulting volume. The increase in volume of the central bore is a measure of the strength of explosive. For the purpose of comparison, 10 g of picric acid is used as a standard explosive charge [83, 84]. According to some reports, BAM has modified the Trauzl or lead block test in terms of preparation of sample, which provides better accuracy and reproducible data.

The 'ballistic mortar test' is considered to be the most satisfactory laboratory test for the measurement of the strength of an explosive. The design is based on the American company Du Pont's design which was accepted as an international standard by the International Committee on Standardization of Tests on Explosives, Belgium in 1962. This has been described in detail by Taylor and Morris [85]. Ballistic Mortar (Du Pont Type) is used in the USA in preference to the Trauzl or lead block test which is considered to be a standard test in some European countries and is well known for research on explosives [86].

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4
Propellants

As discussed in Chapter 1, the other name for low explosive is propellant, which may be defined as an explosive material that burns slowly in a controlled manner resulting in a large volume of hot gases. These gases are used to propel a projectile. In other words, propellants are combustible materials containing within themselves the oxygen needed for their adiabatic combustion and their main function is to impart motion to a projectile, that is, a bullet, shell, rocket or missile. Propellants simply burn and do not generally explode or detonate. Propellants are used in guns as well as rockets and are termed gun propellants or rocket propellants accordingly.

4.1
Classification of Propellants

There are several types of propellant which may be broadly classified on the basis of their application and their physical state. Based on their applications, propellants may be classified as gun propellants or rocket and missile propellants and this classification is shown in Figure 4.1.

Another way to classify propellants is in terms of their physical state (Figure 4.2). Yet another way to classify propellants is based on their nature, that is, whether propellants are homogeneous or heterogeneous (Figure 4.3).

For space exploration and military applications, both solid and liquid propellants are used. However, from the point of view of safety, reliability, simplicity and long storage life, solid propellants are preferred over liquid propellants [1, 2].

4.2
Liquid Propellants

As shown in Figure 4.1, liquid propellants are further classified as mono- or bipropellants. The monopropellants are liquids which undergo controlled exothermic decomposition or combustion reactions in the absence of external oxygen. They have comparatively low energy and low specific impulse (I_{sp}) and are used in

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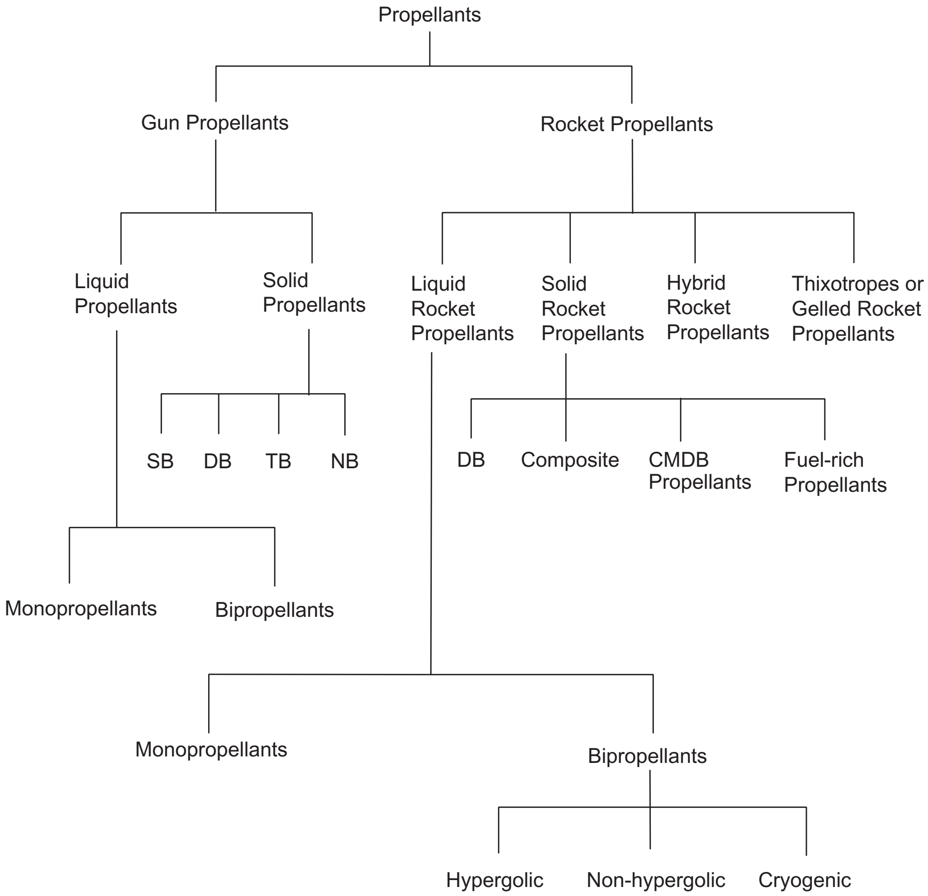


Figure 4.1 Classification of propellants in terms of their applications.

missiles which require low thrust. Examples of liquid monopropellants are isopropyl nitrate, hydrogen peroxide, hydrazine, methyl nitrate and ethylene oxide. However, hydrazine is currently the most widely used monopropellant. The most common liquid propellants are bipropellants. Bipropellants consist of two components – a liquid fuel and a liquid oxidizer, which are stored in separate tanks and injected into a combustion chamber where they come into contact with each other and burn. Some important examples of bipropellants are:

Fuel	Oxidizer
Methanol	Nitric acid (HNO_3)
Kerosene	Nitric acid (HNO_3)
Aniline	Red fuming nitric acid (RFNA)
Ammonia	Nitric acid (HNO_3)

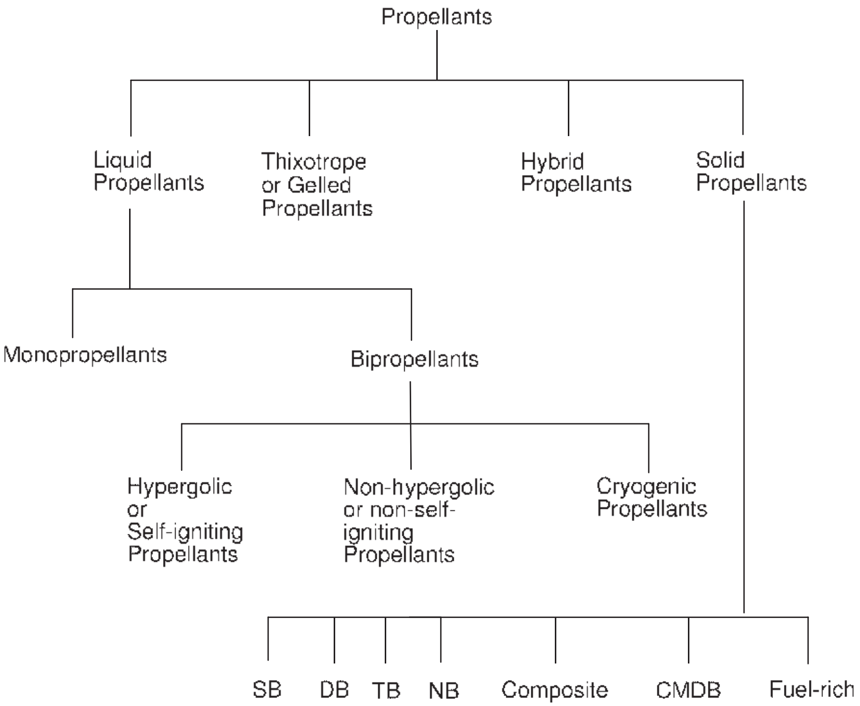


Figure 4.2 Classification of propellants based on their physical state.

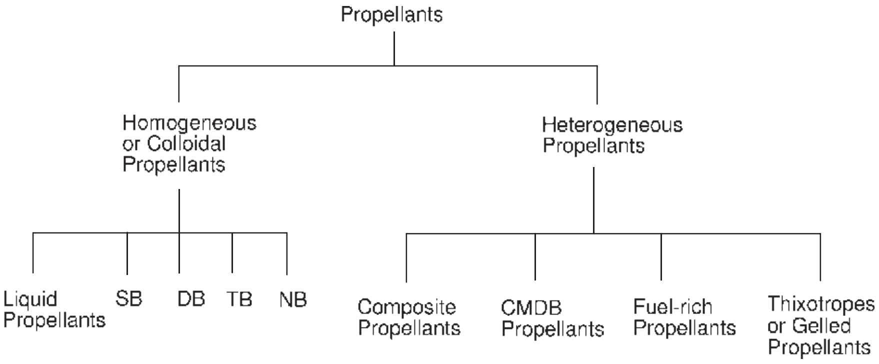


Figure 4.3 Classification of propellants based on their nature.

Hydrazine hydrate	Hydrogen peroxide (H_2O_2)
Hydrazine	Nitric acid/hydrogen peroxide (H_2O_2)
UDMH	Nitric acid/hydrogen peroxide (H_2O_2)/dinitrogen tetroxide (N_2O_4)

Hydrazine gives better performance than hydrocarbons with oxygen, peroxide or nitric acid. Hydrazine does not meet military specification of low freezing point which is achieved with unsymmetrical dimethyl hydrazine (UDMH). UDMH meets the physical properties of a military rocket fuel but gives lower performance than hydrazine as it contains carbon. A mixture of hydrazine and UDMH (50 : 50 also known as Aerozine-50) possesses suitable physical properties and results in better performance. Bipropellants may be hypergolic (self-igniting) or non-hypergolic (non-self-igniting). Since hypergolic propellants do not require a secondary ignition source, they have an added advantage over non-hypergolic propellants. The UDMH–HNO_3 system is hypergolic whereas the gasoline–RFNA system is non-hypergolic but becomes hypergolic when RFNA contains an oxidizing agent such as potassium permanganate ($KMnO_4$).

Most of the liquid propulsion rockets are used where long duration of operation is required. For space missions, usually both oxidizer and fuel used are cryogenic whereas these are non-cryogenic in missiles. Sometimes, a combination is used for space missions, where one component is cryogenic while the other is non-cryogenic. It means that the bipropellant system can be wholly or partly cryogenic. Liquid bipropellants are very powerful systems and are used to power large rockets, space vehicles and some tactical missiles (US Army's Lance battlefield missile). The US Lance missile carries a warhead of 500 kg and it is powered by an UDMH–inhibited RFNA system which is currently the most widely used bipropellant system. UDMH is a derivative of hydrazine and inhibited RFNA is a mixture of nitric acid and dinitrogen tetroxide with about 0.5% hydrofluoric acid to inhibit corrosion of the storage tank.

Today, Russia and China favor a nitrogen tetroxide (N_2O_4)–UDMH system for ballistic missiles and auxiliary engines. On the other hand, the USA started with N_2O_4–(50% hydrazine + 50% UDMH) in the Titan missile. The USA has also used bipropellant N_2O_4–monomethyl hydrazine (MMH) system for several auxiliary engines in many satellites and upper stages. The orbit maneuvring system of the space shuttle uses N_2O_4–MMH system. Many US satellites have also used hydrazine monopropellant for auxiliary engines.

The most widely used cryogenic system which is also a bipropellant, is liquid hydrogen–liquid oxygen (LOX) system. The boiling points of liquid hydrogen and liquid oxygen are −252 °C and −183 °C respectively (at atmospheric pressure) and as a result they are stored in special facilities and filled into the rocket just prior to launch. The main engine of NASA's Space Shuttle and the third stage of the ESA's Ariane IV rocket employ this system.

Russians have done pioneering research in the field of liquid propellants. However, it was mainly directed toward their use in liquid propellant rocket engines (LPREs). They synthesized and tested a new synthetic kerosene (called Sintin) with a higher performance and employed it in a few selected upper stages of space launch vehicles (SLVs) such as Proton. This synthetic fuel in combination with sub-cooled LOX gave about 20 s more I_{sp} than the ordinary LOX–kerosene system, resulting in a substantial increase in the payload. During the last 30 years as a result of a number of trials, they seem to have settled on a few specific propellant combinations, each for a specific category of application:

for example, LOX–kerosene system for LPREs of some SLVs; N_2O_4–UDMH system for military applications, upper stages of SLVs and spacecrafts and power control engines [3]. G-fuel, which is a mixture of xylidine and triethylamine (50/50) in combination with RFNA is used in a number of Indian missiles including the 'Prithvi' missile. A new liquid fuel blend consisting of natural products carene (a distillation product of turpentine) and cardanol [a distillation product of cashew nut shell liquid (CNSL)] in 70 : 30 ratio (by wt.) has recently been reported and exhibits synergistic hypergolic ignition with RFNA and N_2O_4. Some important attributes of this liquid propellant are lower freezing point, higher boiling point, higher density and higher density-impulse compared with most other conventional liquid propellants currently being used. The addition of norbornadiene (a cyclic diene) to the above blend further increases the performance of the propellant. Thus a fuel formulation consisting of carene, norbornadiene and cardanol (40 : 40 : 20, by wt.) with RFNA as oxidizer, holds a tremendous potential as a suitable replacement for G-fuel-RFNA propellant system and trials are in progress [4].

4.3
Solid Propellants

As pointed out earlier, solid propellants are preferred to liquid propellants in view of their safety, reliability, simplicity and long storage life. Solid propellants which are generally used for rockets and missiles are broadly classified into:

1) Homogeneous or colloidal propellants.
2) Heterogeneous propellants.

A brief account of solid rocket propellants is as follows:

4.3.1
Homogeneous Propellants

These propellants are also called colloidal or double-base (DB) propellants and have nitrocellulose (NC) and nitroglycerine (NG) as their principal ingredients. Some ingredients may also be added in small proportions to serve as stabilizer, non-explosive plasticizer, coolant, lubricant, opacifier and burning-rate modifier or other additives to impart desirable properties to the propellants. These propellants are processed into desired shapes by two methods, that is, extrusion and casting. They find wide applications in anti-tank missiles.

Homogeneous or colloidal propellants consist of single, double and triple-base propellants whose salient features are:

4.3.1.1 Single-Base Propellants

A propellant which consists of nitrocellulose (NC) as the only explosive ingredient is called a single-base (SB) propellant. The formulation consists of 90% or more of NC with a nitrogen content of 12.50–13.25%. NC is gelled with the help of a plasticizer such as dibutyl phthalate and stabilized by adding carbamite (which also assists in gelatinization of NC) and then extruded and chopped into the required grain shape and size. The energy content of SB gun propellants (*Q* value) varies from 3100–3700 $\mathrm{J\,g^{-1}}$. SB propellants are used in all kinds of guns from pistols to artillery weapons.

4.3.1.2 Double-Base Propellants

These propellants also contain nitroglycerine (NG) in addition to NC and the proportion of NG depends on the performance desired from double-base (DB) propellants. DB propellants are more energetic than SB propellants and have *Q* value between 3300 and 5200 $\mathrm{J\,g^{-1}}$. There are two disadvantages in the use of DB propellants: higher erosion of the gun-barrel as a result of higher flame temperatures and presence of a muzzle flash which discloses the location of the gun. DB propellants are used in pistols, mortars, rockets and missiles.

4.3.1.3 Triple-Base Propellants

An energetic material nitroguanidine (also called picrite-NQ) is usually added to DB propellants in order to reduce flame temperature and muzzle flash. The proportion of nitroguanidine varies from 50–55% depending on mission requirements. Nitroguanidine is a white crystalline solid which is finely ground before mixing with NC/NG gel to form a homogeneous particulate suspension. The triple-base (TB) propellants have energy values (*Q* values) from 3200 to 3700 $\mathrm{J\,g^{-1}}$, intermediate between SB and DB propellants. TB propellants are used in tank guns and large caliber guns.

4.3.2
Heterogeneous Propellants

These propellants consist of:

4.3.2.1 Composite Propellants

Composite propellants are essentially made up of a fuel or binder and an oxidizer. The binder or fuel constitutes the matrix which retains solid oxidizer such as ammonium nitrate (AN), ammonium perchlorate (AP), ammonium dinitramide (ADN), or hydrazinium nitroformate (HNF) and largely governs their physical properties. The oxidizer acts as a filler. Similar to double-base propellants, the plasticizer may be inert or energetic in nature. For a higher specific impulse (I_{sp}), a higher oxidizer loading is necessary, but this adversely affects the physical properties of propellants. The most widely used oxidizer is still ammonium perchlorate (AP). A number of binders or fuels such as castor oil (CO), polypropylene glycol (PPG), carboxy-terminated polybutadiene (CTPB), hydroxy-terminated polybutadiene (HTPB) etc. are available and the choice depends upon availability, cost, ease of processing and specific impulse required. The I_{sp} can be substantially increased by incorporating aluminum or magnesium powder in propellant formulations.

Aluminum powder (18–22%) gives better I_{sp}. Compounds such as Prussian blue, ammonium dichromate, copper chromite, ammonium sulfate, ferric oxide etc. are used as ballistic modifiers for composite propellants. Polybutadiene prepolymers are considered as high energy fuels for composite propellants. HTPB is a late entrant in this field and permits solids loading up to 91% and still retains mechanical properties within the acceptable limits. Because of the high reactivity of hydroxyl groups in all hydrocarbon environments, HTPB should be processed carefully to avoid premature curing. All polybutadienes are subject to air oxidation with subsequent hardening during storage. Partial or total hydrogenation resulting in hydrogenated HTPB solves this problem but introduces other problems such as higher viscosity and higher glass transition temperature (T_g) with consequent poor low temperature properties. A new polybutadiene prepolymer with lactone terminals called lactone-terminated polybutadiene (LTPB) has been developed by Rao *et al.* [5].

The ageing and low temperature properties of LTPB-based propellants have been reported to be comparable to the conventional CTPB-based propellants. Composite propellants possess higher densities (1.75–1.81 $\mathrm{g\,cm^{-3}}$), higher specific impulse and a wide range of burn rates (7–20 $\mathrm{mm\,s^{-1}}$). Such propellants are generally made by the 'casting technique'. Extruded composite propellants are also currently available.

India's four-stage Satellite Launch Vehicle-3 (SLV-3) which put the Rohini Satellite in orbit on July 18, 1980 used a composite propellant based on terpolymer of butadiene-acrylic acid–acrylonitrile (PBAN) for the first and second stage motors whereas LTPB-based composite propellant was used for the third and fourth stage motors [6].

4.3.2.2 **Composite Modified Double-Base Propellants**

In composite modified double-base propellants (CMDBs), significant amounts of crystalline oxidizer (ammonium perchlorate) and metallic fuel (aluminum powder) are incorporated in a DB propellant matrix resulting in highly energetic propellants. If casting is used for their manufacture, these two ingredients are incorporated in the DB casting powder. These propellants may also be manufactured by a 'slurry cast technique' and an 'inert diluent process' as described in the literature [7]. CMDB propellants are characterized by high energy output (I_{sp}: 260–270 s) coupled with higher combustion temperatures.

4.3.2.3 **Fuel-Rich Propellants**

Fuel-rich propellants (FRPs) with high metal content find use in ram-rockets which operate with the combustion of fuel-rich hot gases generated in the primary chamber or combustor and ram air inducted from atmosphere to a secondary chamber or combustor for full combustion. The rocket system where energy for propulsion is derived in such a manner is termed an integrated rocket-ramjet (IRR). The major benefit of a ram-rocket is substantial reduction in the weight of rocket or missile as the oxidizer need not be carried along with the propellant fuel. Fuel-rich propellant formulations for ram-rockets consist of metal fuels, binder and minimum quantity of oxidizer to ensure sustained combustion. The formulations are prepared and grains are made by extrusion or casting technique [8, 9] but the formulations containing higher solids (>92%) are generally processed by mixing various ingredients followed by pressing in the desired form.

AP is the most commonly used oxidizer for fuel rich propellants. AN is used where a high rate of gas generation is the prime requirement. Sometimes, sodium nitrate also finds application due to its high density, oxygen availability, heat of combustion and affinity of its exhaust species with ram-air. HMX-based fuel-rich formulations which give better performance, are also available.

Polybutadienes (PBs) are the preferred choice as binders for fuel-rich propellants among various polymeric binders. The major advantages of PBs are: superior structural integrity, high load-bearing capability, clean crosslinking reactions and high fuel value [10]. Recently, azide polymers such as GAP, poly(BAMO) and copolymer of BAMO and NiMMO are also emerging on the scene as potential energetic binders for this purpose [11, 12]. The most important attribute of azide polymers is their positive heat of formation (28–42 kcal mol^{-1}) which results in exothermicity during binder degradation. On the other hand, decomposition of PBs is an endothermic process which results in heat sink effect.

Some investigators have also reported Teflon, polyvinylidene fluoride etc. as binders for Mg-based pressed formulations. Hydrocarbons like naphthalene, anthracene etc are also employed for this purpose. Naphthalene sublimes at a low temperature and combustion affinity of exhaust species with ram-air helps in ejecting the condensed particles through the nozzle.

The invention of Lo *et al.* is directed to the manufacture of a fuel-rich solid propellant gas generator for an air-augmented rocket system. The fuel of choice is boron whereas the binder is based on an energetic, thermally stable polymer of a dinitrofluoromethyl epoxide. As opposed to conventional fuel-rich solid propellant gas generator systems based on non-energetic binders wherein solid oxidizer is added to achieve satisfactory burning of the grain in the primary motor, the boron-rich solid propellant gas generator system of this invention requires no addition of solid oxidizer since the binder is energetic. However, high flexibility in the ballistic properties of the gas generator can be achieved by the addition of solid oxidizer.

The most important attributes of this invention are high impulse performance coupled with high exit temperature on primary combustion and favorable boron species in the primary motor exhaust. The system is also insensitive to impact and possesses excellent thermal stability at elevated temperatures. Additionally, the system is readily castable since the addition of solid oxidizers is not required. Further, high flexibility in the ballistic properties of the gas generator can be achieved by the addition of solid oxidizers such as ammonium nitrate, ammonium perchlorate, hydroxylammonium perchlorate, potassium perchlorate, lithium perchlorate, calcium nitrate, barium perchlorate, RDX, HMX etc. The oxidizers are preferably powdered to a particle size of about 10 to 350 microns [13].

4.4
Hybrid Propellants

These propellants consist of solid and liquid component substances in the same system, that is, a combination of solid and liquid propellants. The most widely used hybrid propellant has a hollow solid fuel grain (similar to solid propellant grain) but without oxidizer. The fuel grain may contain energetic solid substances also. The oxidizer is generally a storable liquid such as nitrogen tetroxide or chlorine trifluoride. The fuel grain based on the HTPB–TDI system is very popular for use in hybrid rockets. Some literature reports suggest the use of guanidinium azotetrazolate (GAT) as an additive for HTPB–PAPI (polyisocyanate) system. The addition of GAT improves the regression rate of HTPB fuel grain in hybrid rockets as much as 150% compared with plain HTPB [14].

This system is very rarely used though it has certain advantages; it has not found much favor with missile designers the world over. The use of hybrid propellants extends the range but poses additional engineering and combustion related problems. Figure 4.4 shows a simple hybrid rocket motor.

4.5
Thixotropic Propellants

Thixotropic gels are also useful as propellants for rocket applications. These are commonly called thixotropes or gels. Normal fuels and oxidizers are converted into thioxotropes by the addition of a small quantity of a gelling agent in order to ensure uniform suspension of solid additives (usually metal additives) during storage. It is reported that if very finely pulverized particles of beryllium or aluminum are suspended in the liquid fuel, it is possible to increase the specific impulse substantially.

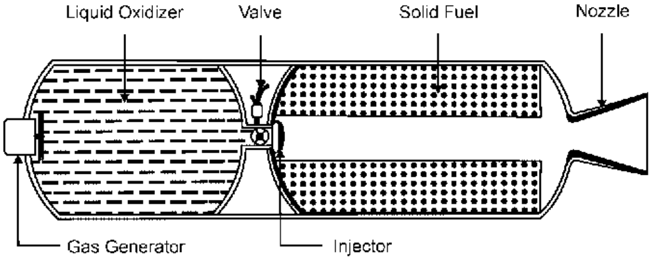


Figure 4.4 A Typical hybrid rocket motor.

4.6
Performance of Propellants

4.6.1
Gun Propellants

A gun is a heat engine in which the chemical energy of the propellant is transformed into kinetic energy of the projectile and the aim to achieve high projectile velocities has been the driving force for gun research. High muzzle velocity directly results in decrease in the time of flight, increase in range, better target penetration, increase in hit probability and magnification of terminal ballistic effects on the target. However, increasing the muzzle velocity may lead to hazards such as increase in blast-over pressure due to rapid displacement of the surrounding atmosphere, violation of safety criteria for gun crew and nearby structures due to high pressure blast waves, improper control of projectile stability and flight behavior, increase of projectile ablation and projectile disintegration as a result of high velocity impact on the target.

The performance of the gun depends on fixed factors such as (i) bore length and diameter; (ii) chamber configuration and its volume, and variable factors such as (i) nature of ammunition; (ii) projectile weight; and (iii) propellant type and its formulation. The gun-propellant system ultimately decides the attainment of maximum pressures. The area under the pressure–time (*P*–*t*) curve is proportional to the projectile velocity achieved by the combustion of the propellant. A propellant which would produce a *P*–*t* curve that would rise quickly to its peak pressure, remain at this value until the completion of combustion of the entire propellant and then fall to zero through adiabatic expansion of the gases, is always preferred. The reason is that this maximizes the area under the *P*–*t* curve and thus maximizes the muzzle velocity. But in reality, the combustion of propellant produces a *P*–*t* curve that rises gradually to peak pressure, remains at this value for only a short time, and gradually drops to zero through expansion of the gases. A gun propellant is considered to be performing well if it produces 85–90% of its maximum potential velocity. Thus, the performance of a gun to a large extent, depends on the propellant.

The propellant is the most vital sub-system of a gun and rocket or missile system and accordingly, the performance of a gun, rocket or missile mainly depends on the propellant used. Some basic performance parameters are used to define the characteristics of these propellants and they are different for gun and rocket propellants.

The major ballistic performance parameters of a gun propellant are its energy expressed in terms of force constant and burning rate coefficients α, β and β_1.

4.6.1.1 **Force Constant**

The force constant is a chief performance parameter of a gun propellant and is defined as the maximum amount of work done by the unit mass of propellant. It is denoted by F or it may be defined as the energy released by the decomposition of unit mass of propellant. This is defined by Equation 4.1:

$$F = nRT_o \tag{4.1}$$

where R = universal gas constant
T_o = adiabatic flame temperature and
n = number of moles of gas in the products per unit mass of propellant

The closed vessel (CV) is used to obtain the values of F and co-volume experimentally by firing the propellant charge at a given loading density. Also, from the measurement of rate of pressure rise, one can calculate the propellant burning rate characteristics. The most extensively used CV is the 700 cm^3 capacity based on the UK design. The testing of propellant in a CV is cost-effective compared with the gun as only about 200–300 g of propellant is sufficient to carry out each firing as against the latter wherein the quantity of propellant required could be in kilograms. The CV technique is also used for controlling the quality of propellant during manufacture or for assessing the usefulness of the propellant during its life by comparison with the known standard propellant.

4.6.1.2 **Burning Rate Coefficients**

1) The propellant burns in terms of 'Piobert's Law' which suggests that the propellant burns in parallel layers (layer by layer) from the exposed surface in a direction perpendicular to the surface. As a natural consequence, it tends to retain its original shape till it is consumed.

2) The burning rate (r) depends on the pressure (P) at the burning surface and is given by the equation $r = \beta P^{\alpha}$ where β = burning rate coefficient and α = pressure index. These coefficients, that is, β and α are constants for a particular propellant formulation. The value of α is in the range of 0.8 to 0.9. The burning rate (r) is controlled by various parameters such as pressure, calorific value, density, thermal conductivity, initial propellant temperature, particle size of crystalline ingredient, content of volatile matter and degree of gelatinization of NC in the propellant etc.

4.6.1.3 **Vivacity**

The way in which a given propellant charge behaves in respect of its mass burning rate during combustion under adiabatic conditions is called 'vivacity'. It is also experimentally determined by CV and given by the ratio β/D where β = linear burning rate coefficient and D = propellant web size.

4.6.1.4 **Muzzle Velocity**

Muzzle velocity (MV) is defined as the velocity at which a projectile leaves the muzzle of a gun. MV is considered to be the maximum velocity of a projectile when it emerges from the bore. As it is very difficult to determine the velocity close to the muzzle, the usual practice is to measure it at a short distance from the muzzle, for example, 23.77 m (78 ft) and then either to correct back to the muzzle for the retardation in flight (as is done for artillery ammunition) or to take it as such (usually done for small arms ammunition). MV is calculated theoretically by means of equations or determined experimentally through the use of chronographs.

4.6.1.5 Efficiencies of Gun System and Charge

Two parameters, that is, piezometric efficiency and ballistic efficiency are commonly employed in order to evaluate the overall performance of a particular gun-charge-projectile system and are defined in the following manner.

1) **Piezometric efficiency:** Piezometric efficiency is defined as the ratio of the mean pressure and the maximum breech pressure. The mean pressure is taken as that pressure which, if uniformly exerted upon the projectile over the entire length of the bore, will produce the observed muzzle velocity. Thus (Equation 4.2):

$$\eta_p = \frac{(1/2)MV_P^2}{A_S.S.P_{BM}} \tag{4.2}$$

   In general, the pressure-travel curve becomes flatter with higher piezometric efficiency.

2) **Ballistic efficiency:** Ballistic efficiency is defined as the ratio of the total work done upon the projectile to the total work potential of the propelling charge, that is, (Equation 4.3):

$$\eta_b = \frac{(1/2)M_E V_P^2}{E_{in}} \tag{4.3}$$

where η_p = piezometric efficiency
η_b = ballistic efficiency
M = mass of the projectile, kg
V_P = projectile muzzle velocity, ms^{-1}
A_s = cross-sectional area of bore, m^2
S = shot travel distance, m
P_{BM} = maximum breech pressure, Nm^{-2}
M_E = effective mass of projectile, kg
E_{in} = total energy content of the propellant, J

A high ballistic efficiency can be obtained by burning the propellant charge as early as possible in the projectile's traverse of the gun bore thereby reducing residual muzzle pressure.

4.6.2
Rocket Propellants

Rockets use the principle of jet propulsion. This is the application of Newton's famous Third Law of Motion that 'action and reaction are equal and opposite'. If a fluid is ejected from a vessel through a nozzle at a high velocity, then the force causing it to be ejected results in an equal force in the opposite direction propelling the vessel in a direction which is opposite to the ejecting fluid. The term 'rocket' is nowadays used to refer to the complete flying object while the actual device in which chemical energy is transformed into energy of motion is called the 'rocket motor'.

Different classes of solid propellants: DB, CMDB, and fuel rich (FR) have been developed in order to meet the requirements of various missions in terms of specific impulse (I_{sp}) and wide range of burn rates with low pressure index (n). High density, low temperature sensitivity and good mechanical properties constitute other essential requirements of these propellants. The salient features of such performance parameters are:

4.6.2.1 **Burn Rate**

The efficiency of a propellant for a specific application depends to a large extent on its burn rate while its usefulness depends on burn rate–pressure relationship. A solid propellant burns at the surface and as the burning proceeds, the burning surface recedes layer by layer, which are parallel to each other and the general geometric configuration of the burning surface is maintained until the web of the grain (web thickness is the minimum thickness of the propellant that must be consumed during combustion) is burnt through. This is known as Piobert's Law (Equation 4.4):

$$\text{Linear burn rate}\,(r) = \frac{\text{Web thickness}}{\text{Time of burning}} \tag{4.4}$$

Generally, burn rate increases or decreases as the pressure is raised or lowered. It is also influenced by the temperature of the propellant and increases with an increase in temperature whereas decreases with a decrease in temperature. It is therefore necessary to fix higher as well as lower temperature limits at the time of development of a propellant keeping in view the mission's requirements. The specified temperature limit for Service applications has been stipulated as −40 °C to +60 °C in India. Burn rate also depends upon the calorific value of the propellant and, other things being equal, the higher the calorific value, the higher the burn rate of the propellant.

The exponential form of burn-rate law (known as Vielle's Law, Equation 4.5), that is,

$$r = aP_c^n \tag{4.5}$$

where r = burn rate which mainly depends on the chamber pressure and initial temperature of the propellant.

P_c = chamber pressure

a = a coefficient which depends on the initial temperature of propellant and ranges from 0.05–0.002.

n = pressure index or exponent and is a function of propellant formulation.

The burn rates of propellants are determined in a strand burner (Crawford bomb/acoustic emission technique) at various pressures using an inert gas for pressurization. This data, when fitted in the empirical relation $r = a.P_c^n$ provides the pressure index n and the coefficient a. This technique is highly useful as a first approximation and is extensively used for propellant screening and quality control. The burn rates at different pressures are also determined by static testing in a ballistic evaluation motors (BEMs) and burn rates are typically scaled up from 1–5% for full scale motors.

The pressure exponent (n) is the characteristic of a specific propellant and also depends on the pressure range. For DB propellants, it is in the range from 0.2 to 0.5 but AP-based composite propellants exhibit relatively low values (0.1 to 0.4). The mathematical derivations clearly show that the value of n can never exceed 1 and a value close to 0 (zero) is always preferred from safety considerations.

The pressure exponent or index is a very important parameter and plays a vital role during rocket operation. The important implications of the value of n are as follows:

1) The effect of variation on chamber pressure due to burning surface (voids or fissures etc) will be minimum if n has a small value.

2) The smaller the value of n, the quicker will the pressure return to equilibrium, that is, a low value of n will allow the design of light-weight rocket motors. Constant n is a measure of the dependence of r on P_c. A value of n of 0.80 indicates a strong dependence of r on P_c, while that of 0.20 indicates relatively low dependence. This is very important because if for some reason P_c increases and n is large, the r increases and P_c rises still further. The cumulative effect of such variations easily lead to rocket motor burst or failure.

4.6.2.2 **Thrust**

The reaction force (F) exerted by the ejection of combustion gases from the rocket nozzle is called 'thrust' and is expressed by Equation 4.6:

$$F = \dot{m}V_e + A_e(P_e - P_a) \tag{4.6}$$

where $\dot{m}$ = mass flow rate
V_e = velocity of gases at nozzle exit
A_e = nozzle exit area
P_e = nozzle exit pressure
P_a = surrounding atmospheric pressure.

The thrust of a rocket motor is measured statically by using load cells where axial thrust is generally measured. A rocket motor is mounted on a trolley placed on rails and the load cell fixed at the head end of the rocket is butted against the thrust block to measure the axial thrust.

4.6.2.3 **Specific Impulse (I_{sp})**

Specific impulse (I_{sp}) is the most important single ballistic property for rocket propellants and its value is of utmost significance for the determination of propellant mass necessary to meet the ballistic requirements. It is defined as the thrust per unit weight flow rate of propellant ($\dot{w}$) (Equation 4.7).

$$I_{sp} = F/\dot{w} \tag{4.7}$$

I_{sp} of a propellant is also a function of chemical parameters and can be calculated according to Equation 4.8:

$$I_{sp} = K\sqrt{nT_C} = K_1\sqrt{T_c/M} \tag{4.8}$$

where K and K_1 are different constants
T_c = flame temperature
n = number of moles of gas produced per unit mass of propellant
M = average molecular mass of gaseous products of combustion.

I_{sp} is also related to the characteristic exhaust velocity (C^*), calculated from the P–t profile, according to Equation 4.9:

$$I_{sp} = C^*(C_F/\mathbf{g}) \tag{4.9}$$

where C^* depends on propellant formulation but is independent of the motor used for firing. C_F is thrust coefficient (ratio of thrust to the product of chamber pressure and nozzle throat area, that is, C_F = ($F/P_c.At$) and depends upon the nozzle design. Its value ranges from 1.1 to 1.8 for chemical propellants and **g** stands for gravitational force. It is usually determined by measuring total impulse and dividing it by the weight of the propellant. The total impulse is given as the integral of the thrust (F) over the useful burning duration and therefore, (Equation 4.10):

$$I_{sp} = {}_0\!\int^{t10} F.\mathrm{d}t\Big/w \tag{4.10}$$

where w is the propellant weight. I_{sp} is usually called 'Figure of Merit' of a given combination of motor and propellant grain.

4.6.2.4 **Chamber Pressure**

The force exerted by combustion gases per unit area inside the rocket motor is called chamber pressure and is denoted by P_c. Rockets generally operate in the pressure range of 70–140 kg cm^{-2} and large rocket motors are designed to operate at lower pressures to reduce the chamber weight. For a given propellant configuration, the ratio of surface area to nozzle throat area controls the chamber pressure. A pressure gradient usually exists in rocket motors. Chamber pressure is measured by using strain gauges.

4.6.2.5 **Characteristic Velocity (C^*)**

Characteristic velocity (C^*) is defined as the ratio of the product of the chamber pressure and throat area to the mass flow rate, that is, (Equation 4.11):

$$C^* = \frac{P_c At}{\dot{m}} \tag{4.11}$$

It is denoted by C^* and depends on the flame temperature, mean molecular mass of the combustion products and propellant formulation. It is a fundamental parameter which gives the energy available on combustion and can be used to compare the efficiency of different chemical reactions independently of the P_c. For propellants, the value of C^* ranges between 1200 and 1600 $\mathrm{ms^{-1}}$. It is determined by firing a propellant grain in a motor and evaluating the area under the P–t profile and using Equation 4.11.

4.6.2.6 **Temperature Sensitivity**

The temperature sensitivity of a propellant is always discussed in connection with:

1) the initial temperature sensitivity of the burn rate r (at constant pressure), $(\pi r)_p$;
2) the initial temperature sensitivity of the chamber pressure (at constant k_N), $(\pi p)k_N$ or $(\pi p)k$.

Temperature sensitivity is a measure of change in burn rate with respect to initial temperature of propellant at constant pressure. It is designated as $(\pi r)_p$ and is derived from Vielle's equation, that is, the mathematical derivation of $(\pi r)_p$ is (Equation 4.12):

$$(\Pi r)_p = \frac{(r_1 - r_2)}{(r_1 + r_2)/2} \cdot \frac{100}{(T_1 - T_2)} \tag{4.12}$$

where r_1 = burn rate at temperature T_1
r_2 = burn rate at temperature T_2
T_1 = conditioning temperature of hot firing
T_2 = conditioning temperature of cold firing

$(\pi r)_p$ represents the variation of the burn rate per unit temperature and expressed in percent per degree. Its value ranges from 0.1 to 0.4 percent per kelvin. Composite propellants having higher self-ignition temperatures are less temperature-sensitive than DB propellants.

The chamber pressure of the motor also changes due to the change in initial temperature of propellant for a fixed nozzle. This coefficient (temperature sensitivity of pressure at constant k) is expressed as (Equation 4.13):

$$(\Pi_p)_k = \left[\frac{\mathrm{d}\ln p}{\mathrm{d}T}\right]_k \tag{4.13}$$

$(\Pi_r)_p$ and $(\Pi_p)_k$ are related by (Equation 4.14):

$$(\Pi_p)_k = \frac{1}{(1-n)} \cdot (\Pi_r)_p \tag{4.14}$$

These parameters are determined by testing BEMs conditioned at the required extreme operational temperatures [15].

The temperature sensitivity is an important parameter of the propellant. It is now well known that low values of temperature sensitivity are essential in order to reduce the cost of the missile or armament system in addition to the uniform performance over a wide range of temperatures. Based on temperature sensitivity data, designers cater for variations in operating pressures in order to provide a sufficient margin of safety. Thus higher temperature sensitivity produces greater variation in operating pressures whereas lower temperature sensitivity results in less variation.

For conventional propellants, it is well known that r increases with increase in chamber pressure (P_c) and gives a straight line on plotting log r against log P_c. (Figure 4.5).

It has been reported that there is a marked increase in r up to a critical pressure range on adding a lead salt to the propellant formulation. Above this pressure range, r becomes independent of P_c for a limited pressure range; for still higher pressures, however, r again increases comparable with that of an unplatonized propellant, that is, propellant without a lead salt (Figure 4.5). The region where r is independent of pressure rise is known as 'plateau' and this process in known as 'platonization'. The compounds which lead to this phenomenon are termed 'platonizing agents'. The curve also shows a fall in the value of r with an increase in P_c which means a negative value of n and this is known as the 'mesa' effect. The addition of 0.5 to 1.0% basic lead stearate gives optimum platonizing effect in DB propellants and higher percentage of lead salt shifts the plateau to lower pressure regions in the curve. The addition of carbon black to propellant formulations platonized with lead salts results in higher plateau region. PbO is the only additive to produce the 'mesa' effect. A large number of ballistic modifiers and their effect on r are discussed in Section 4.9.7.1 on ballistic modifiers.

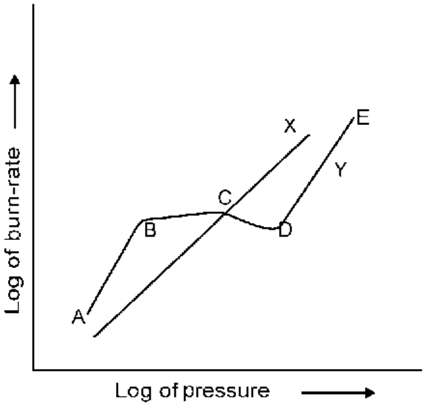


Figure 4.5 Graphical presentation of burning characteristics of propellants.
X-Uncatalysed Propellant and Y-Catalysed Propellant
A-B: Super Burn-rate; B-C: Plateau Region; C-D: Mesa Region; and D-E: Post-Plateau Region.

4.7
Formulation of Gun Propellants

Gun propellants (GPs) are also sometimes called smokeless powders in order to differentiate newly developed NC-based propellants from the traditional gunpowders. They are largely smokeless on firing but are not 'powders' in the ordinary sense of the word and are being produced in different sizes and shapes such as flakes, ribbons, spheres, cylinders or tubes. Conventional gun propellants consist mainly of mixtures of NC or NC and NG or NC, NG and NQ and accordingly, termed single-base, double-base and triple-base gun propellants. These propellants in addition contain a plasticizer, a stabilizer and small amounts of other additives in order to improve processing, life, burn rate and other desirable properties depending on requirements. These propellants are formulated using these ingredients and processed to give different shapes by extrusion technique. Some typical shapes of gun propellants are shown in Figure 4.6.

Gun propellants are formulated on the basis of:

1) The ballistic requirements of a gun, that is, muzzle velocity (V_p) and pressure (P).
2) Gun characteristics viz caliber or bore diameter, shot travel or barrel length, effective chamber capacity and ballistic efficiency of the gun (η_b).
3) Projectile mass (M).

On basis of the above data, the force constant (F) for propellants is arrived at by using Equations (4.15) and (4.16)

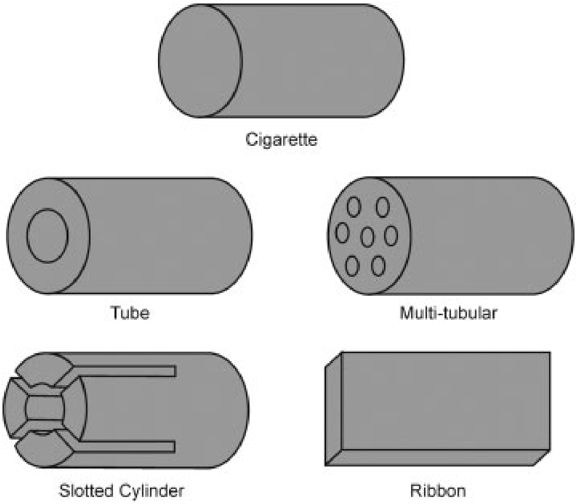


Figure 4.6 Some typical shapes of gun propellants. Reprinted with permission from J. Akhavan, *The Chemistry of Explosives*, 2004; © 2004, The Royal Society of Chemistry, UK.

$$\text{Ballistic efficiency of the gun } (\eta_b) = \frac{(1/2)MV_p^2(\gamma-1)}{F.C.} \tag{4.15}$$

$$F = \frac{(1/2)MV_p^2(\gamma-1)}{\eta_b \cdot C} \tag{4.16}$$

where F = force constant
M = mass of the projectile
V_p = projectile muzzle velocity
η_b = ballistic efficiency
γ = specific heat ratio, that is, C_p/C_v
C = propellant charge mass

A large number of formulations are available for use; the formulation is decided and tailored depending on the requirements of users. However, no single formulation meets all requirements of the user. An ideal gun propellant should possess most of the following properties.

- The raw materials used should be cheap, available in abundance and the process of manufacture should be easy, rapid and safe in all respects.
- Capable of easy and rapid ignition and have low flame temperature.
- High force constant and minor variation of burning rates over a wide range of temperatures.
- Low sensitivity to all modes of initiation: heat, hot spall, impact, friction etc.
- Minimum tendency to produce flash, smoke and toxic fumes.
- Long shelf-life under field conditions.

4.8
Ingredients of Gun Propellants

The gun propellant formulation usually contains one or more energetic compounds as main ingredients. In addition, it includes minor quantities of plasticizer, stabilizer, inorganic salt, surface moderant, ignition improving agent, flash reducing agent, decoppering agent, gun wear reducing agent etc. Some important ingredients are:

- Energetic compounds: NC, NG, picrite, RDX etc.
- Plasticizers: phthalate esters (DEP, DBP, DOP), TA, NG, liquid nitro/azido compounds etc.
- Stabilizers: DPA, carbamite, methyl centralite, 2NDPA etc.
- Coolants: dinitrotoluene (DNT), TNT, carbamite, mineral jelly etc.
- Flash reducing agents: K_2SO_4, cryolite, potassium nitrate etc.
- Inorganic salts: $CaCO_3$. MgO etc.
- Ignition improvement compounds: $Ba(NO_3)_2$, KNO_3, camphor, carbon black etc.
- Surface moderants: carbamite, camphor, DNT, methyl centralite etc.

Table 4.1 Important characteristics of solid gun propellants.

	Single-base	Double-base	Triple-base	Nitramine-base
Density/g cm^{-3}	1.58	1.61	1.62	1.65
Cal val./Cal g^{-1}	700–800	720–1200	750–900	800–1100
Flame temperature/K	2500–3000	2600–3600	2400–3300	2900–3200
Force constant/J g^{-1}	940–1020	940–1180	950–1140	1000–1200

- Decoppering agents: tin, lead-tin foil or lead compounds etc.
- Wear reducing agents: TiO_2/wax, polymer/wax, talc/wax etc.
- Antistatic surface coating material: graphite.

Gun propellants are manufactured by three different methods: (i) solvent method; (ii) semi-solvent method; and (iii) solventless method. The solvent method is that most commonly used for the manufacture of gun propellants. Selection of the method for manufacture basically depends on the properties of the raw materials and the propellant formulation. While there are limitations for the manufacture of gun propellants by solventless and semi-solvent methods, the solvent method may be applied for almost every gun propellant formulation. The solid–liquid ratio of the ingredients and the type of nitrocellulose used usually decide the feasibility of manufacture by the solventless method. Some characteristics of solid gun propellants are given in Table 4.1.

In addition, there are some other types of solid gun propellants which may be categorized as:

4.8.1
High Energy Propellants

The replacement of nitroguanidine/picrite (NQ) in TB propellants by nitramine RDX/HMX/HNIW results in improved performance, that is, higher force constant/muzzle velocity, and such propellants are known as high energy propellants or nitramine-base (NB) propellants. Such propellants are generally used in tank guns for achieving better penetration of armor. Though the performance of such propellants is better, there is a disadvantage of higher gun barrel erosion due to their high flame temperature [16] and vulnerability of formulation to accidental initiation which sometimes may lead to detonation.

4.8.2
Low Vulnerability Gun Propellants

The conventional gun propellants, that is, SB, DB, TB and NB, which are based on NC; NC and NG; NC, NG and NQ and NC, NG and RDX respectively, are highly prone to accidental initiation as a result of external stimuli: fire (hot spall), shock waves and impact (hyper-velocity impact). This leads to the probability of catastrophic killing of armored weapon systems and crew members. This drawback is attributed to the relatively low decomposition temperature of nitrate esters. In order to reduce this risk, low vulnerability ammunition (popularly known by the acronym LOVA) propellants are attractive alternatives for conventional gun propellants. The incorporation of materials possessing higher ignition temperatures into propellant formulations while maintaining superior energetics, is key to the development of LOVA/insensitive propellants [17, 18]. This is usually done by a judicious combination of energetic oxidizers and suitable binders which are described in the subsequent paragraphs.

4.8.2.1 **Ingredients of LOVA Gun Propellants**

The main ingredients of LOVA gun propellants are:

1) **Oxidizers:** Nitramines RDX and HMX are widely used as energetic ingredients of LOVA to achieve low vulnerability, which is due to their higher thermal stability (decomposition temperature >200 °C) than nitrate esters (<180 °C). Nitramines also offer superior impulse due to the low molecular weight of the exhaust gases and positive heats of formation (+14 and +17 kcal mol^{-1} for RDX and HMX respectively). An additional benefit of the nitramines is the increased gun barrel life due to low flame temperature compared with DB propellants of equivalent energy potential. Moreover, nitramines have the other advantages of reduced IR radiation due to reduction of CO_2/H_2O content in the plume, and non-corrosive and non-polluting exhaust [19, 20]. Schedlbauer used triaminoguanidine nitrate (TAGN) which has a decomposition temperature comparable to that of RDX as an oxidizer for LOVA propellants [21]. Narang and Schmitt [22] reported the suitability of oxidizers like hexanitrostilbene (HNS), triaminotrinitrobenzene (TATB) as energetic components for LOVA propellants particularly on the basis of their high decomposition temperatures (>300 °C). However, HNS/TATB/TAGN are less energetic than nitramines. Choudhri *et al.* have evaluated RDX and HMX individually and in combination with HNS and diaminotrinitrobenzene (DATB) to achieve optimization in energetics and sensitivity [23].

2) **Binders:** A binder plays an important role in resisting conductive ignition by hot metal particles. Propellants whose binders decompose endothermically are considered excellent in this context. On the other hand, propellants with exothermically decomposing binders ignite as easily as nitrate ester propellants. Binders can be classified as inert and energetic binders.

   - **Inert binders:** Polybutadiene and cellulose derivatives are used as binders for LOVA formulations [24]. The commonly used polybutadiene-based binders are hydroxy-terminated polybutadiene (HTPB) and carboxy-terminated polybutadiene (CTPB)/poly(butadiene-acrylonitrile) (PBAN) while the most commonly used cellulose derivatives are ethyl cellulose (EC), cellulose acetate (CA), cellulose acetate butyrate (CAB) and cellulose acetate propionate (CAP). The investigation of Mackowiak indicates that polybutadiene-based RDX formulations having higher decomposition temperatures than the conventional propellants deliver a high performance if the RDX content is more than 85%. Among cellulose derivatives, CAB-based formulations give relatively superior energetics to polybutadiene binders. Some other polymers have also been patented as potential binders for LOVA propellants [25, 26].

– **Energetic binders:** A number of researchers have recently reported several energetic polymers as potential binders. Mishra *et al* [27] have patented some binders with high energy and reduced sensitivity to develop LOVA propellants and explosives. Nitrocellulose (NC) is also added to some of the formulations in order to enhance the mechanical properties and improve processibility. NC also enhances overall energy and burning rates, however, incorporation of NC results in increased impact and thermal sensitivity. Energetic azido polymers, like poly[bis(azido methyl oxetane)], poly(BAMO) and glycidyl azide polymer (GAP) have also been considered as binders for LOVA propellants [28, 29]. The mechanical properties of patented propellants are also suitable for gun applications as exhibited by the elongation of 1–3% and modulus of 420–2200 $\mathrm{kg\,cm^{-2}}$.

3) **Plasticizers:** Plasticizers such as acetyl triethyl citrate (ATEC), triacetin (TA) and dibutyl phthalate (DBP) have been used as plasticizers for EC, CA, CAB and CAP binders. Adolf and Kim [30] have claimed the utility of 2,2,2-trinitroethyl-2-nitroxyethyl ether having energy content in between NG and butane triol trinitrate (BTTN) with high thermal stability as an energetic plasticizer for LOVA propellants. This plasticizer is also less volatile and less toxic than NG. The research carried out by Asthana *et al.* has established the potential of low molecular weight GAP as an energetic plasticizer for LOVA propellants [31]. GAP plasticized formulations deliver high energy while retaining low vulnerability.

Wise and Rocchio [32] have discussed the processing techniques for LOVA formulations which invariably depend on the type of binder. The polybutadiene-based formulations referred to as cured systems, are processed through a solventless process whereas formulations based on cellulose derivatives and thermoplastic elastomers as binders are processed by a solvent process similar to standard NC propellants. In conclusion, LOVA formulations offer unique propulsion systems for tanks with the potential to offer high energy and low vulnerability.

The shelf-life of propellants is evaluated from the stabilizer content and is defined by the period of storage (number of years) in which the stabilizer content is reduced to half of the initial value. Gun propellants of low web size <0.2 mm can burn very fast which may lead to mass detonation and accordingly gun propellants with low web size fall under UN Hazard Classification 1.1 whereas others fall under 1.3 (see Chapter 6).

The leading gun propellant technologists are of the opinion that the conventional solid gun propellants have reached their saturation level in terms of energy output and there is a need to develop high performance propellants for future gun ammunition to propel projectiles with hypervelocity [33], that is, projectiles with muzzle velocity in excess of $2000\,\text{ms}^{-1}$. The high muzzle velocity provides weapons with higher range, quicker response time and better accuracy in addition to armor-defeating capability. The solid gun propellants containing cyclic nitramines such as RDX, HMX, CL-20, especially formulations with a higher percentage of RDX, lead to problems associated with gun barrel erosion [34]. Therefore, research and development efforts commenced on alternative concepts of gun propulsion systems such as liquid gun, rail gun, coil gun, electrothermal gun, electrothermal chemical gun etc. The liquid gun propellants possess some advantages over solid gun propellants in respect of lower flame temperature, lower muzzle flash, lighter in weight, continuous zoning capability, good storage stability, insensitivity (less vulnerable to accidental initiation), better logistics and lower costs.

4.8.3
Liquid Gun Propellants

The origin of use of liquid propellants for guns lies in the analogy of liquid rocket propellants. As discussed earlier, liquid propellants can either be monopropellants or bipropellants. However, there are potential advantages to the use of bipropellants in rocketry and as a result, serious consideration was given for their use in guns [35]. Several mono- and bipropellants were evaluated for gun applications but results were not satisfactory. The logistics and engineering difficulties associated with the use of bipropellants, and the toxicity and corrosivity of their ingredients are such that no practical bipropellant gun system is currently available in the Services. Extensive research and development efforts of UK, German and US scientists have led to the discovery of many liquid monopropellants and their formulations and some salient features of important liquid monopropellants are given below.

4.8.3.1 Hydroxyl Ammonium Nitrate Liquid Gun Propellants

Hydroxyl ammonium nitrate (HAN) is a relatively new synthetic propellant material but with combined hydrogen and nitrogen (fuel ingredients) and oxygen (oxidizer ingredient) in the same molecule. It is an opaque, hygroscopic material when pure and is a clear, colorless, odorless liquid in aqueous solutions. Solid HAN has a specific gravity of 1.84. The melting point of HAN is 48 °C and it forms mixtures with water that are liquids at room temperatures at concentration as high as 95%. The liquid is corrosive, toxic, denser than hydrazine monopropellant and does not seem to be carcinogenic. The liquid is incompatible with alkaline materials, many metals and other materials. Even with very compatible materials, HAN solutions decompose slowly during storage and a satisfactory stabilizer is needed.

HAN is a potential solid propellant ingredient and liquid HAN solution is a potential monopropellant. Both can be made to burn smoothly and several catalysts have been effective in obtaining controlled decomposition. The use of a

HAN-based aqueous system as a gun propellant was first proposed by the personnel at the Naval Ordnance Station, Indiana Head, MD, USA.

HAN, which is a salt of hydroxyl amine and nitric acid: $(NH_3OH)\ NO_3$, contains more oxygen than is required to oxidize its hydrogen to water. It can therefore also serve as an oxidizer to form energetic mixtures when combined with a suitable fuel. Further, in contrast to other types of liquid propellants, HAN–H_2O mixtures show no shock sensitivity to a range of stimuli that are expected in gun applications [36, 37]. In addition to the traditional benefits of liquid propellants such as low cost, efficient logistics and high volumetric impetus, HAN-based liquid gun propellants (LGPs) offer a number of improvements over propellants considered in the past. The most important is safety in handling. It is very difficult to ignite these materials unless heavily confined. Also they do not deflagrate under ambient conditions but decompose slowly in by fizzing. Further, the vapor pressure of the liquid is low which eliminates flame and toxicity hazards inherent in many other liquid propellants.

The fuel selected for use with HAN should be totally compatible and therefore, nitrate salts of amines are the natural choice for this purpose. Based on a study with aliphatic, aromatic and heterocyclic amines, aliphatic amines are considered a better choice and a formulation containing the nitrate salt of triethanolamine (TEA), that is, TEAN $[(CH_2OHCH_2)_3\ NHNO_3]$ is currently in use. HAN-based propellants consist of HAN, water and TEAN. Some typical formulations of LGP are given in Table 4.2 along with their properties. These three propellants differ from one another only in respect of the amount of water which they contain.

LP 101 is the mixture which has been mostly used in UK in the program whereas Americans studied the propellant designated as LGP1846 extensively. Burning rate measurements of LGP 1846 reveal an interesting feature of its combustion, that is, volumetric burning rate shows a marked decrease with an increase in pressure in the pressure range of 6.7–34.0 MPa. Further, HAN-based propellants provide the best balance of characteristics between performance on the one hand and safety in handling on the other.

The I_{sp} of monopropellant is in the range of 200–265 s depending on the water content of the HAN–aqueous or HAN–fuel system. The use of diethanolammonium methylcubane nitrates such as *N*,*N*-diethanol-ammonium methylcubane

Table 4.2 Formulations and properties of some liquid monopropellants.

Designation		Formulation/%, by mass			Density/g cm^{-3}	Impetus/J g^{-1}	Flame temperature/K
US	UK	HAN	TEAN	Water			
LGP 1845	LP 101	63.2	20.0	16.8	1.46	973	2730
LGP 1846	LP 102	60.8	19.2	20.0	1.42	935	2570
–	LP 103	58.5	18.5	23.0	–	–	–

nitrate and 1,4-bis (*N*,*N*-diethanolammonium methyl) cubane dinitrate in HAN solution has also been suggested to improve its performance [38]. Similarly, the performance of HAN solution may be enhanced by the addition of non-metallic salts of 3-nitramino-4-nitrofurazan {where the cation is selected from the group consisting of NH_4^+, $(NH_3OH)^+$, $(NH_3NH_2)^+$ and dinitroazetidinium [39].Further, the ionic salts of cage molecules: adamantyl tetrakis(ammonium nitrate), adamantyl and cubyl poly(ammonium nitroformate) which have high density, high energy and water-solubility, appear to be attractive in HAN-based liquid gun propellant formulations and are currently being investigated for such applications.

In summary, HAN-based propellants are markedly superior to other liquid propellants and also appear to possess physical properties and a number of other characteristics necessary for their use in a practical gun. Their performance may be further enhanced by the use of some additives. These propellants are also biodegradable so that disposal is not a problem [40, 41]. The data generated as a result of extensive characterization and hazard testing indicate that HAN-based propellants are suitable for military use. The HAN-based liquid propellants also appear to offer low vulnerability characteristics comparable to the LOVA propellants [42–44].

4.8.3.2 **DMAZ Liquid Gun Propellants**

As discussed earlier, hypergolic mono- and bipropellants have been employed in small to medium scale propulsion systems and MMH is regarded as most widely used hypergolic fuel for bipropellants. Although MMH is a high performance hypergolic fuel, it is a highly toxic and carcinogenic fuel. Therefore, there is a requirement for a non-toxic and non-carcinogenic replacement for MMH similar to UDMH. US Army Aviation Missile Command (AMCOM) has recently identified a fuel: 2-(dimethylamino) ethyl azide [DMAZ: $(CH_3)_2N.CH_2.CH_2.N_3$)] which appears to be very attractive as a potential candidate to replace hydrazine derivatives in certain hypergolic fuel applications and also as a monopropellant using a heated catalyst bed. DMAZ is a colorless, pungent, volatile and low-viscosity energetic liquid. It is also soluble in most organic solvents and compounds at almost all temperatures (dry ice-bath temperature, 0 °C and 70 °C). It is classified as 'toxic by inhalation' according to the guidelines of the US Occupational Hazard and Safety Administration [45–47]. However, the current status regarding its use for military applications is not known. DMAZ is non-carcinogenic and much less toxic than MMH.

DMAZ is hypergolic and also meets all the requirements for military use. However, its ignition delay is significantly longer than MMH when used in combination with inhibited RFNA (i.e. IRFNA). The longer the ignition delay, the larger must be the combustion chamber so as to avoid pressure spikes that could rupture the engine. Therefore, an ideal fuel would have the properties of DMAZ with ignition delay comparable to that of MMH. Sengupta and Raman, based on their ab initio theoretical calculations using COSMO-RS and thermodynamic methods for tertiary amine azide fuels, concluded that most of the molecules have better properties: density, heats of formation, vapor pressures, heats of vaporization, specific impulse, density-impulse etc. than the currently used propellants [48]. These molecules, due to their negligible vapor pressures, are expected to be environmentally friendly. Finally the fuel, 3-azidoimidazole dimethyl *t*-amine is considered to be the best balance of characteristics between performance on the one hand and non-toxic and non-carcinogenic nature on the other. However, this molecule should be synthesized and the theoretical predictions should be validated through experimental research.

The use of liquid gun propellants appears to be very attractive. However, the problems encountered such as gun design and ignition system along with combustion instability limit their application and at present no liquid gun propellant is in use. Therefore, solid gun propellants based on novel energetic ingredients are thought to be the ultimate choice for future applications [34, 49].

4.9
Ingredients of Solid Rocket Propellants

Modern rockets and missiles generally use composite propellants. These composite propellants are based on three basic components: an organic polymer which serves as both a binder and gas-forming combustible fuel; an oxygen-rich solid oxidizer which is the source of oxygen for oxidation purpose; and a combustible metal additive which is the primary source of additional thermal energy resulting in an increase in their performance. In addition to these three basic major ingredients, some other minor ingredients such as BRMs, plasticizers, bonding agents and stabilizers or anti-oxidants are also incorporated in propellant formulations.

4.9.1
Oxidizers

The oxidizer is a major ingredient of composite propellants and constitutes more than 70% (by weight) of the propellant. An oxidizer should possess: compatibility with other ingredients, high oxygen content, low heat of formation, high density, high thermal stability and low hygroscopicity. It should be non-metallic in nature so as to produce large volumes of gaseous products and should also be safe to handle. Long shelf-life, that is, storability without changes like phase transition, is another important aspect which is given due consideration when an oxidizer is selected. A number of oxidizers are used in composite propellants and their important characteristics are given in Table 4.3.

Ammonium perchlorate satisfies most of the requirements and is used most widely in composite propellants all over the world. The greatest advantage of AP is the immense experience and vast information on AP-based propellants available over several decades which impart more confidence in this oxidizer. Other non-metallic oxidizers have also been investigated in detail but have not been found suitable for use for one reason or the other. Nitronium perchlorate (NP) which has positive 'heat of formation' and highly favorable oxygen balance was also

Table 4.3 Some important characteristics of oxidizers for composite propellants.

Oxidizer	Molecular formula	Density/ g cm^{-3}	Available oxygen/ %	Salient features
Ammonium nitrate (AN)	NH_4NO_3	1.73	19.5	Cheap. Phase transition takes place at 32.5 °C accompanied by volume change which is not desirable
Ammonium perchlorate (AP)	NH_4ClO_4	1.95	34.0	Most commonly employed oxidizer
Potassium perchlorate (KP)	$KClO_4$	2.52	46.2	High burn rates but solid particles are present in the exhaust
Lithium perchlorate (LP)	$LiClO_4$	2.43	60.1	Expensive and highly hygroscopic
Nitronium perchlorate (NP)	NO_2ClO_4	2.22	66.2	Not compatible with binders and also highly hygroscopic

investigated extensively in early 1970s but was discarded because of its instability in the presence of moisture.

Although AP is the most widely used oxidizer for composite propellants, it is not environmentally friendly, and results in acid rain and the hazard of ozone depletion. Also its exhaust signature leads to problems of detection and tracking of rockets or missiles [50–54].

The use of energetic organic ingredients as a replacement for AP has been the goal of a number of groups of investigators and as a result, several energetic ingredients with no chlorine in their molecular structures have emerged as potential contenders. A few energetic ingredients such as NC, NG, PETN, RDX and HMX containing nitro- or nitrate groups appeared promising at first sight. However, their application in large rocket motors is ruled out on the ground of sensitivity of these propellants to shock, friction and temperature. The focus automatically shifted to those oxidizers which have a positive oxygen balance, positive heat of formation, and can deliver higher energy on decomposition and are less sensitive. New energetic oxidizers such as AN, ADN, HNF, HNIW (also called CL-20) and TNAZ appear likely to fulfill the major criteria to emerge as candidate oxidizers to replace AP in propellant formulations.

The size, shape and size distribution of the solid particles of oxidizer, metal fuel or RDX/HMX in the propellant have a major influence on composite propellant characteristics. The particles should be spherical in shape because this allows easier mixing and higher percentage of solids in the propellant than shapes with sharp-edged natural crystals and consequently, better performance.

4.9.1.1 **Ammonium Nitrate**

Ammonium nitrate (AN) imparts slower burn rates but is a high gas producer and accordingly is used for gas generator propellants. AN has an oxygen balance ≈ 20%, density ≈ 1.73 g cm^{-3} and it decomposes endothermically at atmospheric pressure with heat energy of −365.04 kJ mol^{-1}, leading to low burn rate and low specific impulse compared with AP. At the same time, use of AN as a propellant ingredient is not without some significant technical challenges and the most important drawback of AN is that a solid-state phase transition occurs at room temperature [55, 56] along with significant volume change. Ammonium nitrate crystal is thermally sensitive and undergoes five stable polymorphic transformations with volume change in the temperature range of −200 °C to 125 °C. The transition temperatures with their phase structures are reported as follows:

$$\mathrm{VI} \xrightarrow{-200^{\circ}\mathrm{C}} \mathrm{V} \xrightarrow[\text{Tetragonal}]{-18^{\circ}\mathrm{C}} \mathrm{IV} \xrightarrow[\substack{\text{Tripyramidal}\\ \text{Rhombic}}]{32^{\circ}\mathrm{C}} \mathrm{III} \xrightarrow[\text{Rhombic}]{84^{\circ}\mathrm{C}}$$

$$\mathrm{II} \xrightarrow[\text{Tetragonal}]{125^{\circ}\mathrm{C}} \mathrm{I} \xrightarrow[\text{Cubic}]{}$$

Efforts have been made by many research workers in the past to modify or suppress the phase-transition of AN by phase stabilizing it with the help of some suitable chemical compounds induced in the AN lattice or by modifying its properties with the application of surfactants, or by changing the method of preparation of AN itself in order to make it acceptable for use in propellant formulations.

Engel and coworkers [57] have reported the manufacturing process of phase stabilized ammonium nitrate (PSAN) by inducing metal complexes into AN lattices and by using surfactants to modify its properties. Kim [58] has prepared PSAN by precipitation with KNO_3 from a solution of their salts by the addition of acetone. Kempa *et al.* [59] have incorporated diammine copper (II) in the AN lattice to improve the phase-transition behavior. Krishnamurthy [60] has reported modification of phase IV–III transition by co-crystallization of AN with KF and KNO_3. On the other hand, Mishra [61] has reported KF as an effective phase stabilizer for AN. A small fraction of NiO (Nickel oxide, typically 3%) imbedded into the AN crystals is also used for phase stabilization.

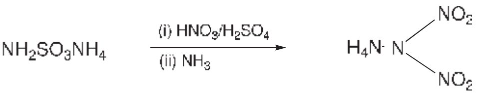
Ammonium nitrate (AN) was considered early as an environment-friendly alternative to AP but its multiple crystal phase-transitions at low temperatures and its poor performance precluded its use. The nitramine-based propellants are also likely to emerge as potential eco-friendly propellants as the combustion products are non-toxic and non-smoky, although the present day nitramine propellants do not match the high performance and high burn rates of AP-based composite propellants [62, 63]. At the same time, high pressure exponent and unstable combustion prevent their application in large rockets due to safety considerations [20]. The inclusion of Al powder and other additives increases the burn rate and also eliminates the combustion instability.

In search of a high performance and eco-friendly oxidizer, extensive research has been going on in this area for more than two decades and as a result, two oxidizers: ammonium dinitramide (ADN) and hydrazinium nitroformate (HNF) have emerged as strong contenders of AP in composite propellants and their important aspects are as follows.

4.9.1.2 **Ammonium Dinitramide**

Ammonium dinitramide (ADN) [$NH_4N(NO_2)_2$] is a relatively newly discovered inorganic solid salt, mainly intended as an oxidizer for composite propellants and it is widely known at present. Dinitramide salts were reported [64, 65] from USA in 1996 while Russians [66] used these salts in their various missile programs in 1971.

ADN is an energetic material with high density ($1.82\,g\,cm^{-3}$), positive oxygen balance (+25.8%) and a negative heat of formation ($-150.60\,kJ\,mol^{-1}$) higher than that of AP and AN. ADN has a needle-shaped structure but it does not show any phase transition and volume change, unlike AN. ADN has been synthesized with the use of N_2O_5 and nitronium tetrafluoroborate (NO_2BF_4, also made with the help of N_2O_5). An excellent overview of the different synthetic routes and properties of ADN has recently been published by Venkatachalam *et al.* [67]. The authors have concluded that the method invented by Langlet *et al.* is most suitable for scaling-up. In this method, ADN [Structure (4.1)] is synthesized by reacting ammonia sulfate derivatives such as $NH(SO_3H)_2$, $NH_2SO_3NH_4$, NH_2SO_3H or $NH(SO_3NH_4)_2$ with mixed acid nitrating agent (HNO_3/H_2SO_4) followed by reaction with ammonia as shown in Equation 4.17:



(4.17)

Structure (4.1): Ammonium dinitramide (ADN)

The reaction is carried out at −40 °C using fuming HNO_3 (>98%) and conc. H_2SO_4 (98%). Similarly, the potassium salt is prepared [68] by employing potassium sulfamate as a starting material and neutralizing the dinitramidic acid with KOH. Additional experimental details are given in a subsequent publication [69]. This is currently the most important route for ADN and also suitable for further scaling-up. This method was developed by chemists at the Swedish Defence Research Agency (FOI) and ADN/other dinitramides are today commercially produced on a pilot-plant scale by Eurenco Bofors, Sweden under licence from FOI. Some reports suggest that Eurenco is today the only commercial manufacturer of ADN worldwide. Some physical, thermal and explosive properties of ADN are given in Table. 4.4.

ADN is more hygroscopic than AN and has lower critical relative humidity (ADN ≈ 55.2% whereas AN ≈ 61.9% at 25 °C). Hence, to prevent ADN from absorbing moisture during handling, storage and processing [70], RH in the atmosphere must be below 55%. A brief on some important properties of ADN from the point of view of end-use will be presented while comparing ADN with HNF.

Apart from the ammonium salt of dinitramidic acid, many different stable oxygen-rich salts with a variety of cations are possible which could provide a new class of energetic materials. The presence of $-N(NO_2)_2$ groups in these compounds imparts high heat of formation, density and oxygen balance and hence has received a lot of attention in recent years. The alkali metal dinitramide

Table 4.4 Some physical, thermal and explosive properties of ADN.

Property	Characteristic data
Melting point/°C	92.0
Density/g cm^{-3}	1.80–1.84
Decomposition temperature/°C	127.0
Temperature of ignition/°C	142.0*
Enthalpy of formation/kJ mol^{-1}	–150.6
Friction sensitivity/N	72.0
Impact sensitivity/Nm	5.0
Electrostatic discharge/J	0.45
Vacuum stability (80 °C for 40 h, Cm^3/5 g)	0.73

* 167.0 °C (by FOA)

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derivatives are synthesized for use in pyrotechnic flare compositions. These metal dinitramide salts provide pyrotechnic effects and increase the density of the formulation in addition to providing extra energy. The inorganic derivatives of dinitramide have higher stability because of negative charge delocalization through the seven atoms in $[N(NO_2)_2]^-$. On the other hand, the amine salts of dinitramide are considered as explosives or components of energetic mixtures because of their good thermal stability and low susceptibility to hydrolysis [71]. Apart from the thermal stability, these amine salts have better non-hygroscopicity and positive oxygen balance and therefore may find applications in new high energy formulations.

N-guanylurea dinitramide (commonly known as FOX-12) has low sensitivity and is an excellent candidate for insensitive munitions [72]. It is neither hygroscopic nor soluble in water. Its thermal stability is comparable to RDX and superior to that of ADN. The substitution of ammonium in dinitramide by an organic cation results in the change of combustion temperature and reactivity of the fuel.

The cubane and azetidine salts of dinitramide are of great interest because of their high strain energy and density and may have potential applications in advanced propellants. Azetidine-based explosives are expected to have excellent performance because of the associated high strain energy with the four-membered ring. The 3,3-dinitroazetidinium cation has a high oxygen balance and is useful as an energy-rich substitute for the conventional cations such as ammonium, guanidinium, hydrazinium etc. and these are likely to prove useful as propellant ingredients [73].

In a nutshell, ADN appears to be an efficient oxidizer for the high performance eco-friendly propellants and is now envisaged as a suitable and better successor to AP. The use of ADN in composite solid propellants eliminates the emission of chlorinated exhaust products from rocket motors and gives 5–10 s more I_{sp} than conventional AP-based propellants.

4.9.1.3 **Hydrazinium Nitroformate**

Another high energy and environment friendly oxidizer which has recently come to prominence as a result of painstaking research at the European Space Agency (Aerospace Propulsion Products Division) and its sub-contractors (TNO-PML, Delft University of Technology and the University of Delaware) is hydrazinium nitroformate [$N_2H_5.C\ (NO_2)_3$: Structure (4.2)] a salt of hydrazine (N_2H_4) and nitroform or trinitromethane [$HC(NO_2)_3$], reported to have been discovered in 1951. Of course, this is made without the use of N_2O_5. It is prepared as a precipitate [74] by acid–base reaction between nitroform and hydrazine, Equation 4.18.

$$N_2H_4 + HC\ (NO_2)_3 \longrightarrow N_2H_5C\ (NO_2)_3 \tag{4.18}$$

Structure (4.2): Hydrazinium nitroformate (HNF)

Since the reaction is highly exothermic, it is carried out under controlled temperature of 5 °C in ethylene dichloride as the reaction medium. HNF is a yellow-orange needle-shaped crystalline material with monoclinic packing. The crystallographic results indicate that $[N_2H_5]^+$ ions are hydrogen bonded to neighboring $[C(NO_2)_3]^-$ ions. It is a water soluble salt at elevated temperatures. It may also be in an equilibrium state with its pre-dissociated form.

The most crucial step in the synthesis of HNF is the production of nitroform where a number of accidents have been reported. Almost all aspects relating to HNF: synthesis, characterization, properties (physical, chemical and explosive), thermal behavior and toxicity etc., have been reported in the literature [75–81] as a result of extensive research of ESA, TNO-PML and FOI.

The particle size of HNF crystals is estimated to be between 5 to 10 μm. However, a method has recently been developed to recrystallize HNF to produce particle size between 200 and 300 μm. The stability of HNF depends on its purity and pure HNF has sufficient stability. The European Space Agency established a production facility at Aerospace Propulsion Products (APP) in 1993 to meet the increasing demand of good quality HNF. At present, the pilot plant has a maximum capacity of ≈300 kg per year. All commercially available European HNF is manufactured in this facility. A new propellant based on HNF and glycidyl azide polymer (GAP) binder has recently been reported in Europe. This new propellant containing HNF and GAP promises two new clear advantages:

1) A performance substantially higher (≈7%) than the best presently known AP/Al/HTPB propellant;
2) Chlorine-free exhaust products.

The m.p. of HNF lies in the range of 115–124 °C depending on its purity and it is suitable for processing of propellant formulations. The m.p. of an oxidizer is important because curing of composite propellants is usually done at elevated temperature. Further, there is no measurable moisture uptake for HNF.

Its practical use is primarily hampered by its tendency to attack double bonds in unsaturated binders such as HTPB causing gas evolution and hence swelling of the propellants. However, the most satisfying characteristic of HNF is its compatibility with the recently reported energetic binders such as GAP, poly(NiMMO), poly(GlyN) and poly(BAMO). HNF in conjunction with modern binders like GAP, poly(GlyN) and poly(NiMMO) not only gives a substantial increase in the performance of solid rocket propellants but also an environmentally benign exhaust as the combustion gases are free from chlorine. The friction and impact sensitivity of HNF/Al/GAP propellants are acceptable and comparable with other propellants and explosives being used presently.

Recent studies by European countries suggest that poly(NiMMO)/HNF is one of the most promising in the propellant family. This formulation consists of aluminum (Al) as a secondary fuel, an isocyanate as curing agent, a burn-rate modifier (BRM) and a bonding agent. The curing agent crosslinks the binder molecules by the formation of a polyurethane network. The BRM is used to modify the burn rate beyond what can be done with variation of the particle size of solids. The bonding agent serves as a wetting agent for the solids and increases the cohesion between the binder and oxidizer. HNF and HNF-based propellants exhibit very high burn-rate exponents. The uncatalyzed HNF/Al/Poly(NiMMO)-based propellant shows a pressure exponent (n) of ≈ 0.85 while generally accepted values in rocket propulsion are <0.6. In order to reduce the pressure exponent (n) of these propellants, two approaches are followed (i) replacement of a part of the HNF by AP and (ii) use of BRMs. Many of the catalysts investigated in the past were found to be incompatible with HNF, however, recently several potential BRMs were identified which are compatible with HNF. For HNF-based propellants, three families of organic bonding agents: aziridines, epoxies and glycerophosphates were studied and epoxy bonding agent was found to be the best trade-off between improvement in the mechanical properties and compatibility with HNF. However, the names of the most suitable BRM and epoxy bonding agent are not disclosed. Further, HNF-based solid propellants are also of interest for military applications as these propellants eliminate the smoke trail caused by AP and Al in the currently used AP/Al/HTPB-based propellants. For short range missiles (anti-tank, theater ballistic missiles, surface-to-air missiles) and rockets, this smoke trail is a very serious tactical disadvantage. At the same time, accepting some smoke (from Al) could strongly increase the range of missiles.

HNF being a new oxidizer for applications in defense (rockets and missiles) and space (launch vehicles), the following aspects of HNF need special emphasis.

1) **Compatibility:** The work of several investigators suggests that HNF is incompatible with HTPB and isocyanates. The presence of –C=C– in the HTPB backbone is reported to be the cause of HNF/HTPB incompatibility when these two materials are used in conjunction; the –C=C– bonds of HTPB are oxidized by HNF resulting in the deterioration of mechanical properties of the propellants. On the other hand, the incompatibility of isocyanates is reported to be due to the transfer of hydrogen from HNF to nitrogen of the –N=C=O group of TDI, HMDI etc. In other words, before incorporation of HNF in propellant systems, a method to introduce a protective barrier to coat it is essential, so that it does not react with either HTPB or isocyanates and also becomes a free-flowing powder.

Similarly, ADN has also been reported to be incompatible with isocyanates (spontaneously reacting and decomposing in their presence) in one of the recent references on ADN [82]. This means that a large number of polymers such as HTPB, NHTPB, GAP, poly(NiMMo) and poly(GlyN) etc. which undergo polyurethane bonding cannot be used with ADN without introducing a protective coating on it, similar to HNF.

2) **Stability:** This was ascertained by performing a vacuum stability test at 60 °C for 48 h, and gas evolution in the range of 2–10 $cm^3 g^{-1}$ was reported by various researchers. Some researchers are of the opinion that excessive gas evolution from raw HNF is attributed to the presence of solvents and other impurities. However, high purity HNF or recrystallized HNF with controlled particle size is reported to evolve 0.1–0.5 $cm^3 g^{-1}$ and use of some stabilizer may further increase its stability. The order of stability of HNF among other oxidizers is HNF < ADN < NC < CL-20 < RDX < HMX, that is, it is a most unstable substance. Nevertheless, the stability of HNF is such that it may be stored at 25 °C for several years [83] until it reaches a mass loss of 1%.

3) **Sensitivity:** Impure HNF shows a value of impact sensitivity of <1 Nm while pure or recrystallized HNF of the same batch exhibits an improvement to the level of ≥15 Nm. Some researchers have reported friction sensitivity of 25 N. However, the data on impact and friction sensitivity reported by various groups suggest that sensitivity depends not only on purity but also on particle size, shape of crystals and the type of contaminants. There is a lot of variation in the data reported by various investigators and it appears that this variation is attributed to differences in purity, particle size and morphology of HNF synthesized by different groups [84].

4) **Toxicity:** It is non-toxic, non-corrosive and non-irritating to skin and eyes and no indication of danger exists with respect to inhalation. It is classified as 'harmful' only for oral ingestion [85]. For satellite and on-orbit propulsion, hydrazine with a suitable catalyst is considered essentially the only monopropellant due to its rapid and well reproducible decomposition. Similarly, hydrazine derivatives, MMH and UDMH are considered ideal as bipropellant components for in-space propulsion due to their long-term storability, hypergolic reactions with the storable N_2O_4 oxidizer and high and reproducible performance. Due to the extreme toxicity of hydrazine and its derivatives, there was a need for more environmentally benign and non-toxic replacement. Currently several research efforts are under way globally to identify advanced 'green' monopropellants that could replace hydrazine, currently state-of-the-art monopropellant. HNF dissolved in water with or without a fuel is considered an ideal high performance and green monopropellant for space applications. The addition of a fuel to HNF further improves its performance because its decomposition yields oxygen as one of the reaction products as shown in Equation 4.19:

$$4\,N_2H_5C(NO_2)_3 \rightarrow 10\,H_2O + 4\,CO_2 + 10\,N_2 + 3O_2. \tag{4.19}$$

and this oxygen leads to combustion of fuel yielding an extra amount of energy that is beneficial to the performance of the mixture. In other words, there are essentially two major aspects that make HNF-based monopropellants very attractive:

- High performance potential, that is, I_{sp} of up to 295 s with the addition of a fuel and thus HNF solid has the higher performance compared with ADN and HAN.
- Favorable handling and operational aspects due to its non-toxicity and environmentally benign nature.

ADN and HNF are two powerful oxidizers mainly intended to be used in solid propellants. They have the potential to increase I_{sp} above that of AP-based propellants and also they are environmentally benign. A comparative study of ADN and HNF was conducted by two European pioneers [ADN: FOI Stockholm, Sweden and HNF: TNO-PML Netherlands] and the gist of their findings [86] is reproduced below:

- Needle like crystals are formed while synthesizing ADN and HNF. Spherical particles with a low aspect ratio are desired in order to obtain high solids loading in a propellant.
- The density of ADN is 1.823 g cm^{-3} whereas for HNF it is in the range of 1.846–1.869 g cm^{-3}. The melting peak for ADN was found to be at 92.7 °C but enthalpy of melting and onset of the exotherm for HNF could not be determined since decomposition starts during its melting.
- The ignition temperature for ADN is between 167 °C (no reaction) and 174 °C (two reactions) whereas for HNF it is between 115 °C (no reaction) and 120 °C (4 reactions)
- HNF shows better vacuum stability at 70 °C than ADN. Surprisingly, at 60 °C ADN is less stable than at 70 °C/80 °C which cannot be explained at present. A stabilizer will probably be needed for both ADN and HNF to increase their thermal stability further,
- ADN is very hygroscopic whereas HNF is not. Therefore, ADN needs drying at 40 °C under vacuum before its use/testing. On the contrary, there is no measurable moisture uptake for HNF and its hygroscopic point is 94%.
- ADN and HNF have approximately the same impact sensitivity at 16.7% probability. However, ADN is somewhat less sensitive than HNF at 50% probability. The exhaustive data generated by FOI and TNO-PML on impact sensitivity suggest that both ADN and HNF should be considered to be more sensitive materials compared with conventional explosives RDX and HMX. Further, HNF is roughly 10 times more sensitive to

friction than ADN. HNF does not meet the UN criteria with respect to friction sensitivity and thus it can only be transported with special precautions.

4.9.2
Binders

The performance of solid propellants is mainly governed by the solids loading which the polymer binder can take up while the mechanical integrity is governed by the nature of the polymer binder used. The scenario has, however, now changed in the last two decades or so with the advent of energetic polymer binders.

Most of the advanced missiles make use of composite propellants mainly because of higher I_{sp} resulting in higher range or payload. Asphalt (naturally occurring bitumens or an end product of the distillation of certain crude oils) was the first binder for preparing a composite propellant which was used in Jet Assisted Take-Off (JATO) rockets. These propellants have a very narrow temperature range for their applications and also their I_{sp} is low. Further, in the initial stages of development of composite propellants, a number of polymers were used as fuel-binders which are polyethylene, polyester, polyisobutylene, polyvinyl chloride, polyacrylonitrile, polysulfide etc. The binders employed in the initial stages of development of rocketry are only of historical importance now. The use of these polymers as binders for composite propellants is not favored mainly due to poor I_{sp} and mechanical properties of the resulting propellants. The recent trends in the field of binders for composite propellants are research and development on polybutadiene with terminal functional groups and energetic binders.

4.9.2.1 Characteristics of Binders

A polymer to be suitable as binder for composite rocket propellants should possess a number of desirable properties but important among them are:

1) The binder should be compatible with the other ingredients of the propellant, that is, oxidizer, metal powder, plasticizer, bonding agent, stabilizer and ballistic modifier etc.
2) The binder should have polymer backbone with high C/H ratio.
3) The no. av. mol. wt. ($\overline{M}_n$) and wt. av. mol. wt. ($\overline{M}_w$) should be in the range of 2000 to 3500 and at the same time, molecular weight distribution should be as narrow as possible in order to impart better and reproducible mechanical properties to propellants.
4) The binder should not be very viscous enabling high solids loading (oxidizer and metal fuel) resulting in higher I_{sp}.
5) The binder, on incorporation of solids ≈ 85 to 90%, should possess reasonably high tensile strength, elongation and Young's modulus etc. in order to enable rocket propellant grains maintain their structural integrity during flight.

6) The extent of 'post-curing' of propellants on storage should be as low as possible so that there is no considerable change in their properties during storage.
7) The binder should preferably be capable of room temperature curing so that manufacturing of propellant is not too time consuming and also, at the same time, production is cost-effective due to the saving of energy.
8) The binder should have low T_g and long shelf-life.

Poly(butadiene-acrylic acid), that is, PBAA was the earliest prepolymer in the category of polybutadiene wherein the functional –COOH groups are randomly distributed along the backbone. The uneven spacing of carboxyl groups which give rise to poor mechanical properties in the PBAA-based composite propellants, is improved by the introduction of acrylonitrile (AN) groups in PBAA molecules. The resulting terpolymer, that is, poly(butadiene-acrylic acid-acrylonitrile) (PBAN) has more reproducible properties and is widely used as a fuel prepolymer in high energy solid propellants. However, for better low temperature properties and improved performance, carboxy-terminated polybutadiene (CTPB) is preferred to PBAN. The solid composite propellants used the world over for space and military applications are based on PBAN, CTPB or HTPB. HTPB is the most recent entrant and permits solids loading up to 91% and retains mechanical properties within acceptable limits. At present, HTPB is regarded as a 'work horse' binder for composite propellants and most commonly employed for this purpose.

4.9.2.2 **Polyurethanes as Binders**

Polyols and polyisocyanates are major ingredients for polyurethane (PU)-based composite propellants in addition to chain extenders and catalysts etc. A brief description on these materials is considered necessary in order to understand the chemistry of composite propellants in a better way. Polyols are the largest group of raw materials for PUs. The properties of PUs/PU products are largely determined by their chemical composition and molecular mass. They may be broadly classified [87] as:

- Polyether polyols
- Polyester polyols
- Castor oil and its derivatives.

The details are already available in the literature. However, some important aspects of popular polyols i.e. castor polyols and HTPB, diisocyanates/ polyisocyanates, other ingredients and preparative methods of PUs are given in this section.

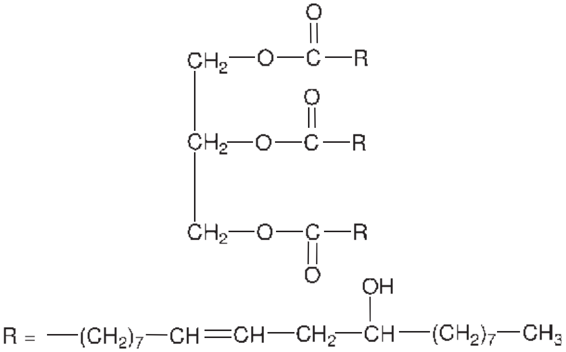
1) **Polyols:**
   - **Castor polyols:** Castor oil (CO) is mainly available in India and Brazil although the USA also produces a considerable quantity. Castor oil is produced either by expression or by solvent extraction from its seeds, also known as 'castor beans'. It is a viscous liquid with a characteristic unpleasant taste and can be made odorless and tasteless by neutralization and subsequent deodorization. The grade of castor oil is decided by its

Table 4.5 Typical properties of castor oil.

Oil	% volatile (moisture)	Hydroxyl value/mg of KOH g^{-1}	Acid value/mg of KOH g^{-1}
DB oil (urethane grade)	0.02	163	1.0
No. 1 oil	0.2	163	2.0
No. 3 oil	0.3	154	12.0

color, clarity and acidity. There are three principal industrial grades of refined castor oil and some of their properties are listed in Table 4.5. Since the moisture content and acid value should be very low for urethane applications, the best grade of CO is usually a natural choice.

Castor oil [CO: Structure (4.3)] is a triglyceride of ricinoleic (12-hydroxyoleic) acid; about 90% of the fatty acid portion of the molecule consists of ricinoleic acid and 10% in the form of non-hydroxy acids consisting largely of oleic and linoleic acids. Small amounts of stearic and dihydroxystearic acids are also found in some industrial grades.



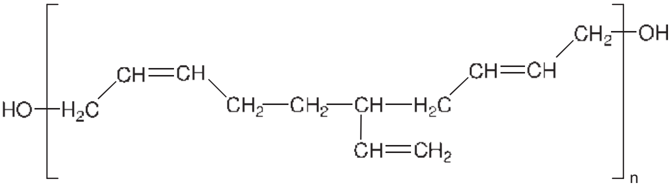
$$R = -(CH_2)_7-CH=CH-CH_2-\overset{\displaystyle OH}{\overset{|}{C}H}-(CH_2)_7-CH_3$$

Structure (4.3): Castor oil (CO)

Castor oil can be considered to be a mixture of about 70% pure glyceryl triricinoleate and 30% glyceryl diricinoleate–mono-oleate or –monolinoleate. Hence, from the standpoint of isocyanate use, it is approximately 70% tri- and 30% difunctional. Because of the long fatty acid chain, castor oil imparts nonpolar characteristics to urethane polymers which are reflected in some of the resulting polymer properties particularly in terms of good water resistance and flexibility. The low temperature properties of CO are excellent and no solid residue is deposited even on long storage at low temperatures. At the same time, the triol structure of castor oil produces crosslinking resulting in thermosetting resins.

The three secondary hydroxyl groups in the 12-position are somewhat slow to react with diisocyanates and generally require heat for the completion of reaction. This can be of advantage or disadvantage depending upon the specific application. Modifications of CO and particularly of ricinoleic acid through esterification results in products that are of considerable interest as polyols for various urethane applications [88, 89].

- **Hydroxy-terminated polybutadiene:** HTPB [Structure (4.4)] prepared by emulsion polymerization has the configuration: *trans*-1,4: 60%, *cis*-1,4: 20% and vinyl-1,2: 20% with predominantly primary terminal hydroxyl groups of the allylic type. The –OH functionality varies from 2.4–2.6 and gives high reactivity with aromatic isocyanates.



Structure (4.4): Hydroxy-terminated polybutadiene (HTPB)

This structure has superior water-resistant properties in comparison to conventional polyols used for PU synthesis. Room temperature cures are easily obtained with typical urethane catalysts. Short chain diols, fillers and plasticizers may also be used in their formulations in order to vary physical properties. Formulations usually with NCO/OH ratio of 1.05 are used for this purpose. Such urethanes are reported to be flexible down to about –70 °C. HTPB is regarded as a 'work horse' binder for composite propellants and PBXs. HTPB also successfully competes with widely used room temperature vulcanizing (RTV) silicones and special epoxy resins for the encapsulation of electronic components. HTPB-based PUs are superior in this respect as epoxy resins change their mechanical properties widely with temperature.

2) **Diisocyanates/polyisocyanates:** Aliphatic and aromatic polyisocyanates are used to obtain PU networks for composite propellants.

   - **Aliphatic polyisocyanates:** The most important aliphatic polyisocyanates are given in Figure 4.7.
   - **Aromatic polyisocyanates:** Aromatic polyisocyanates are primarily used for a wide variety of PU foamed plastics, elastomers, and adhesives. More than 90% of PUs are produced from aromatic polyisocyanates. The isocyanate group bonded to an aromatic ring is more reactive toward water or hydroxyl groups than that bonded to an aliphatic compound. The most important aromatic diisocyanates are also given in Figure 4.7.

Aromatic isocyanates with the NCO group in the benzyl position behave like the cycloaliphatic isocyanates with regard to reactivity and light stability [90].

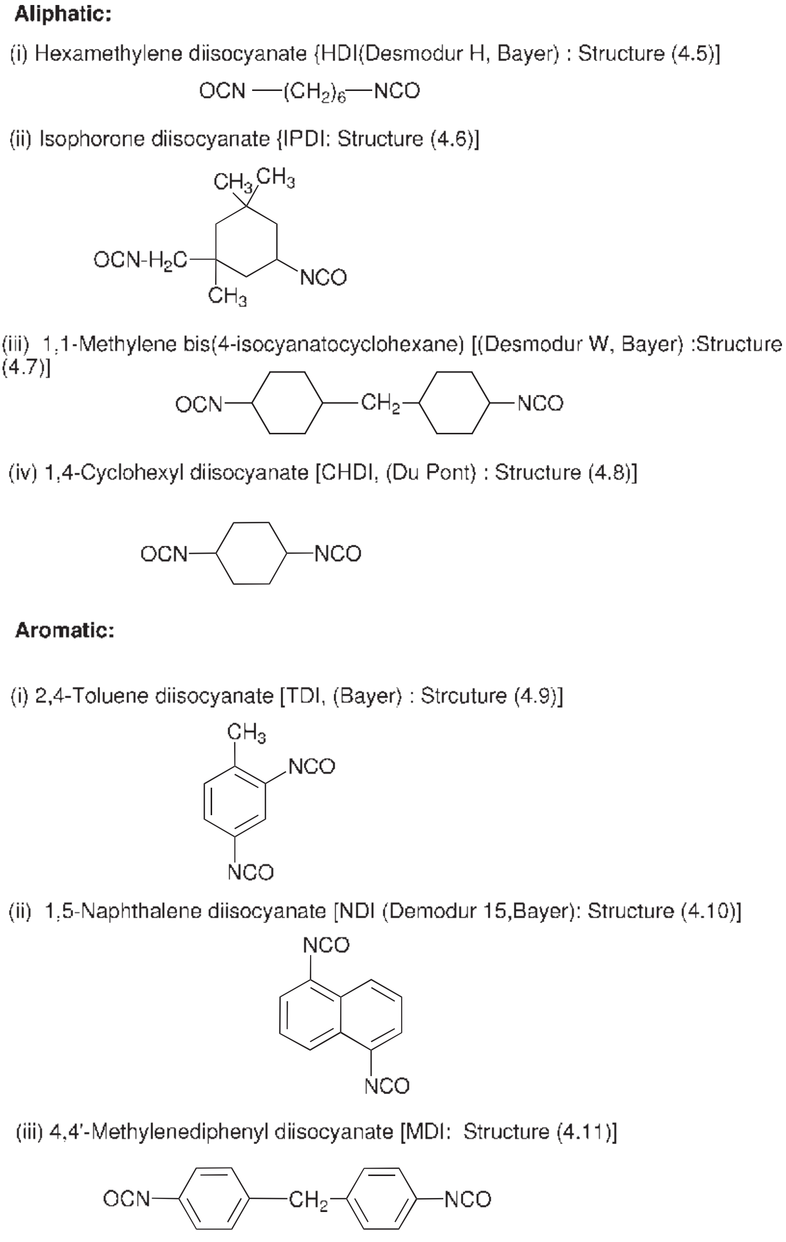


Figure 4.7 Structures of some aliphatic and aromatic polyisocyanates.

MDI- or NDI-based PUs usually have better mechanical properties than PUs obtained from aliphatic polyisocyanates. The effect of various diisocyanates on the thermal stability of their PU elastomers is given below for a polycaprolactone (mol. wt. 2000)/diisocyanate/BDO type elastomer of molar ratio 1 : 2.6 : 1 and synthesized using the prepolymer technique.

$$\text{CHDI} > \text{PPDI} > \text{MDI} > \text{TDI}$$

That is, the thermal stability decreases in this order.

The most commonly employed curative for HTPB is TDI which is comparatively more reactive than other curatives except MDI. Due to this, the pot-life of TDI-cured propellant is only ≈4–5 h. IPDI is another curative which is preferred to TDI mainly on account of its slow reactivity resulting in extended pot-life, that is, 15–18 h and low toxicity [91]. It is only recently that a bicurative system consisting of TDI and IPDI (70 : 30) has been developed and compared with TDI and IPDI-based systems. Compared with pot-life of TDI system (4–5 h), bicurative system has got 7–8 h pot-life. At the same time, viscosity build-up is less in bicurative system revealing an edge over conventional TDI-based system for smooth processing of a propellant slurry [92].

3) **Chain extenders:** Diols and diamines are generally used as chain extenders in PU industry and choice of chain extender influences elastomer properties considerably. The standard diol chain extender used for the synthesis of PU elastomer is 1,4-butane diol (BDO). Compared with a diol, better physical properties usually result when a diamine is employed as an extender. This is probably due to the introduction of urea linkages which enter into strong hydrogen bonded interactions. A diamine is usually chosen as the chain extender when a relatively unsymmetrical diisocyanate is employed. Diamines also function as efficient catalysts in addition to chain extenders.

4) **Catalysts:** Catalysts are widely used for PU manufacture. Sometimes a combination of two or three catalysts is required to obtain the desired balance of reaction rates between compounds of differing active hydrogen activity. Metal compounds, especially organotin compounds, are much more efficient catalysts than tertiary amines for the –OH/NCO reaction. In addition to more commonly used dibutyltin(IV) dilaurate, dibutyltin(IV) diacetate, dialkyltin(IV) oxide or salts of divalent tin with a variety of carboxylic acids such as stannous octoate, hexoate and naphthenate etc. are available for this purpose. Combination of tin catalysts with tertiary amines has been reported to lead to a synergistic increase in catalytic activity.

5) **Preparation:** The two usual routes of chemical formulation for all urethanes [93] are:

   - **Prepolymer method:** This consists of two steps. The diisocyanate and polyol are reacted together to form an intermediate polymer called ‘prepolymer’ which is normally a thick viscous liquid. This prepolymer is

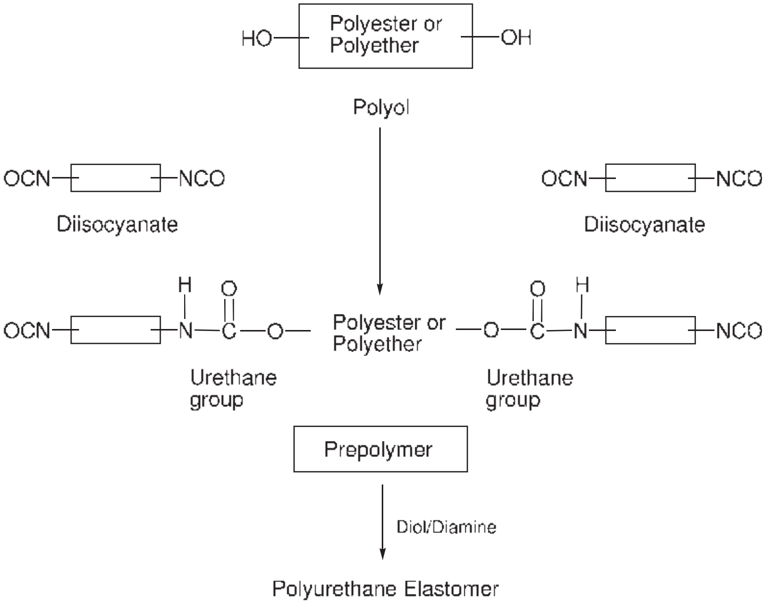


Figure 4.8 Prepolymer route for polyurethane elastomer preparation.

then converted into a final high molecular weight polymer by further reaction with a diol/diamine chain extender (Figure 4.8).

- **One-shot method:** In this process, the entire polymer formation may be carried out simultaneously mixing together polyol, diisocyanate and chain extender (along with catalysts). The PU formation through this route is schematically represented in Figure 4.9.

The prepolymer route imparts greater regularity of structures which results in better low temperature properties.

4.9.2.3 **Novel Binders**

These binders may be classified into two classes: inert or non-energetic binders and energetic binders.

Inert or Non-Energetic Binders: The use of conventional polymers for explosive and propellant formulations brings down the overall energy of such systems. At present, HTPB is regarded as the state-of-the-art binder for composite propellants and PBXs. The use of HTPB for composite propellants meets the requirements of missiles and launch vehicles, that is, simplicity and high reliability (the hallmark of solid propellants) in addition to low cost. It has a low viscosity allowing a high solids loading and also has well-established isocyanate cure chemistry. The polymer binder acts by wetting the solid filler to provide a void free matrix which gives enhanced mechanical properties and allows the formulation to be cast into

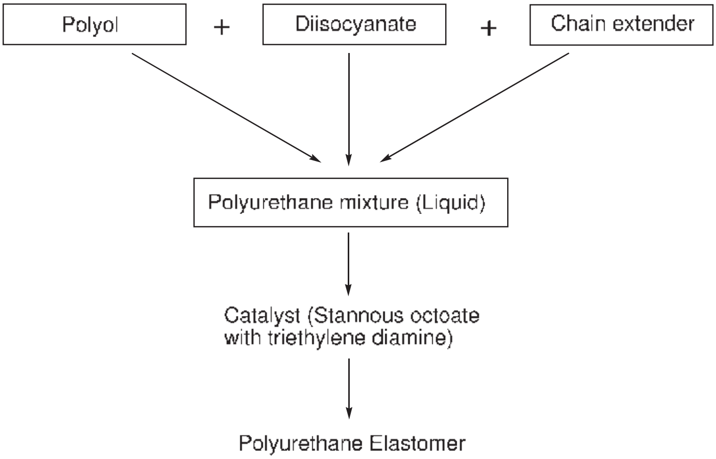


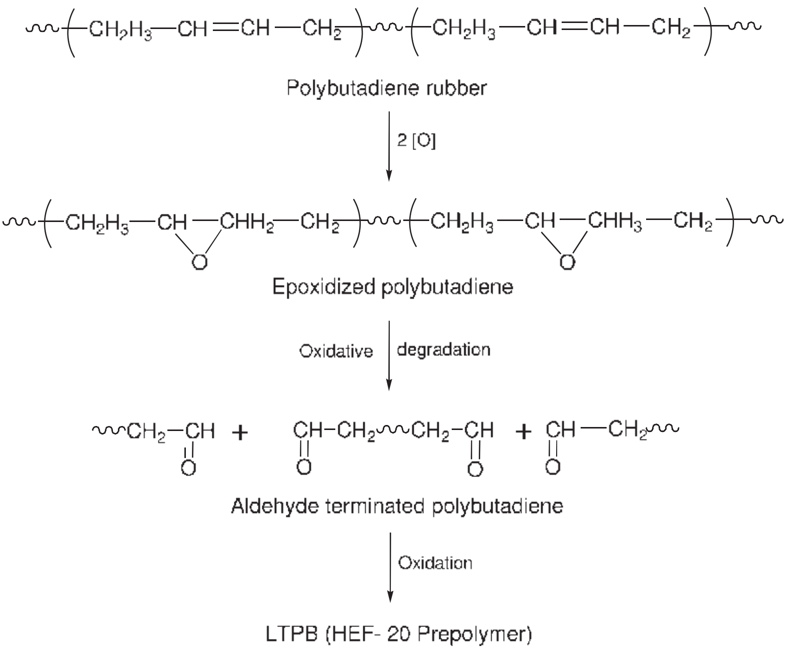
Figure 4.9 One-shot process for polyurethane elastomer preparation.

large motors. HTPB is however, non-energetic and thus the performance of the formulation is limited unless there is still high solids loading. At very high solids loading, there are processing problems and vulnerability related problems. Reduction of the solids loading, mainly oxidizer, would reduce the vulnerability to stimuli since the oxidizer is the sensitive ingredient. Therefore, to reduce vulnerability without lowering the performance, energy can be added to the propellant through the use of an energetic binder enabling a lower solids loading or alternatively maintaining the same solids loading resulting in increased performance. This is the genesis of the use of energetic binders which has led to a lot of research on both the synthesis and formulation of various types of energetic polymers.

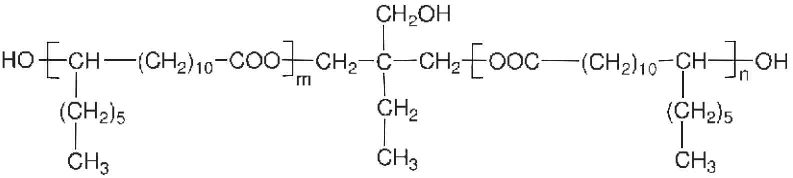
Indian Space Research Organization (ISRO) has developed three new polymeric binders for use in solid composite propellants and some salient features of these binders are:

1) **Lactone-terminated polybutadiene (LTPB):** This is also known as HEF-20 and is synthesized by Scheme 4.1. HEF-20 is a substitute for CTPB and was used in the upper stages of Satellite Launch Vehicle-3 (SLV-3), Augmented Satellite Launch Vehicle (ASLV) and in Apogee Kick Motor to position the 'Apple' satellite into orbit using Ariane, European Space Agency's (ESA's) launch vehicle [5]. The data indicate that the LTPB-based propellants are better than CTPB-based propellants in respect of ageing and low temperature properties and marginally better in terms of I_{sp}, mechanical properties and density.

2) **ISRO polyol:** ISRO polyol [Structure (4.12)] is based on castor oil and is a saturated ester with a low molecular weight (≈2000) nearly bifunctional prepolymer having a viscosity of about 2000 cPs at 30 °C. The hexyl-pendant groups impart good low temperature properties in addition to making it a self-plasticized system. The chemical structure of this prepolymer may be represented as:



Scheme 4.1 Synthesis of lactone-terminated polybutadiene (LTPB).



Structure (4.12): ISRO polyol

It is cured with isocyanates like TDI/MDI and trihydroxy compound such as trimethylol propane (TMP) is often served to tailor mechanical properties. The binder can take different solids loading and I_{sp} is ≈247 s at ≈87% loading.

ISRO polyol is considered to be a substitute for HTPB binder and propellants based on it are used in sounding rockets (RH-300). Such propellants are also considered as candidate propellants [94] for the booster stages of Polar Satellite Launch Vehicle (PSLV). The easy availability of castor oil coupled with its low cost makes ISRO polyol more attractive compared with current binders [95] like PBAN, CTPB and HTPB.

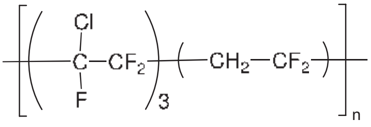
3) **Hydroxy-terminated natural rubber (HTNR):** It is a honey-colored viscous liquid and is prepared by the depolymerization of masticated natural rubber (NR) in the presence of H_2O_2 in toluene. Similar to other polyols, it is curable with TDI/MDI. Some important attributes of HTNR are:

- Ease of availability of the starting material, that is, NR and also ease of depolymerization.
- All-cis configuration yields a low viscosity to the propellant slurry.
- Higher calorific value compared to HTPB and therefore better ballistic performance.
- Compatible with a variety of ingredients of composite propellant formulations.
- Absence of pendant vinyl groups (contrary to HTPB) leads to the formation of more uniform polymer networks.
- Exhibits a good environmental resistance to temperature changes.
- Room temperature curing characteristics resulting in energy savings specially in the case of larger propellant grains [96].

However, its application for bulk manufacture of composite propellants for missiles or satellite launch vehicles is not reported in the literature.

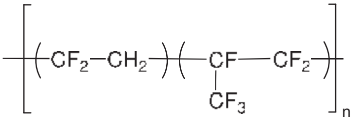
Energetic Binders: The term energetic polymer implies the presence of energetic moieties such as fluoro (F), nitro ($-NO_2$), nitrate ($-NO_3$) or azide ($-N_3$) in binders. There are two possible approaches for synthesis of energetic polymers viz. (i) polymerization of a nitrated monomer and (ii) introduction of energetic groups to an inert polymer. The former approach has been applied to the synthesis of energetic polyoxetanes poly(BAMO), poly(NiMMO) and poly(GlyN) whereas the latter approach has been applied to synthesize GAP and NHTPB.

The copolymer of vinyl ferrocene (VF) and butadiene has also been reported in the literature for use as a binder for composite propellants. It does not require any burn-rate (BR) accelerator because of the presence of iron (Fe) in vinyl ferrocene which is converted to finely divided Fe_2O_3 (a well-known BR accelerator) during combustion. A few groups of scientists have also studied fluorocarbon polymers as binders for composite propellants because of their excellent compatibility with oxidizers and fuels coupled with high density. Accordingly, Kel-F elastomer (a copolymer of vinylidene fluoride and chlorotrifluoroethylene, trade name of 3M, USA) and Viton-A (copolymer of hexafluoropropylene and vinylidene fluoride, trade name of Du Pont, USA) have also been reported for this purpose. The structures of Kel-F 800 [Structure (4.13)] and Viton-A [Structure (4.14)] are:



$$\left[\left(\mathrm{CCl(F)}-\mathrm{CF_2} \right)_3 \left(\mathrm{CH_2}-\mathrm{CF_2} \right) \right]_n$$

Structure (4.13): Kel-F 800



$$\left[\left(\mathrm{CF_2}-\mathrm{CH_2} \right) \left(\mathrm{CF(CF_3)}-\mathrm{CF_2} \right) \right]_n$$

Structure (4.14): Viton-A

This gives a family of solid propellants with higher I_{sp} leading to higher range or payload. Similarly, another binder is prepared by reacting a nitro- or fluorodinitromethyl-containing polycarboxylic acid diol type polyester with an isocyanate or a carboxyl reactive crosslinking agent. Du Pont, USA has also developed perfluoro elastomer which is better than Viton-A and is considered ideal for aerospace applications (space shuttles). The fluorinated polyols are an entirely new class of polyol intermediates produced by Montedison. The structure of a typical –OH-terminated perfluoropolyether [Structure (4.15)] is shown below:

$$HO-CH_2-CF_2-(OC_2F_4)_p-(O-CF_2)_q-OCF_2-CH_2OH$$

Structure (4.15): Hydroxy-terminated perfluoropolyether polyol

Its average molecular weight is 2000 ± 400 with functionality ≈ 2.0. The cost of these fluorinated polyols is high. However, PU elastomers with unique chemical resistance and other exceptional properties are produced.

Paris-based Société Nationale des Poudres et Explosifs (SNPE) France has recently developed a new binder known as butacene (a ferrocene derivative chemically bound to the HTPB backbone) for composite propellants. The butacene-based composite propellants are available for use and have higher burn rates compared with HTPB. In addition, the chief advantage of this binder is that the same facilities which are used for the manufacture of HTPB-based propellants, can be used for the manufacture of butacene-based composite propellants as well.

The recent trend is to use energetic binders such as nitrated cyclodextrin polymer, poly(CDN), glycidyl azide polymer (GAP), nitrated HTPB, poly(NiMMO) and poly(GlyN) etc for composite propellants and PBXs. Energetic polymers have been researched extensively over the last 30 years as alternatives to hydroxy-terminated polybutadiene (HTPB) binder [97]. The advantage of an energetic binder over traditional non-energetic binders is the lower solids loading of sensitive fillers required to achieve similar performance. Lower filler levels reduce the vulnerability of the system to external stimuli such as fire, impact, shock waves etc. and therefore, greatly increase the safety of the munitions containing them. Poly(3,3-nitratomethyl) methyl oxetane [Poly(NiMMO)] and polyglycidyl nitrate [Poly(GlyN)] are commercially available energetic binders which have been studied extensively in the UK as replacements for non-energetic binders. In this section, these energetic polymers are discussed in detail.

1) **Nitrated cyclodextrin polymers [Poly(CDN)]:** MACH I Inc. USA has completed a small Business Innovation Research Programme of the US Air Force to evaluate nitrated cyclodextrin polymers, [(Poly(CDN)] as possible components of insensitive and minimum smoke producing propellants [98, 99]. A systematic study on the synthesis, purification and characterization of the following polymers [100]

    (a) γ-cyclodextrin polymer crosslinked with 1-chloro-2,3-epoxy propane;

(b) γ-cyclodextrin polymer crosslinked with 4,4′-methylene-bis (phenyl isocyanate);

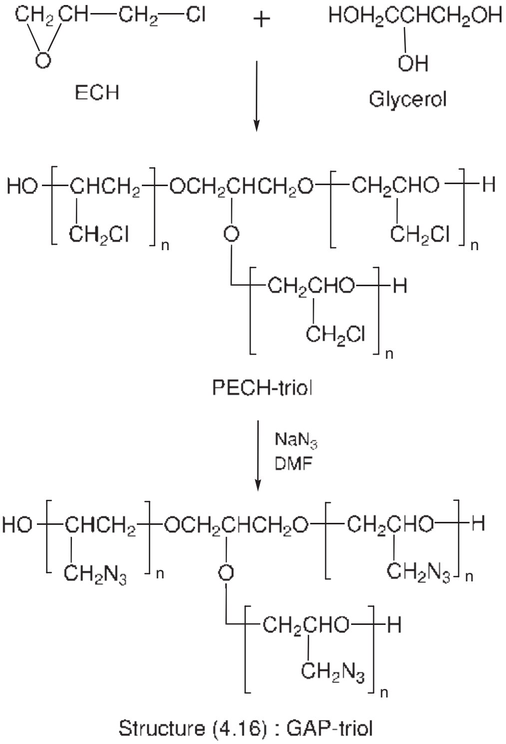
(c) a linear polymer with pendant γ-cyclodextrins;

(d) a linear tube consisting of α-cyclodextrins crosslinked with 1-chloro-2,3-epoxy propane;

was carried out and the resulting polymers on their nitration according to different protocols, give their nitrated compounds. The polymers (a), (c) and (d) were nitrated using nitric acid and their nitrated forms have nitrogen 11.6%, 19.9% and 9.55% respectively. However, polymer (b) cannot be nitrated using nitric acid and therefore was nitrated using N_2O_5 in liquid carbon dioxide as a medium. The encapsulation trials of RDX with nitrated polymers followed by sensitivity measurement indicate that the shock sensitivity of RDX comes down dramatically on encapsulation. Further, evaluation of these nitrated polymers indicates potential of the nitrated polymer (a) as insensitive munition (IM) energetic candidate.

2) **Glycidyl azide polymer (GAP):** GAP is one of the most widely studied energetic polymers and was first synthesized in 1972 by Vandenburg [101] by the reaction of NaN_3 with polyepichlorohydrin (PECH-triol) in DMF. Subsequently, several groups of researchers have been active in developing GAP for use as an energetic plasticizer and an energetic binder. GAP possesses a high density ($1.3\,g\,cm^{-3}$) compared with other polymers used as binders for composite propellants and PBXs, a positive heat of formation ($+42\,kcal\,mol^{-1}$) and capability to desensitize nitroglycerine (NG), a major ingredient of DB and CMDB rocket propellants. Hence, it has been employed both as a plasticizer ($\overline{M}_n \approx 400$–$500$) and as a binder ($\overline{M}_n \approx 2500$–$3000$) in propellants in an effort to enhance specific impulse (I_{sp}). A number of publications are available in the current literature [102–110] which deal with almost all aspects of GAP: synthesis, characterization, thermal behavior, explosive properties and its evaluation in propellant formulations as a plasticizer and as a binder. GAP was found to be very insensitive (did not explode) when impacted with ≈5.5 kg drop weight and height 130 cm in drop weight machine coupled with a high speed camera even in the presence of additives or gas bubbles [111]. The properties of GAP reveal that it may open a new era in the field of explosives in the near future. Based on the analogy of hydroxy-terminated polybutadiene (HTPB), it is believed that GAP may prove to be a very interesting binder for explosive formulations, PBXs and propellants. SNPE, France has already set up a pilot plant for the manufacture of GAP under licence from Rockwell International, USA, in order to cater for requirements of European countries [112]. It is currently the most readily available energetic binder due to its relatively straightforward and low cost synthesis and shows excellent binder properties in its pure form.

Frankel and coworkers at Rocketdyne [108] first synthesized PECH-triol by polymerization of epichlorohydrin (ECH) with glycerol as initiator followed by synthesis of GAP-triol [Structure (4.16)] as in Scheme 4.2.

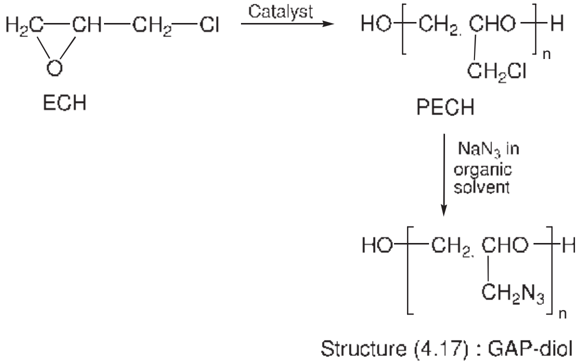


Scheme 4.2 Synthesis of GAP-triol.

Similarly, GAP-diol [Structure (4.17)] may be made by Scheme 4.3 where *n* is the degree of polymerization. GAP may then be crosslinked with isocyanates to give an extended polymer network.

The general process of synthesis of GAP-triol can also be used to produce linear GAP-diol and branched GAP-diol polymer [113]. As PECH-diol is commercially available, azidation can be carried out directly and GAP having desired molecular weight and functionality may be obtained in one step only.

Linear GAP has a functionality of ≈2 and in order to achieve the desired level of mechanical properties, it must be raised by the addition of triols or crosslinked with triisocyanates to generate the desired extended polymeric matrix. Gas evolution is a serious problem during the curing of liquid GAP with isocyanates which react with moisture to give carbon dioxide. This carbon dioxide (CO_2) remains trapped in the voids of the crosslinked binder networks and results in decreased mechanical properties and performance. Some organometallic compounds such as dibutyltin dilaurate (DBTDL) and triphenyl bismuth (TPB) are reported to suppress CO_2 formation and at the same time, accelerate the curing process [114].



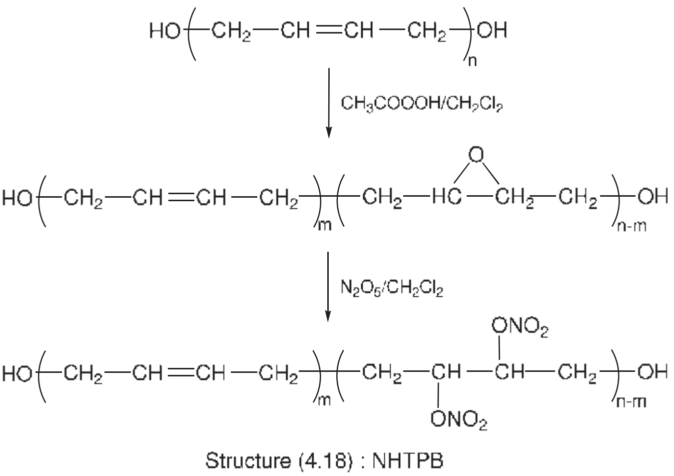
Scheme 4.3 Synthesis of GAP-diol.

GAP has a low $T_g \approx -45\,^\circ C$ and a low weight percentage of polymer weight-bearing chain which results in an energetically favorable binder. However, GAP is hard and brittle at low temperatures as a consequence of the rigid conjugated $-N_3$ groups limiting the flexibility of the polymer backbone.

Branched GAP (B-GAP) consists of a long GAP backbone chain to which shorter GAP chains have been grafted. It is synthesized by the simultaneous degradation and azidation of high mol.wt. ($\approx 10^6$) solid PECH with NaN_3 and a basic degradation catalyst in the presence of an inhibitor in a polar organic solvent. The reaction is completed [115] in less than 16 h. As a result of this unique degradation and simultaneous azidation process, branched hydroxy-terminated GAP is obtained in a single step thereby reducing time and cost. A pilot plant for the manufacture of 5 kg per batch of branched GAP is in operation at the Defence Research Establishment, Valcartier (DREV), Canada [116, 117]. Rocket propellants based on AN and B-GAP have also been cast and their salient features are minimum smoke, low vulnerability and good mechanical integrity.

3) **Nitrated HTPB:** The potential to nitrate HTPB was recognized many years ago. The synthetic route in the early stages involved epoxidation of HTPB in a manner similar to that reported by Zuchowska [118] using 'in situ' peracetic acid as the epoxidation reagent. Reaction of the epoxide groups with N_2O_5 in dichloromethane gives a polymer with a percentage of double bonds converted to dinitrate ester groups depending upon the epoxide content of the intermediate polymer. Nitrated HTPB, an energetic binder which combines the excellent elastomeric properties of HTPB coupled with energy associated with nitrate ester groups is potentially useful for propellant, explosive and pyrotechnic formulations.

NHTPB [Structure (4.18)] is a liquid polymer, whose viscosity can be varied by changing the percentage conversion of double-bonds to dinitrate ester groups. It is made by conversion of a percentage of the double bonds in HTPB to epoxide groups and then to nitrate-ester groups by the reaction with



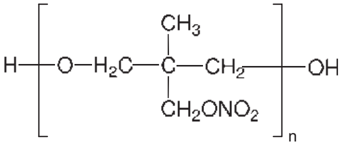
Scheme 4.4 Synthesis of Nitrated Hydroxy-terminated Polybutadiene(NHTPB).

N_2O_5, a powerful nitrating reagent. The outline of its synthesis is given in Scheme 4.4.

Nitrated HTPB with 10% double bonds converted to dinitrate ester groups is good for use as a binder. It has viscosity sufficiently low both to make it easy to process and to permit a high solids loading [119]. It can be cured by using aliphatic or aromatic diisocyanates. Its T_g is however, slightly higher than that of HTPB ($T_g \approx -63\,°C$) but unlike HTPB, it has the advantage of being miscible with energetic plasticizers. Its thermal stability is also acceptable. NHTPB synthesized by selective nitration using N_2O_5 from cheap precursors, has undergone scale-up and evaluation trial and the initial data suggest its suitability for binder application [120, 121].

Some energetic monomers {candidate molecules such as 3-nitrato methyl-3-methyl oxetane (NiMMO) and glycidyl nitrate (GlyN)} have also been synthesized by selective nitration [122] with N_2O_5. These monomers yield polymers of the desired molecular weight range and suitable hydroxyl functionality. The OH-terminated molecules may be subsequently crosslinked to give polyurethane rubbers which constitute a new class of energetic rubbers with potential applications in explosives and propellants. Such rubbers enable high-performance and low vulnerability propellant formulations [123].

4) **Poly(NiMMO):**
NiMMO is also synthesized by the selective nitration of the hydroxyl group present in 3-hydroxymethyl-3-methyloxetane (HyMMO) using N_2O_5. In order to aid scale-up of the monomer, NiMMO is now routinely made in a flow nitration system giving excellent yields and purity in dichloromethane solution which can be directly polymerized [124]. The resulting monomer (NiMMO), on cationic polymerization, yields a pale yellow viscous liquid [97,

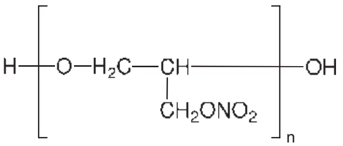


Structure (4.19): Poly(3-nitratomethyl-3-methyloxetane) [Poly(NiMMO)]

125] called poly(NiMMO) [Structure (4.19)]. The cationic polymerization of (NiMMO) is done using an initiator system consisting of BF_3 and a diol. The polymerization depends on many factors such as reaction temperature, initiator system, reaction time, monomer addition rate etc. which have effects on the molecular weight, polydispersity, viscosity, hydroxyl functionality and presence of cyclic species etc. The standard poly(NiMMO) is difunctional since butanediol is the initiating alcohol. However, higher functionality can be achieved by the use of a triol ultimately giving a harder binder. Furthermore, molecular weight can be varied by changing the monomer feed rates and ratio of diol to Lewis acid co-initiator. In particular, by using a large excess of diol with a strong acid initiator, the reaction proceeds by a different mechanism and lower molecular weight but more structurally defined product results. This product can also be end nitrated to give a non-hydroxylated oligomer of NiMMO which can act as an effective plasticizer for the prepolymer [126]. This process has been scaled-up by the UK Defence Research Agency (DRA) and the technology transferred to ICI. The T_g of the prepolymer (measured by DSC) is −25 °C. The thermal stability of the polymer is reasonable (decomposition starts at 170 °C). It is now being evaluated as a propellant and explosive binder in large scale tests. Use of this binder increases the overall energy of a formulation and reduces the vulnerability. DRA has developed a plastic bonded explosive (PBX) called CPX 413 [based on poly(NiMMO)/HMX/NTO/Plasticizer (K-10)] which matches the performance goal of Composition B (RDX/TNT 60/40) while passing the UN Series-7 Tests, ranking it as an Extremely Insensitive Detonation Composition [127]. The formulation of CPX 413 is NTO 45%, HMX 35%, Poly(NiMMO) 10% and K-10 10%. The binder poly(NiMMO) is cured with the commercially available isocyanate, Desmodur N100 and an energetic plasticizer K-10 was used to lower the viscosity of the mix and glass transition temperature (T_g) of the cured PBX. CPX 413 has a measured density of $1.70\,g\,cm^{-3}$ and VOD ≈ $8150\,m s^{-1}$ as against $1.66\,g\,cm^{-3}$ and $7840\,m s^{-1}$ respectively reported for RDX/TNT (60/40) in the literature.

Poly(NiMMO) has been used in a variety of applications, not solely in explosives but also in gun and rocket propellants [128]. British scientists have done extensive research on synthesis, characterization and application of poly(NiMMO) as a binder for gun and rocket propellants. A team led by Leach examined a range of composite LOVA propellants based on poly(NiMMO) in combination with various fillers and plasticizers. At the end of their investigation, they concluded that it is possible to formulate propellants with an impetus of up to $1300\,J\,g^{-1}$ which still show a low response to shaped charge attack [129]. In another study conducted by Flynn *et al.* at the British Aerospace, Defence Royal Ordnance, UK, a composite propellant based on poly(NiMMO)–AP–AP was made. The results from small scale firing of motors indicate high burn rate and high I_{sp} without the use of any BRM although their use is not precluded. Further, pressure exponent is low which is advantageous to rocket designers in addition to its low smoke level compared with a standard HTPB–AP–DOS composite propellant [130].

5) **Poly(GlyN):**
   Glycidyl nitrate (GlyN) is synthesized in a similar manner to NiMMO by selective –OH nitration of glycidol using N_2O_5. The yield and purity are both high. GlyN is polymerized into poly(GlyN) [Structure (4.20)] by using the same technique used [131, 132] to form poly(NiMMO). GlyN, like its oxetane counterpart NiMMO, is now prepared using N_2O_5 in a flow reactor to give dichloromethane solution in high yields and high purity requiring no further purification before polymerization. However, polymerization of GlyN is more difficult than that of NiMMO and is carried out by a different polymerization mechanism. The polymerization is effected by controlling the reaction parameters to induce an active monomer mechanism (AMM) by using a strong acid initiator such as HBF_4. A more detailed account of the synthesis and properties of high-molecular-weight poly(GlyN) can be found in the literature [131]. Poly(GlyN) is a pale yellow liquid that can be crosslinked with diisocyanates to yield rubbery materials. The polymer imparts high density, high energy and low vulnerability to both propellant and explosive formulations. Its T_g is reported as −35 °C.



$$H\left[O-H_2C-\underset{CH_2ONO_2}{\underset{|}{CH}}-\right]_n OH$$

Structure (4.20): Poly(glycidyl nitrate) [Poly(GlyN)]

The synthesis of α, ω-hydroxy telechelic, low molecular weight oligomers (degree of polymerization less than 10) of GlyN and NiMMO by the activated monomer mechanism has also been reported by the researchers at DRA, UK. The end-nitration of these compounds by dinitrogen pentoxide (N_2O_5) in dichloromethane gives α, ω-nitro telechelic oligomers that are envisaged to be energetic and fully compatible (miscible) plasticizers for the new generation of energetic binders such as poly(NiMMO) and poly(GlyN) in propellant and explosive applications [133].

Uncured poly(GlyN) prepolymer exhibits good chemical stability and has a satisfactory shelf-life. However, the ageing characteristics of isocyanates cured PU rubbers are unsatisfactory contrary to (NiMMO) rubbers which have good ageing characteristics. Long term ageing trials have shown that the cured rubbers undergo degradation and liquefaction can occur within a period of 12 months. Further, degradation is not prevented by the addition of stabilizers such as 2-NDPA, p-NMA and calcium carbonate etc. at 1% level or by the exclusion of oxygen. The exhaustive study conducted by scientists at DERA, UK suggests that this degradation of Poly(GlyN) rubber is attributed to a low activation energy degradation associated with chain scission at the urethane linkage and has little to do with the normal nitrate ester degradation process. Further, this instability of poly(GlyN) prepolymer is its inherent problem and does not depend on the isocyanate used. This is supported by the fact that such chain scission is not possible in case of poly(NiMMO) which does not possess labile hydrogen atom available for transfer [134].

The above problem was overcome by modifying poly(GlyN) at the crosslink site to convert terminal GlyNs to chlorohydrin units. This end modified poly(GlyN) showed considerable promise at eliminating the shelf-life related problem [135] found in unmodified poly(GlyN).Unfortunately, the modified poly(GlyN) still exhibited some gassing behavior. An alternative modification of poly(GlyN) end groups by ring closure of the primary –OH group to form an epoxide followed by hydrolysis with H_2SO_4 to give a secondary/primary diol appeared initially very promising [136]. Subsequently, it was noticed that this modified material also exhibited minor gas evolution [137]. As a result of painstaking research at ICI Explosives, UK, the scientists proposed treatment of end-modified poly(GlyN) with potassium carbonate solution. This was found to be the most effective way of removing the instability of Poly(GlyN) and thereby improving the shelf-life of the modified poly(GlyN). Finally, the H_2SO_4 hydrolyzed/K_2CO_3 stabilized end modified poly(GlyN) exhibits far superior long term chemical stability than those shown by earlier types of poly(GlyN). Poly(NiMMO) and poly(GlyN) are being manufactured by Nobel Energetics (now Chemring Energetics) UK on a regular basis and they are reported to be of use in explosives, gun and rocket propellants [138, 139].

The polymerization of GlyN was also investigated using hexafluoroantimonate/dibromoxylene initiating system because of its higher initiating efficiency and better stability and control available compared with the traditional tetrafluoroboric acid/diol system. The preliminary results are promising and indicate that it is a better polymerization system and these materials are expected to exhibit superior mechanical properties to those available commercially [140].

A family of high performance and clean space motor/gas generators and large launch vehicle solid propellants based on poly(GlyN) binder, ammonium nitrate oxidizer and small amounts of aluminum and/or boron with optimized performance at low solids loading (without the presence of plasticizers) and also poly(GlyN) binder, ammonium nitrate oxidizer and aluminum or magnesium fuel have been reported in the literature [141, 142]. These solid propellant formulations produce essentially no HCl or chloride ions in the exhaust and are considered eco-friendly.

Similarly, high performance solid propellants consisting of Poly(GlyN) binder, ammonium perchlorate oxidizer and beryllium/beryllium hydride fuel which also do not require the presence of plasticizers and offer optimum performance at low solids loading have been reported for space launch vehicles [143].

To summarize, the cost of production of NHTPB is lower than that of poly(NiMMO) or Poly(GlyN). However, NHTPB's performance is poor in comparison to them. On the basis of trials conducted so far, it seems likely that poly(GlyN) will prove to be a world leader in the field of energetic polymers. A summary of the properties of energetic binders for use with both explosives and propellants is given in Table 4.6a,b.

Current methodologies for the manufacture of energetic materials such as NHTPB, Poly(NiMMO) and Poly(GlyN) etc. use environmentally undesirable solvents such as dichloromethane. However, the adoption of the 'Montreal Protocol' by most of the countries has limited the use of these halogenated hydrocarbons. To address current and futuristic legislations, DERA Scientists have developed various strategies to enable the manufacture of energetic materials in an environmentally friendly manner. Such an approach is to use liquid or supercritical carbon dioxide as a solvent. Carbon dioxide exhibits supercritical fluid behavior at a temperature >31.1 °C and a pressure >73.8 bar. At this point, it acts as a 'super solvent', that is, it possesses high solubilizing properties of liquid and also high diffusivity of a gas. This allows possibility of tuning solvent characteristics for highly specific reactions or separations and also possibility of synthesizing novel materials due to the milder conditions incorporated in the process. With the use of liquid CO_2 as the reaction medium, DERA has also developed a method of introducing $-NO_2$ and $-ONO_2$ functionalities by using dinitrogen pentoxide (N_2O_5) as a nitrating agent and has obtained similar or superior results. Nitrations of various alcohols, silylethers and silylamines were also carried out using N_2O_5/CO_2 as the reaction medium. Cationic ring opening polymerization of various energetic oxetanes and oxiranes was also carried out in liquid or supercritical CO_2 to form energetic prepolymers for use as binders in composite propellants and explosives. The preliminary results indicate that the use of liquid/supercritical CO_2 for manufacture of energetic materials is very promising in place of

Table 4.6a Some physical properties of energetic polymeric binders.

Polymer	$\overline{M}_n$ (by GPC)	Density/g cm^{-3}	Viscosity/Poise (at 30 °C)	T_g/°C
GAP	500–5000	1.30	50	–40
NHTPB	≈2500	1.20	120	–58
Poly(NiMMO)	2000–15 000	1.26	1350	–25
Poly(GlyN)	1000–3000	1.42	163	–35

Table 4.6b Some thermal and explosive properties of energetic binders for explosives and propellants.

Binder	Thermal sensitivity		Vacuum stability (at 100 °C for 40 h)/cm^3 g^{-1}	Impact sensitivity (by liquid rotter impact tester)	Friction sensitivity	Special features
	Ti/°C	Tm/°C				
GAP	120	212	≥3.0 (200 h)	Very insensitive	Very insensitive	Acts as a binder and plasticizer. Gas evolution during curing is a serious problem
NHTPB	156	209	0.50	F of I is out of range i.e., very insensitive	very insensitive	Miscible with all energetic plasticizers in current use i.e., NG, DEGDN, TEGDN, MTN, K-10 and BDNPA/F etc.
Poly(NiMMO)	170	229	0.54	very insensitive	very insensitive	Miscible with similar plasticizers. Similar to GAP, acts as a binder and plasticizer depending on molecular weight.
Poly(GlyN)	145	222	0.65	Its sensitiveness to impact and friction is classed as too low to require classification as a Class 1 Explosive		End-modified, H_2SO_4 hydrolyzed and K_2CO_3 treated material meets the requirements. Similar to GAP and poly(NiMMO) acts as a binder and plasticizer depending on molecular weight.

halogenated hydrocarbons [144] and thus conforming to the provisions of the 'Montreal Protocol'.

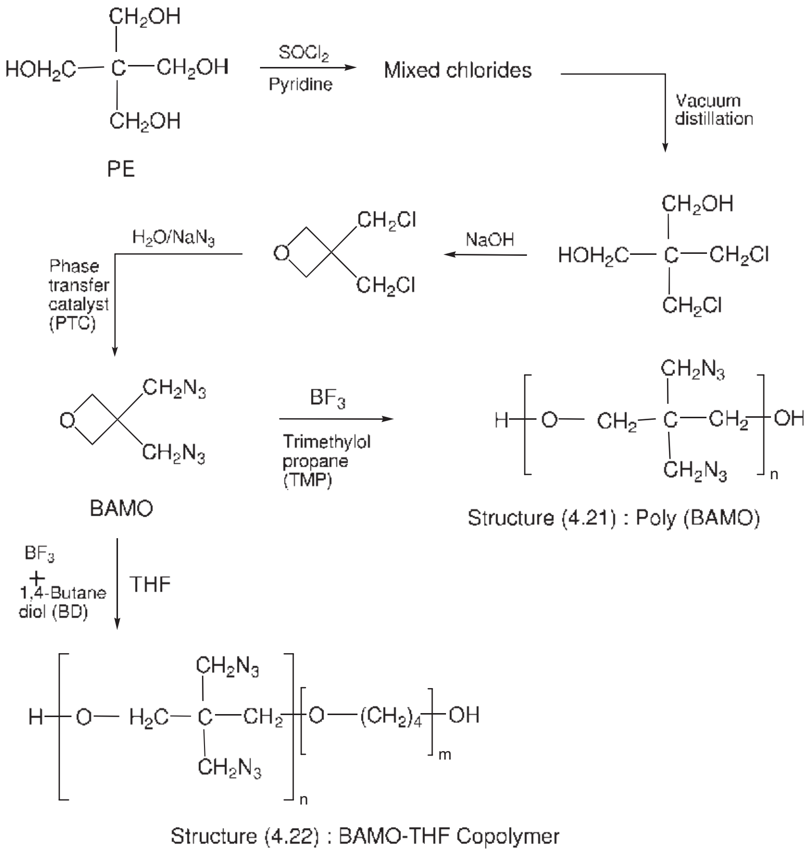
6) **Energetic thermoplastic elastomers:** In addition to energetic binders such as GAP, NHTPB, poly(NiMMO) and poly(GlyN), poly[3,3-bis(azidomethyl) oxetane] [Poly(BAMO)], poly(3-azidomethyl-3-methyl oxetane) [Poly(AMMO)] and their copolymers are also emerging on the world scenario as potential contenders for binder application. The future requirements of recyclability or environmentally compliant disposal of explosives and propellants are very important. The main problem associated with the current binders is that they use an isocyanate cure which is irreversible, toxic, causes gassing, has a finite pot-life and is generally not environment friendly. Such cured rubbers cannot be easily recycled without extensive degradation of polymer and their disposal also poses problems. In order to overcome these problems, use of energetic

thermoplastic elastomers (ETPEs) has been investigated by many groups all over the globe [145, 146]. The main effort has been into the combination of a hard block (A) and soft block (B). Energetic copolymers consisting of blocks of various energetic polymers such as poly(BAMO), poly(NiMMO), and poly(AMMO), and variants thereof have been studied. The results show that the ideal system is a pure ABA block copolymer where A blocks have a suitable melting temperature for processing whereas B block has a low T_g to satisfy the Service requirements. These polymers negate the use of isocyanates and can be easily processed and recycled by simply melting the material. The ETPEs having hard and soft segments are useful since their co-crystallization itself forms the necessary 3-dimensional network of interlinked soft unsymmetrical polymer blocks. Crosslinkers are not used in the solidification process. However, block length is critical to obtain the required thermal and mechanical properties and is therefore, carefully controlled during the polymerization. The QinetiQ's work has demonstrated that poly(NiMMO) can be produced with excellent molecular weight control. Further, poly(GlyN) can be produced in much higher molecular weight than commercially available material. ETPEs based on high molecular weight poly(NiMMO) and poly(BAMO) have also been produced. Such ETPEs have the potential to play a major role in the next generation of propellants, explosives and pyrotechnics.

The synthesis of BAMO involves treatment of 3,3-bis(chloromethyl) oxetane (BCMO) with sodium azide in the DMF medium at 85 °C for 24 h. Similarly, AMMO which is a monofunctional analog of BAMO is synthesized by the azidation of chloro/tosylate product of 3-hydroxymethyl-3-methyl oxetane (HyMMO) with sodium azide in DMF medium at elevated temperatures. These energetic monomers are readily polymerized to liquid curable prepolymers with the help of boron trifluoride etherate/1,4-butanediol initiator system and the outlines of synthesis [147–150] of poly(BAMO) [Structure (4.21)] and its copolymer with THF, that is, BAMO-THF copolymer [Structure (4.22)] are shown in Scheme 4.5.

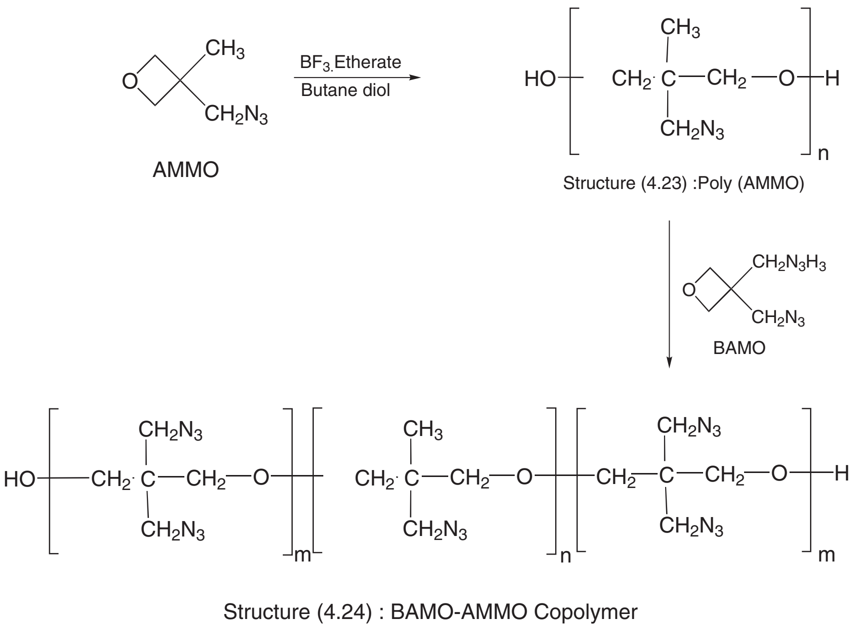
Similarly, the outlines for synthesis of poly(AMMO) [Structure (4.23)] and its copolymer with BAMO, that is, BAMO-AMMO copolymer [Structure (4.24)] are [151, 152] given in Scheme 4.6.

BAMO is perhaps the most prominent among the azido oxetanes class in terms of the number of polymers and copolymers reported so far. Due to its symmetrical azido groups, it assumes special significance as a hard block repeating unit in a thermoplastic elastomer. However, the homopolymer is solid and cannot be used directly for binder applications because of its crystalline nature. Also, poly(BAMO) shows relatively poor mechanical properties as a binder for solid rocket propellants [153]. Many copolymers of BAMO with non-energetic co-monomers like tetrahydrofuran (THF) have been reported. The BAMO-THF copolymer is an excellent candidate for binder applications with its energetic BAMO content coupled with the THF block which affords



Scheme 4.5 Synthesis of poly(BAMO) and BAMO-THF copolymer.

good processibility and mechanical properties [154]. However, the performance of propellants based on such copolymers comes down and at the same time, the thermoplastic character disappears. This led to the emergence of AMMO as a preferable component of BAMO-based copolymers. BAMO-AMMO copolymers yield ETPEs which are of considerable interest for extruded propellants and explosives. BAMO-AMMO copolymer (80/20) offers the most attractive features for use as ETPE binder in futuristic propellant and explosive formulations [155]. Similarly, ETPEs, based on high molecular weight poly(NiMMO) and poly(BAMO) have also been reported [156]. BAMO-NiMMO copolymer with a molar ratio of 7 to 3 possesses very interesting characteristics in respect of sensitiveness, mechanical properties and heat of decomposition and is a potential thermoplastic energetic binder for explosives and propellants for insensitive munitions [157].



Scheme 4.6 Synthesis of poly(AMMO) and BAMO-AMMO copolymer.

Hamilton and coworkers designed a rocket propellant formulation based on BAMO-AMMO Copolymer TPE and 80% total solids (AP and Al) and it was directly cast into a phenolic case and required no liner or insulation. The results of firing of a 18 kg test motor exhibited completely acceptable ballistic properties. The authors claimed it to be the 1st demonstration of a high energy TPE motor firing [158]. Prior to this, Wardle and his team reported BAMO-AMMO copolymer and CL-20-based potentially attractive high energy ETPE gun propellants.

4.9.3
Metal Fuels

Metal powders are incorporated in propellants primarily to achieve high volumetric energy release due to their high heat of reaction with oxygen, improvement of propellant density, reduction in pressure exponent (n) and suppression of combustion instability [159, 160]. Occasionally metals are also introduced in the form of wires, foils etc. to enhance burn rates and improve mechanical properties. Aluminum, magnesium, boron and zirconium have found wide application in propellant formulations. Powdered aluminum is extensively used in propellant formulations for extra energy, that is, higher heat of combustion, higher propellant density, higher combustion temperature and thus higher I_{sp} and also to promote stable burning. Although powdered beryllium has a higher theoretical energy value than aluminum, it is seldom used because of its extreme toxicity, relative scarcity and higher cost. In addition, beryllium has poor combustion efficiency with most of the hydrocarbon binder-fuels available. However, this could be improved with the use of unique and advanced binders like fluorocarbons. Magnesium is a preferred metal fuel for fuel-rich propellants. Boron was the star metal fuel during the 1960s but things changed subsequently mainly because of combustion related problems due to the formation of boron oxide on its surface. Use of zirconium or titanium has also been reported for use in propellants which require high density-impulse (product of density and I_{sp}).

Both zirconium and hafnium have extreme electrostatic discharge (ESD) sensitivities that create significant safety issues and have limited their use in energetic formulations. MACH I, U.S., has expanded its in-house technology for coating high melting refractory metals with a low melting soft metal and thus, aluminum-coated hafnium and zirconium were explored. Aluminum coating improved ESD sensitivity to aluminum like levels, a substantial improvement. MACH I is currently working with Aerojet Inc. to develop high density-impulse solid propellants based on aluminum-coated zirconium.

Using similar technology, MACH I is developing a magnesium coated boron for commercial applications. Boron, due to its high heat of oxidation and low atomic weight, is one of the highest energy-density materials known. Unfortunately, it is very difficult to ignite it due to its inherent reactivity and coating of its surface with oxide. Magnesium, by comparison, is relatively easy to ignite and by coating a boron particle with magnesium, the ignition characteristics of boron increase substantially. In this application, burning magnesium heats the boron particle, as well as keeping the surface relatively clear of boron oxide [161].

Zirconium could offer a higher performance alternative to aluminum powders in propellants but it is extremely combustible or pyrophoric in nature. Zirconium could provide up to a 20% higher density-impulse than other metals such as aluminum which is most commonly used in composite propellants. Having a propellant with a higher density-impulse should allow planners of space or military missions to achieve higher payload and/or range capability for a rocket or missile. Raw zirconium has an ESD of 0.5 millijoules meaning it could be set-off easily by normal static electricity (a person can quickly generate 20 millijoules of static electricity during a casual stroll). It means that ESD of zirconium should be increased to a much safer level ≈200 millijoules, the same as the ESD of aluminum.

MACH I, Inc. USA, has developed a process to make zirconium powder as safe as aluminum powder (passivated Zr powder) and is in the process to develop propellants with high density-impulse for potential use in the ballistic missile defense system. These propellants would produce a high degree of impulse or thrust per unit of volume.

Some reports also suggest that an alloy of Be and Li is best when AP is used as an oxidizer. However, the drawbacks of Be cannot be ignored with the use of this alloy.

4.9.4
Plasticizers

Plasticizers are high boiling point liquids, usually organic esters which are added to propellant and explosive formulations in order to modify their properties. The presence of ester groups in plasticizers impart oily characteristics to them. The addition of plasticizers improves flexibility which in turn improves low temperature characteristics of propellants and explosives. The introduction of a plasticizer between two segments of a polymer used as a binder separates the polar groups apart, thereby reducing the monotone of configuration and improving flexibility. In addition, use of a plasticizer improves processibility and also improves explosives or solids loading of the formulations leading to their better performance.

4.9.4.1 Classification of Plasticizers

Plasticizers are generally classified as inert or non-energetic and energetic plasticizers. The non-energetic plasticizers modify tensile strength, elongation. toughness and softening point but reduce energy of a system. Some of the well-known non-explosive plasticizers which are being used for the manufacture of rocket propellants are triacetin (TA), diethyl phthalate (DEP), dioctyl azelate (emolein) and dioctyl adipate (DOA).

The energetic plasticizers also enhance flexibility and elasticity in addition to increase in the overall energy of a system and its spontaneous ignition properties. In explosives and propellants, they are preferred over non-energetic plasticizers because of their contribution to energy. The energetic plasticizers invariably contain functional moieties such as nitro, fluoronitro, fluoroamino, azido etc. in addition to long carbon-carbon chains [162].

These non-energetic and energetic plasticizers may be non-reactive or reactive. A plasticizer which when added to a polymer, does not chemically combine with the polymer and modifies the polymer's properties because of its presence in between the polymer chains, is known as non-reactive plasticizer. For example, diethyl phthalate (DEP), dibutyl phthalate (DBP), dioctyl phthalate (DOP), triacetin (TA) etc. The most important drawback of such plasticizers is that they tend to ooze out from the system during storage. On the other hand, a plasticizer which chemically reacts with polymers and improves their flexibility and low temperature properties is known as reactive plasticizer. Novolac epoxy plasticizers and monoepoxy long chain compounds are its important examples. Sometimes, these plasticizers are also referred to as flexibilizers as flexibility increases because of their addition. The most important attribute of such plasticizers (flexibilizers) is that they do not tend to ooze out or migrate after manufacture and during storage.

The efficiency of a plasticizer is judged from its ability to bring about a desired effect. The more the plasticizer that is required to produce the desired effect, the less efficient it is. The plasticizers are invariably added in the proportion varying from 3 to 5%. It is however, desirable to have high plasticizing effect with its minimum concentration.

4.9.4.2 **Characteristics of Plasticizers**

All moderately high molecular weight liquids or low melting solids or esters of long chain carboxylic acids do not function as plasticizers. Some of the important characteristics of a plasticizer are:

- Chemical compatibility with polymer used as a binder, low volatility and high resistance to extraction and migration.
- Should not be very viscous. According to Leilich's Rule, more viscous plasticizers are less efficient than the less viscous ones.
- Non-toxic, non-sensitizing to skin, absence of eye irritation and neuro-toxicity.
- Free from strong odor and mottling.
- Fastness to light, washing and solvent.
- Capable of mixing and dissolving polymer mutually to yield a homogeneous mass.
- Should not affect the mechanical properties of the polymer significantly. Also, it should not induce shrinkage or early stiffening of plasticized polymer.

4.9.4.3 **Functions of Plasticizers**

The addition of a plasticizer to a polymer or resin imparts the following changes:

- Brings down the viscosity of a liquid polymer. Also, lowers the melt viscosity of a thermoplastic polymer. Thus it improves the workability and enhances the loading capability of a polymer with explosives, fillers or oxidizers. This is of special interest in the field of explosives or propellants where the amount of an explosive or oxidizer ingredient considerably increases leading to improvement in their performance.

- Also brings down modulus and tensile strength and as a result, increases elongation which improves the low temperature characteristics. This may also lower T_g of the polymer or resin and thus facilitates their processing at a lower temperature. Some aliphatic dicarboxylic acid esters such as bis (2-ethyl hexyl) adipates, sebacates, azelates, etc. are most effective for this purpose.

- Sometimes, addition of plasticizer imparts flame retardant characteristics in addition to other properties. Phosphate esters such as tris(2-ethyl hexyl) phosphate (TOP), tricresyl phosphate (TCP), chlorinated paraffin hydrocarbons etc. impart excellent flame retardant characteristics to many polymers.

- Last, but the most important is improvement in terms of safety, that is, processing of the explosive or propellant formulations becomes safer.

4.9.4.4 **Migration of Plasticizers**

When plasticized polymers are in contact with the mother polymers, plasticizers are likely to migrate to mother polymers and the extent of their migration depends on a number of factors such as polymer–plasticizer system, polarity of polymer and plasticizer, crosslink density of polymer, molecular weight of plasticizer etc.

It is reported in the literature that small migration does not change the properties of a polymer significantly but extensive migration severely affects their properties. A number of techniques have been employed to reduce or prevent migration of plasticizers but it is still a difficult problem which requires attention of the scientists working in this field. It is well known that if elongation of a polymer is higher, plasticizer migration is also higher. It has recently been reported that some novel unsaturated polyesters, synthesized by an indigenously developed a 3-step polyesterification process possess higher elongation and lower explosive plasticizer (NG) migration – a unique combination of two contradictory properties reported for the first time in the literature [163].

Some of the well-known plasticizers used in the field of explosives or propellants are given in Table 4.7a,b.

Table 4.7a Some inert/non-energetic plasticizers for explosive and propellant formulations.

Plasticizer	Applications
Triacetin (TA) Diethyl phthalate (DEP)	Function as plasticizers and also desensitizer for nitroglycerine (NG) used as an explosive plasticizer for DB and CMDB propellants.
Dioctyl azelate (trade name – Emolein) Dioctyl adipate (DOA)	Bring down viscosity of HTPB and consequently, increase solids loading which improve performance of propellants and PBXs.
Isodecyl pelargonate (IDP)	Improves low temperature characteristics
Tris (2-ethyl hexyl) phosphate (TOP) Tricresyl phosphate (TCP) Tributyl phosphate Triethyl phosphate	Flame retardant plasticizers for inhibition of DB rocket propellants
Bis (2-ethyhexyl) sebacate	Improves low temperature characteristics of explosive formulations
Novolac epoxy flexibilizers	Improve low and high temperature characteristics of novolac epoxy resins for inhibition of composite rocket propellants [164].
Epoxidized soyabean or linseed oils	Plasticizers for novolac epoxy resins. Also prevent auto-catalytic decomposition of NG during storage
Silylferrocene polybutadiene-based plasticizer	Improves combustion rates of thermoplastic binders-based propellants which are suitable as gas-generator for air bags [165, 166].
Acetyl triethyl citrate (ATEC)	Excellent plasticizer for NC and CAB-based propellants. Also imparts desirable non-vulnerability properties and was used in the original XM-39 LOVA gun propellants [167].

Table 4.7b Some energetic plasticizers for explosive and propellant formulations.

Plasticizer	Applications
Bis (2,2-dintropropyl) formal (BDNPF)	Energetic plasticizer for explosive/propellant formulations
Glycidyl azide polymer (GAP) ($\overline{M}_n \approx 400$–500)	Energetic plasticizer for explosive/propellant formulations
Bis (2,3-diazidopropyl) adipate	Energetic Plasticizer for composite propellants
1,2,4-Butanetriol trinitrate (BTTN)	Energetic Plasticizer/co-plasticizer which minimizes loss in strain capability.
Trimethylolethane trinitrate (TMETN)	Energetic Plasticizer or co-plasticizer for high viscosity nitrocellulose (NC) and most preferred plasticizer for cyclodextrin nitrate polymers
Metriol trinitrate (MTN)	Non-migrating plasticizer
Azidomethyl bis (fluoro dinitro ethyl) amine	Enhances energy and at the same time, minimizes smoke level
6-Azidohexyl-6-azidohexanoate	Minimizes flame in the exhaust
Nitroglycerine (NG)	Energetic plasticizers for DB and CMDB propellants
Ethylene glycol dinitrate (EGDN)	
Diethylene glycol dinitrate (DEGDN)	
Triethylene glycol dinitrate (TEGDN)	
Nitroisobutanetriol trinitrate (NIBTN)	Nitronitrate plasticizers for DB and CMDB propellants
2, 2-dinitropropanediol dinitrate (DNPDN)	
Trinitroethyl nitrate (TNEN)	
2,2-Dinitro-1,3-bis (nitrooxy) propane (NPN)	Imparts similar plasticizing effect on poly(NiMMO) as butyl NENA. However, its thermal stability is poor [168].
2-Methyl-2-nitro-1-azidopropane	Potential plasticizer for explosive and propellant formulations [169].
2-Nitro-1,3-diazidopropane derivatives	Potential plasticizers for explosive and propellant formulations [170].
Bis(2-azidoethyl) adipate (BAEA)	Potential replacement of DEP/TA in propellant and explosive formulations [171].
2-Polynitroalkyl-5-perfluoroalkyl-1,3,4-oxadiazole	Plasticizer for explosive formulations [172]
2,2-Bis (azidomethyl)-1,3-propanediol dinitrate (PDADN)	A new energetic azide plasticizer which is beneficial for thermal decomposition of modified DB propellants and hexogen. Also improves combustion properties [173].
3,3-Bis (difluoroamino)-1,5-dinitratopentane	Useful for energetic formulations based on CAB and plasticized NC [174].

Table 4.7b *Continued*

Plasticizer	Applications
2,2-Dinitro-1,3-propanediol diformate	Novel low sensitivity, energetic plasticizer useful for composite and multi-base explosive and propellant formulations [175].
1,5-Diazido-3-nitrazapentane (DANPE)	A potential energetic plasticizer for triple-base gun propellants for improved ballistic performance [176].

The methods of synthesis of most of the energetic plasticizers are available in the literature [177]. Some energetic plasticizers have been evaluated in propellant and explosive formulations and therefore these energetic plasticizers need more attention.

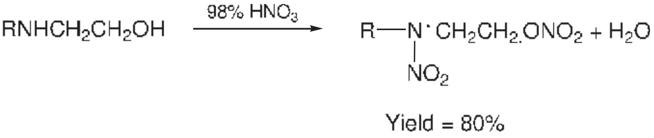
4.9.4.5 **Novel Plasticizers**

Nitroxyethyl Nitramine Plasticizers Nitroxy ethyl nitramine (NENA) plasticizers are a new family of energetic plasticizers which have emerged recently. These are effective plasticizers in energetic formulations, particularly in nitrocellulosic systems. NENAs contain both nitrate ester and nitramine functionalities and possess the general structure: RN $(NO_2).CH_2.CH_2.ONO_2$ where R is methyl, ethyl, propyl, isopropyl, butyl and pentyl.

NENAs were originally discovered in the 1940s at the University of Toronto [178] but keen interest for their use has only recently resurfaced which is due to the following key features:

- Starting materials are commercially available at low cost.
- Synthesis is simple and easily scalable.
- Readily plasticize NC and other cellulosic binders.
- Generate low molecular weight combustion gases.
- Less sensitive to impact than conventional nitrate esters.

In a nutshell, NENAs provide higher impetus at any given flame temperature than many conventional energetic ingredients and it is regarded as their most outstanding feature [165]. A general method for the manufacture of Alkyl NENAs [Structure (4.25)] is by the nitration of commercially available alkyl ethanolamine (Equation 4.20):



$$RNHCH_2CH_2OH \xrightarrow{98\%\ HNO_3} R{-}\underset{\displaystyle NO_2}{\underset{|}{N}}\cdot CH_2CH_2.ONO_2 + H_2O \qquad (4.20)$$

Yield = 80%

Structure (4.25): Alkyl NENAs

One notable member of NENAs family known as dinitroxy ethyl nitramine (DINA) was scaled-up and used [179–181] in a Naval flashless gun propellant (Albanite) way back in 1942.

NENAs possess good thermal stability, readily plasticize NC and other binders, generate low molecular weight combustion products and impart favorable impact sensitivity. Butyl NENA has edge over others because it imparts better low temperature properties as well [182]. The use of NENAs as plasticizers in gun and rocket propellant formulations imparts excellent properties such as high burn rates, reduction in flame temperature and molecular mass of combustion products and high force constant or specific impulse [183].

The data reported in the literature suggests that the replacement of DEP by Bu-NENA in the Dense NC/NG+ DEP/AP/Al/RDX-based composite modified double-base (CMDB) propellants results in increase in the burn rate by 18–20% at $70\,\mathrm{kg\,cm^{-2}}$ pressure. The calorimetric value and percentage elongation also increase significantly. Further, thermal stability and sensitivity of such propellants are comparable with DEP-based CMDB propellants [184]. Bu-NENA is also a component of low vulnerability ammunition (LOVA) propellants [185, 186]. The introduction of butyl-NENA into SB, DB and TB gun propellants results in improvement of their mechanical properties and energetics and reduction in their sensitivity [187].

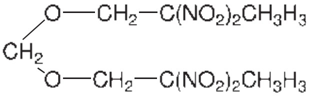
NENAs are low molecular weight molecules and as a result, are volatile and migrate readily from the binder systems. Consequently, propellant formulations based on NENAs do not possess the stipulated minimum of 10 years Service life [188] and therefore, this issue should be resolved by HEMs community before it is used in Service explosives and propellants.

Polynitro Aliphatic Plasticizers Americans commenced their research on polynitroaliphatic plasticizers in the late 1940s with a view to their application as energetic plasticizers (by virtue of their higher densities and higher oxygen content) in explosive and propellant formulations [189]. The most useful products which emerged from their research are bis(2,2-dinitropropyl) acetal (BDNPA) and bis (2,2-dinitropropyl) formal (BDBPF). Subsequently, it was discovered that a mixture consisting of equal amounts of acetal and formal, designated as nitroplasticizer, was more effective as a plasticizer rather than the individual compounds. Nitroplasticizer has a blend of properties: good thermal and chemical stability, low hazard rating, convenience of handling and compatibility with propellant ingredients etc. The formal is a solid whereas the acetal is a liquid. These are used to form a 50/50 eutectic mixture possessing lower m.p. than the formal. This eutectic mixture also imparts better low temperature properties to explosive and propellant formulations [190].

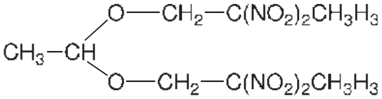
These nitro compounds act as good plasticizers for nitrocellulose (NC). In addition, these compounds when mixed with nitroglycerine (NG) reduce its sensitivity and thus act as efficient desensitizers for its safe handling and transportation. The enhancement in performance characteristics of PBXs or propellant formulations is mainly due to the fact that the conventional non-energetic plasticizers such as

DEP, TA and DOP etc. have high negative calorimetric values or heats of combustion (–6280 to –840 Jg^{-1}) whereas BDNPA/F have high positive calorimetric values approximately +2930 Jg^{-1}.

BDNPF/A [Structures (4.26) and (4.27)] was first synthesized by oxidative nitration of nitroethane to 2,2-dinitropropanol (DNPOH) with silver nitrate as a catalyst followed by the reaction with acetaldehyde/formaldehyde [191]. This process was not economical and later modified to include an additional selective chlorination step of nitroethane to 1-chloronitroethane. BDNPA/F has been produced commercially for many years using this process which is economical, efficient and highly reproducible. Unfortunately, this process involves several environmentally unfavorable materials. The process developed at the Thiokol Corporation is also based on oxidative nitration but using aqueous and non-chlorine chemicals or solvents [192]. This process produces material which meets all specification requirements without any further purification and is now being used for large scale pilot plant production of BDNPA/F.



Structure (4.26): Bis(2,2-dinitropropyl)formal (BDNPF)



Structure (4.27): Bis(2,2-dinitropropyl)acetal (BDNPA)

A study was conducted to find out the effect of addition of these nitroplasticizers on ballistic properties of AP and RDX/HMX filled CMDB propellants. The data generated clearly indicated that the incorporation of nitroplasticizer, that is, 1 : 1 mixture of BDNPF and BDNPA in place of diethyl phthalate (DEP) for AP and nitramine based CMDB propellants improved the burn rates as well as I_{sp} and thermal decomposition behavior of these propellant formulations [193].

Rowanite 8001 or K-10 Plasticizer A mixture of 2,4-dinitro ethyl benzene and 2,4,6-trinitroethyl benzene (2 : 1 mixture) is known as Rowanite 8001, more popularly known as K-10 plasticizer. It. is a clear, yellow/light orange liquid with a UK Hazard Classification of 6.1 (Toxic) and is manufactured by Royal Ordnance in the U.K. It finds use as a nitroaromatic energetic plasticizer in PBXs and also in some propellant formulations.

Azido Plasticizers A large number of compounds with azide functionality have been reported in the literature [194–199] and they appear to be potential energetic plasticizers. A brief summary of these azidoester plasticizers, that is, synthesis, characterization, thermal and explosive properties was presented by Mehrotra *et al.* at the JANNAF Propulsion Meeting [200].

The low molecular weight GAP plasticizer is synthesized by the azide displacement of chlorine from epichlorohydrin (ECH) monomer without a catalyst [201]. Similar to nitrate esters such as trimethylol ethanetrinitrate (TMETN) and butanetriol trinitrate (BTTN) etc., GAP plasticizers are also miscible and compatible with GAP polymer. GAP diol and triol plasticizers have also been reported for this purpose [202]. The hydroxyl groups of GAP plasticizer react with isocyanate curing agent invariably used in such formulations and as a result, its plasticizing function is lost. With this in mind, Ampleman [203] developed a diazido-terminated glycidyl plasticizer without terminal hydroxyl groups. This is a pale yellow liquid with low molecular weight, low T_g and good stability. This GAP plasticizer which is free of hydroxyl groups can be used as an energetic plasticizer in PBXs and gun and rocket propellants.

A new family of energetic plasticizers consisting of azido-acetate ester functionality has recently been reported and 4 new compounds, that is, ethylene glycol bis (azidoacetate) [EGBAA], diethylene glycol bis(azidoacetate) [DEGBAA], trimethylol nitromethane tris (azidoacetate) [TMNTAA] and pentaerythritol tetrakis(azidoacetate) [PETKAA] have been synthesized and characterized in this family. The new plasticizer EGBAA when combined with poly(NiMMO) at 50% plasticizer level gives a rubbery product with a $T_g \approx -66.7\,°C$ coupled with a good stability [204].

We have also synthesized bis(2-azidoethyl) adipate (BAEA) by the reaction of bis(2-chloro ethyl) adipate (BCEA) and sodium azide in ethanol medium and characterized the product for solubility, density, refractive index, impact sensitivity, thermal behavior and moisture content [171]. These properties suggest that a part of non-energetic plasticizers, that is, TA, DEP, DOP etc. can be replaced by BAEA in propellant formulations thereby resulting in increase in their I_{sp}.

Energetic Oligomeric Plasticizers Migration of plasticizers is one of the major problems encountered with their use in binders for explosive and propellant formulations. In order to obviate this problem, the most effective approach is to design plasticizers which resemble closely to the polymer matrix. With this in mind, oligomers of 3-nitratomethyl-3-methyl oxetane (NiMMO) and glycidyl nitrate (GlyN) have been developed for use with energetic binders such as poly(NiMMO) and poly(GlyN) respectively as energetic plasticizers [205].

UK DRA/DERA scientists have done extensive research on cationic polymerization of oxetanes and oxiranes by varying different conditions and obtained energetic binders with desirable molecular weights and functionality. For preparing oligomeric molecules for their use as potential plasticizers, control of molecular weight and functionality is very important which has been achieved via Activated Monomer (AM) polymerization technique [133]. UK scientists achieved oligomerization by using HBF_4 in conjunction with butane-1,4-diol as initiating system through AM mechanism. By conducting a series of experiments with different ratios of cationogen (HBF_4) to co-initiator (butane-1,4-diol), oligomers with desirable molecular weight (consisting of 5–10 monomer units) and molecular weight distribution were obtained [206]. In order to make these oligomers useful as plasticizers, the terminal hydroxyl groups were nitrated. Nitration is easily carried out using N_2O_5 at −10 °C for 30 minutes. As a result, clean conversion of parent oligomers to nitratoterminated oligomers occurs. In case of (NiMMO) oligomer, it is likely to contain unreacted NiMMO monomer which is converted into TMETN on nitration with excess N_2O_5. The end-product, although a mixture, is still considered useful as an energetic plasticizer.

Some functional poly(glycidyl nitrate) oligomers and nitrated poly(glycidyl nitrate) oligomers have also been reported by a team working on energetic binders in U.S. in addition to UK team of scientists. This class of plasticizers offers a number of advantages over traditional nitrate ester plasticizers such as TEGDN, TMETN, BTTN etc. and these advantages include excellent miscibility with binder, low volatility, a low T_g (ca −40 °C), decreased plasticizer mobility and excellent enthalpies of combustion and explosion characteristics [207]. The authors have claimed that these are excellent plasticizers for binders for energetic formulations, that is, explosives, propellants and pyrotechnics and other such formulations.

Nitrate Ester Plasticizers As discussed in Section 2.2.4 of Chapter 2, nitroglycerine (NG) is a high performance nitrate ester and is considered the first energetic plasticizer for commercial explosives.

Some of the major nitrate esters are ethylene glycol dinitrate (EGDN or nitroglycol), diethylene glycol dinitrate (DEGDN), triethylene glycol dinitrate (TEGDN), trimethylol ethane trinitrate (TMETN) or metriol trinitrate (MTN), 1,2,4-butanetriol trinitrate (BTTN) and 1,2-propanediol dinitrate (PDDN). The main aim of development of these energetic nitrate esters was to explore their use as additives to NG to lower its freezing point and at the same time, to reduce impact and friction sensitivities of NG thus rendering its manufacture, handling, transportation and storage safer. TEGDN (chemically stable and less impact sensitive than NG) and BTTN (lower density than NG but offers improved stability) are currently being investigated in the UK, USA and France as alternatives to NG in propellant and explosive formulations [208, 209]. PDDN has found practical use as a high energy monopropellant for marine applications, that is, torpedoes [210, 211].

4.9.5
Bonding Agents

Modern rockets and missiles require high energy composite propellants possessing acceptable mechanical properties to sustain stress and strain during flight, particularly when the acceleration during flight is of a high order. One of the major factors which enhances the mechanical properties of propellants is the adhesion between filler particles and polymeric matrix and this strong adhesion between binder and filler is important for obtaining high tensile strength.

Ammonium perchlorate (AP) is one of the major ingredients of composite propellants based on HTPB as a binder. Though it is an excellent oxidizer, it is a non-reinforcing filler for HTPB-based polyurethane matrix. As a consequence of poor adhesion between PU matrix and AP particles, mechanical properties of the composite propellants are not up to the mark. The binder-filler adhesion and hence mechanical properties of these propellants may be improved by the use of surface active agents which are called 'bonding agents'.

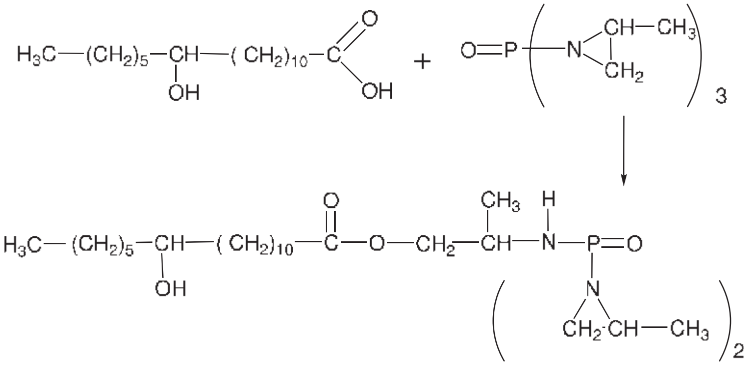
Bonding agents function to promote the interaction between solid particles and binder. This interaction occurs by reactions and/or secondary intermolecular attraction [212, 213]. Therefore, bonding agents help to incorporate solid oxidizer particles into the polymeric binder system, improving the mechanical properties, ageing characteristics, resistance to moisture and reducing brittleness [214] of propellants. In other words, bonding agents perform the function of strengthening the interface between the oxidizer solid particles and binder, reducing dewetting which decreases mechanical properties [215].

Only a few bonding agents are available for use and they are discussed here briefly.

One such bonding agent is the reaction product of equimolar quantities of tris[1-(2-methylaziridinyl) phosphine oxide] (MAPO) and 12-hydroxystearic acid as in Scheme 4.7 shown below [216]. This bonding agent is popularly known as RX bonding agent [Structure (4.28)].

The two aziridine rings which remain as such after reaction are the groups of interest and their presence imparts high reactivity to the bonding agent. Further, these two aziridine rings open-up and homopolymerize over the particles of oxidizer covering their surface and forming a hard and tough shell around them followed by linking them to the polymeric matrix [217–219].

Another bonding agent which is the reaction product of MAPO (2 moles) and mixed adipic acid (0.7 mole) and tartaric acid (0.3 mole) is also available for use. It improves TS of composite propellants [220] [Formulation: AP 67.0%, Al powder 17%, Fe_2O_3 1.0% and HTPB and plasticizer 15% with bonding agent 0.5 parts] to 20.4 kg cm^{-2} compared with TS of control propellant ≈5.1 kg cm^{-2}. The use of



Structure (4.28) : RX Bonding Agent

Scheme 4.7 Synthesis of RX bonding agent.

dihydroxyethyldimethylhydantoin (DHE) in combination with this bonding agent further improves mechanical properties of these propellants.

Some organotitanates especially organophosphate and pyrophosphate titanates have also been reported as bonding agents for liquid elastomer-based propellants. In addition to the increase in tensile strength and elasticity of propellants, these bonding agents [221] also reduce the burn-rate exponent (n).

Americans have claimed that the use of a 'Schiff's Base' produced by the reaction of polyoxyalkyleneamine (Jeffamine) with *p*-nitrobenzaldehyde and glycidol as a bonding agent for solid propellant formulations [222]. The bonding agent provides superior performance by bonding the propellant matrix by means of the hydroxyl groups and to align with oxidizer such as AP by means of the 'Schiff's Base'.

The use of isophthalic acid–2-methyl aziridine was also reported as a bonding agent for composite propellants in the literature. Based on this fact, its analog, that is, isophthalic dimethyl oxaziridine (reaction product of oxaziridine unsubstituted on the nitrogen and isophthaloyl dichloride) also appears to be a potential bonding agent [223] but needs to be evaluated in propellant formulations.

Contrary to composite propellants, which are heterogeneous in nature, DB propellants are homogeneous and therefore do not require the use of bonding agents. The DB propellants are produced by the diffusion of desensitized NG into NC/casting powder. The diffusion of desensitized NG to NC/casting powder knits the two components system into a single monolithic system (grain) which is a homogeneous and coherent mass.

4.9.6
Stabilizers

The Armed Forces demand a long shelf-life (min 10–12 years) for propellants for use in different rockets and missiles. However, the shelf-life of propellants is limited. There are some chemicals which on their addition to these propellants during their manufacture retard the processes responsible for their deterioration and consequently, increase their shelf-life. The main purpose of addition of these chemicals in propellant formulations is to enhance their shelf-life without adversely affecting their manufacturing processes and properties. Such chemicals or additives are known as stabilizers in case of DB and composite modified double-base (CMDB) propellants whereas anti-oxidants in the case of composite propellants. The additives for this purpose are therefore selected depending on the type of propellant.

Nitrocellulose (NC) and nitroglycerine (NG) which are nitrate esters of cellulose and glycerine respectively and major ingredients of DB and CMDB propellants, are inherently unstable. NC and NG gradually decompose at room temperatures to form oxides of nitrogen, mainly nitrogen dioxide (NO_2). These decomposition products further accelerate decomposition of propellants unless these oxides are chemically removed from the system as soon as they are formed, thus shortening the shelf-life of these propellants. Therefore, there is a need for addition of a stabilizer to DB and CMDB propellants during their manufacture in order to neutralize the products of propellants' decomposition. The desirable properties of such stabilizers are (i) should be inert to NC and NG before and after reaction with their decomposition products (ii) should be able to neutralize acids (iii) should be able to absorb oxides of nitrogen and lastly (iv) should be able to form colloidal solution with NC and NG. The compounds most commonly employed for this purpose [Structures (4.29–4.33)] along with their characteristic features are given in Table 4.8.

On the other hand, substituted *p*-nitroaniline compounds are preferred as stabilizers for isocyanate crosslinked CMDB propellants. The author of this patent claimed that such compounds have good solubilities in the propellant matrix and thereby impart good stabilization properties [224].

The present trend in the field of binders for composite propellants indicates extensive use of polybutadiene with terminal functional groups as binders because these binders are considered as high energy fuels and hydroxy-terminated polybutadiene (HTPB) has been extensively used as a binder-cum-fuel and permits solids loading up to 91% with comparatively better mechanical properties. In view of higher solids loading, the resulting propellant produces 2 to 3 s higher specific impulse (I_{sp}). However, the structure of HTPB contains olefinic double bonds and is prone to oxidative degradation and hence there is a need to incorporate small amount of an anti-oxidant to retard the process of ageing and enhance the shelf-life of a propellant.

Most of the work on the inhibition of oxidative degradation of HTPB by incorporating anti-oxidants is in the form of patents or classified reports [225–227]. The use of *N*-phenyl-β-naphthylamine (PBNA) has been extensively studied [226, 228] for this purpose but it is reported to be a carcinogenic material and hence banned for use as a propellant ingredient in developed countries.

We studied comparative efficacy (effectiveness) of some commercially available anti-oxidants (given in Table 4.9) with the help of thermal techniques: differential thermal analysis (DTA) supplemented by differential scanning calorimetry (DSC).

Table 4.8 Some stabilizers for single-base, double-base and triple-base propellants.

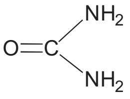
Compound	**Characteristics and structure**	**Application**
Chalk Calcium carbonate ($CaCO_3$)	Odorless white powder	Added as an inorganic stabilizer for NC (used in propellants) to neutralize residual traces of H_2SO_4 in the fibers of NC
Urea	White powder, m.p. 132.7 °C  **Structure (4.29)**	Readily absorbs nitrogen oxides which result from the decomposition of NC and NG but too strong a base to be used as stabilizer. Initially tried and discarded.

Table 4.8 *Continued*

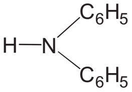
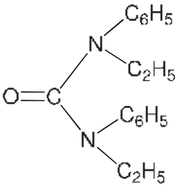
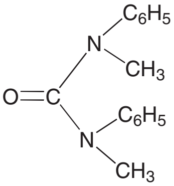
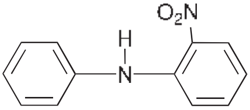
Compound	Characteristics and structure	Application
Diphenylamine (DPA)	White crystalline solid, m.p. 50 °C  **Structure (4.30)**	Mainly used for single base propellants but too basic for DB and TB propellants
Ethyl centralite/carbamite (Sym.diethyl diphenyl urea)	White crystals, melts at 72.5 °C.  **Structure (4.31)**	Very weak base due to the presence of phenyl groups and useful as a stabilizer, gelatinizer and coolant. Also imparts better rollability to rocket propellant formulations.
Methyl centralite (Sym. dimethyl diphenyl urea)	White crystals, melts at 121 °C.  **Structure (4.32)**	Methyl analog of carbamite and is useful as a stabilizer and surface gelatinizer (moderant) for NC powders
2-Nitrodiphenylamine (2-NDPA)	Yellowish orange solid material, melts at 76–78 °C.  **Structure (4.33)**	Superior replacement of DPA. Generally used for rocket propellants i.e., high web-sized propellants. Better than carbamite but processability/rollability becomes slightly difficult.

Table 4.9 Some commercially available anti-oxidants for composite propellants.

Antioxidant	Trade name	Manufacturer
N-Phenyl-β-naphthylamine (PBNA)	–	Fluka Chemie AG, Bucks, Switzerland
2,6-Di-*t*-butyl-*p*-cresol/butylated hydroxytoluene (BHT)	ANTOX-QT	Quality Industries, India
Dioctyldiphenylamine (DODPA)	GOODRITE 3191	BF Goodrich, USA
1,2-Dihydro-2,2,4-trimethyl quinoline (polymerized) (DHTMQ)	GOODRITE 3140	BF Goodrich, USA
N,*N*′-Diphenyl-*p*-phenylene diamine (DPPDA)	–	Fluka, AG Bych SG
2,6-Di-*t*-butylphenol (DTBPh)	–	Aldrich Chemical Co., USA
4,4-Methylene bis(2,6-di-*t*-butylphenol [M bis (DTBPh)]	–	Aldrich Chemical Co., USA
2,5-Di-*t*-butylhydroquinone (DTBHQ)	–	Merck-Schuchardt, Munchen, Germany
2,2-Methylene bis(4-methyl-6-*t*-butylphenol)	BKF	Bayer, Leverkusen, Germany
p-Phenylenediamine (*p*-PDA)	–	Merck-Schuchardt, Munchen, Germany

The activation energy was also determined by recording thermograms at different heating rates (10–25 °C min^{-1}) by following Ozawa's and Kissinger's methods. The research on optimization of concentration of these anti-oxidants indicates that 1% anti-oxidant is sufficient to retard auto-oxidation. Further, comparative data on their effectiveness, viscosity build-up and ageing characteristics indicate that M bis (DTBPh), DTBHQ and BKF are potential candidates for replacement of PBNA in HTPB-based composite propellants [229]. The results had also been validated by static evaluation of these propellants [230]. The results of this study are in agreement with the findings of several researchers who investigated the use of these anti-oxidants for different rubbers [231–233].

4.9.7
Burn-Rate Modifiers

In addition to fuel, oxidizer and inert/energetic plasticizer, various additives are also included in the propellant formulations in order to improve their mechanical or ballistic properties. One such additive is termed a burn-rate (ballistic) modifier which alters inherently high dependence of the burn rate on chamber pressure. The use of an additive for this purpose depends on the type of propellant, that is, DB, composite or composite modified double-base (CMDB). Tables 4.10–4.14 depict various BRMs employed for this purpose.

4.9.7.1 Burn-Rate Modifiers for DB Propellants

It can be seen from Table 4.10 that various compounds of lead impart high catalyzing influence on the burn rate of medium and high energy DB rocket propellants.

Depending on their content, these compounds increase the burn rate of the propellants and in addition, decrease the burn-rate dependence on pressure and initial temperature of the propellant. Further, the influence of lead compounds on

Table 4.10 Burn-rate modifiers for double-base rocket propellants.

Compound	Special features
Lead compounds	For the first time, Avery *et al*. observed the unusual behavior of lead compounds on ballistics of DB propellants [234].
Lead salts of aliphatic acids	Burning characteristics remain substantially unaffected by variations in pressure during operation. Such propellants are suitable for use in rockets and guided missiles [235].
Oxides of lead, basic lead stearate, lead-2-ethyl hexoate, basic lead salicylate	Render the burn rate of DB rocket propellants independent of pressure over a certain pressure range [236]. Such salts are effective only with cooler propellants i.e., cal. val. below ≈850 cal g^{-1}.
1) Inorganic lead compounds such as PbO, PbO_2, Pb_3O_4, PbS, lead molybdate and lead perchlorate 2) Lead salts of organic acids such as 2,4-dihydroxy benzoic acid, salicylic acid, acetyl salicylic acid and methoxy propionic acid	i) Effective with propellants of cal. val. less than 900 cal. g^{-1} ii) Lead salts of aromatic acids are effective with propellants of higher cal. val. [237].
Combination of lead and copper salts of aliphatic and aromatic carboxylic acids	Extend mesa region compared with lead salts alone in propellants having cal. val. ≈600–1250 cal g^{-1} i.e., both cooler and hotter propellants [238, 239].
Short sections of thin metal wires (good conductor of heat) such as Ta, Pb, Al, Cu, Ag and Mo	Increase burn rates of DB propellants containing ballistic modifiers such as lead salts of salicylic and 2-ethylhexanoic acid without any adverse effect on the plateau region [240].
Zinc oxide in conjunction with one or more conventional ballistic modifiers – lead stearate, lead acetophthalate, lead-β-resorcylate and basic copper salicylate etc.	Propellants exhibit good quality plateau burning over a useful pressure range for a wide range of burn rates [241].

Table 4.11 Less toxic or non-toxic burn-rate modifiers for DB rocket propellants.

Compound	Special features
Bismuth derivatives: • Oxides (Bi_2O_3, Bi_2O_4 and Bi_2O_5) and hydroxide $Bi(OH)_3$ • Organic salts of Bi	Copper compounds and carbon black (Soot) further enhance the effect of Bi derivatives [242, 243].
Rare-earth compounds: lanthanum compounds	Not only increase burn rate of DB propellants but also exhibit plateau or mesa combustion in the middle or high pressure range [244].
1) Barium oxide, barium salicylate and/or other organobarium salts 2) Organometallic salts of lanthanum, hafnium and tantalum and their oxides	Replacements for lead and copper compounds currently employed for ballistic modification. Particularly attractive due to production of considerably less smoke during combustion of propellants [245].
Mixture of bismuth and copper salts of hydroxy substituted benzoic acids	Produce plateau and mesa burning characteristics in propellants [246].
Cobalt stearate, salicylate and acetyl acetonate etc.	Promising platonizers and catalysts for DB Propellants [247].
Ultrafine carbon fibers	Non-toxic burn-rate modifiers for cast DB propellants in the absence of lead salts [248].

Table 4.12 Specification of butacene 800 prepolymer (SNPE France).

Properties	Specification
Appearance	Brown viscous liquid
Viscosity at 25 °C/Poise	≤1200
Hydroxyl value/eq kg^{-1}	0.35 ± 0.05
Iron/wt.%	8.00 ± 0.50
Moisture/wt.%	<0.10
Solvents/ wt.%	<0.20
Butylferrocene/wt.%	<0.50
T_g/°C	−55 ± 5
Anti-oxidant (Ionol)/%	1.0 ± 0.2

Storage: To be stored in the original container filled under argon or nitrogen. Also to be kept away from light and high temperature >40 °C; Shelf-life: 6 years from the date of manufacture in original container.
Reprinted with permission from B. Finck, 'Product Bulletin Butacene800', SNPE, France.

Table 4.13 Effect of iron oxide and butacene 800 on burn rate of composite propellants.

Catalyst	Burn rate (*r*)/mm s^{-1}	Pressure exponent (*n*)
Fe_2O_3 (Fe: 0.8% SA: 130 $m^2 g^{-1}$)	28.0	0.59
Butacene 800 (Fe: 0.50% SA: –)	40.75	0.35

Table 4.14 Burn-rate modifiers for composite propellants.

Compound	Special features
Prussian blue	Decreases the magnitude of the pressure exponent (*n*)
Amorphous boron powder	A dramatic effect on ballistic properties is reported when used with Fe_2O_3/Prussian Blue/Al_2O_3. [249]
Metal phthalocyanines	Burn-rate enhancement in HTPB-based propellants is in the order of Fe > Cr > Cu > V > Mn > Ni > Zn. CuPc also increases pot life of the propellant mix. The use of FePc has also been reported in propellant igniter compositions [250, 251].
Silane ballistic modifiers	Silicon compounds having Si–H, Si–N and Si–C bonds are reported to be effective as catalysts for HTPB-based propellants. Burn rate of propellant varies as a function of the Si content in the propellant formulation [252]
Nano Al powder and Carbon nanotubes (CNTs)	Burn-rate accelerators for composite propellant formulations [253]
Mechanically alloyed Fe–B (50%) powder	Reduces combustion temperature and at the same time, functions as a combustion catalyst for HTPB-based propellants [254]

burn rate increases remarkably in the presence of copper compounds [238, 239] and carbon black [255, 256]. The existing ballistic modifiers, in general are chemically unstable and hydrolyze during propellant processing and storage to create serious problems. In order to take care of all these problems, Alley *et al*. proposed a new class of ballistic modifiers. These modifiers are chelate type compounds consisting of lead and/or copper with 2-hydroxy benzoic acid, 2,4-dihydroxy benzoic acid, 2,5- dihydroxy benzoic acid, 0-acetamido benzoic acid, 4-acetamido salicylic acid, salicylamide and benzoic acid. When they are used in amounts ≈0.5–6.0% (by weight) in DB propellants, mesa and/or plateau burn-rate characteristics are imparted to the propellants over a wide pressure range and also reduce their temperature sensitivity. The most significant property of these modifiers is that they are chemically very stable and as a result, are not altered during propellant processing and subsequent storage. This stability imparts improved propellant ballistic repeatability and reliability. These new modifiers are adapted for application in DB propellants made by the solvent or solventless process where many current modifiers are inherently ineffective or are chemically unstable and hence not satisfactory [257].

4.9.7.2 Less Toxic and Non-Toxic Burn-Rate Modifiers for DB Propellants

Because of the toxic and dangerous nature of lead and its compounds, their use is highly undesirable in the propellant formulations. It is in this context that some researchers pursued their work with other metals and their compounds which are either less toxic or non-toxic and a brief account is given in Table 4.11.

4.9.7.3 Burn-Rate Modifiers for CMDB Propellants

Much work has not been done on ballistic modification of CMDB propellants and only a few studies have been conducted and reported in the literature. Basic lead salicylate (BLS) was found to be a superior ballistic modifier compared with metallic salts and oxides for minimum signature CMDB propellants [DB Matrix 79%, RDX 12, AP 6% and Al 3%]. BLS : C. Black (3 : 1) gave the best synergistic effect and highest catalytic activity was exhibited by BLS : Cu_2O : C.Black (3 : 1 : 1) combination [258]. However, none of the ballistic modifiers among basic lead salicylate (BLS), lead methylene disalicylate (LMDS) and lead stannate was found to be effective in either enhancing burn rates or reducing *n* values of CMDB formulation (with 20% RDX and 10% Al). It is in agreement with the findings of Fifer [20].

The catalysts (lead and copper salts of aromatic acid in combination with carbon black) which were effective for DB and RDX-CMDB propellants were also found effective for dinitropiperazine (DNP) containing CMDB propellants [259]. Copper chromite (CC) and ferric oxide which are generally used for ballistic modification of composite propellants are also effective for CL-20-based aluminized CMDB propellants. However, CC is a better BRM [260].

4.9.7.4 Burn-Rate Modifiers for Composite Propellants

The simplest way to modify the burn rate of composite propellants is by means of catalysts or ballistic modifiers. The solid catalysts that have been in use for many years can be classified into two groups.

- Oxides and metal salts with variable valency : iron (III) oxide, copper (II) oxide, copper chromite, copper chromate etc.
- Solid or liquid organometallic compounds such as ferrocene and its various derivatives, iron (III) acetyl acetonate, metal chelates etc.

High energy composite propellants consist of largely solid phase in themselves and therefore, introduction of solid catalysts in large amounts may generate unfavorable changes in the propellant rheological properties such as increase in viscosity of propellant mix, reduction in pot life, decrease in elongation and growth of elastic modulus [261]. A brief account of various solid and liquid BRMs for composite propellants is given in the following paragraphs.

Metallic Oxides A number of metallic oxides have been studied to catalyze burn rate of composite propellants. The research of Jacobs *et al.* suggests that CuO is a better catalyst in comparison to both Cu_2O and copper chromite and that the high temperature decomposition of AP is enhanced considerably [262]. In order to understand the mechanism of thermal decomposition of copper chromate and chromite, TGA and DTA thermal techniques were employed. The successive stages of decomposition of both these compounds have been found to be identical at higher temperatures and both yield Cu_2O ultimately as shown ion Equation 4.21:

$$\begin{aligned}&\text{Copper chromate} \xrightarrow{450\text{–}510\,^\circ\text{C}} \text{Cupric chromite}\\&\text{Cupric chromite} \xrightarrow{900\,^\circ\text{C}} \text{Cuprous chromite}\\&\text{Cupric oxide} \xrightarrow{2100\,^\circ\text{C}} \text{Cuprous oxide}\end{aligned} \tag{4.21}$$

Thus it is not copper chromate which acts directly as a catalyst but it first gets converted to CuO or Cu_2O which actually catalyzes the reaction [263]. Rastogi *et al.* have reported that $CaCO_3$ is a better catalyst in comparison to CuO in PS/AP composite propellants [264].

AP is a major ingredient of composite propellants and it amounts to ≈70–72%. Therefore, the mechanism of increase in the burn rate of composite propellants due to the addition of catalysts or BRMs largely depends on the decomposition of AP. This has been postulated by Rastogi and his team in their publication [265] and it is briefly as follows.

AP is stable at room temperature and it decomposes with a measurable rate at temperatures above 150 °C. Further, it undergoes decomposition due to auto-catalytic reaction of the following type at temperatures below 300 °C (Equation 4.22):

$$\text{Solid (A)} \rightarrow \text{Solid (B)} + \text{Gas} \tag{4.22}$$

This auto-catalytic reaction stops after about 30% decomposition. This is usually called low temperature decomposition (LTD) and it is believed that the electron transfer mechanism is operative in this region. At temperatures above 350 °C, high temperature decomposition (HTD) takes place usually by proton transfer mechanism and finally AP decomposes into NH_3 and $HClO_4$ (Equation 4.23):

$$NH_4ClO_4 \rightarrow NH_4^+ClO_4^- \xrightleftharpoons{\text{Catalyst}} NH_3 + HClO_4 \tag{4.23}$$

These molecules diffuse over to the surface of the catalyst and are adsorbed by it. NH_3 is oxidized whereas $HClO_4$ is further decomposed. Thus catalyst provides some additional surface on which NH_3 and $HClO_4$ are adsorbed, react and increase the rate of forward reaction.

Burn-rate modifiers probably affect most of these combustion steps, that is, the endothermic and exothermic reactions and heat losses. Rastogi *et al.* have shown that burn rate, surface temperature, flame temperature and rate of decomposition are enhanced in case of catalyzed propellants while these are lowered in case of burn-rate retarders. This may be due to heat produced in catalytic reactions in the former case whereas burn rates are reduced on account of endothermicity of the condensed phase reactions on the propellant surface in the case of retarders. It is also reported that carbonates of copper and chromium are better catalysts than their oxides. It is perhaps due to the fact that the carbonates are ultimately converted to their oxides with finer particle size at the propellant surface. The freshly prepared and finer oxides contain a large number of defects and dislocations providing active sites for adsorption and causing acceleration in the rate of reaction. It seems that the role of catalysts can be better understood on the basis of adsorption theory. Therefore, the requirements for positive catalysts are: (i) finer particle size having large number of defects and dislocations in the crystal lattice and (ii) good adsorption capacity and large surface area.

Ferric oxide (Fe_2O_3) with a particle size ≈0.4–0.5 μm is the most extensively used catalyst for composite propellants [266, 267] and it is generally used at the level of ≈1%. The composite propellants for Indian missiles invariably contain ferric oxide as BRM. Recently, MACH I, U.S. has developed Nanocat Superfine Iron oxide (SFIO) which enhances burn rate of composite propellants several times [268] more than the conventional Fe_2O_3. NANOCAT SFIO is amorphous ferric oxide with much finer particle size and greater specific surface area than any other commercially available form. It excels as a catalyst for chemical processes including synthesis, cracking, and oxidation. In composite propellants, it provides high burn rate, low pressure exponent, and improved safety. It is synthesized by a unique vapor-phase process and is free from impurities that poison conventional catalysts. Typical Properties of Nanocat SFIO are:

Composition	Synthetic Amorphous Ferric oxide
Color	Reddish brown
Physical form	Free flowing powder
Pigment character	Transparent
Particle size, nm	3 (0.003 μm or 30 angstrom)
Surface area, $m^2 g^{-1}$	250
Bulk density, gcm^{-3}	0.05

NANOCAT Superfine Iron Oxide(SFIO) is a novel burn-rate catalyst and performs superbly in solid rocket propellants based on ammonium perchlorate (AP). SFIO provides a higher burn rate and lower pressure exponent compared with commercial iron oxides at equal concentrations. Some characteristics of NANOCAT SFIO as a burn-rate catalyst are as follows:

- It is the finest form of iron oxide available today.
- It is the best burn-rate catalyst for propellants based on AP.
- Better than other iron oxides because it gives higher burn rate, lower pressure exponent, greater effective impulse (hence greater range, velocity, payload) and improved mission versatility.
- It differs from catocene and other ferrocene derivatives in respect of safety and ageing stability, that is, it is much safer and gives better ageing stability.
- It is available in commercial quantities and is less expensive than ferrocene derivatives.

Ferrocene Derivatives Ferrocene and its derivatives have also been reported to impart high burn rates to HTPB-based composite propellants. These are highly effective burn-rate catalysts for AP containing composite propellants and are superior candidates for application in rocket motors with high thrust and acceleration power. They are chemically well mixable with other ingredients of propellants, particularly the binder system. They do not adversely affect the pot life and mechanical properties and show minor influence on sensitivity and ageing stability, only in higher concentrations [269]. A large number of derivatives such as *n*-butyl ferrocene; 2,2′-bis (ethylferrocenyl)propane (catocene); 2,4-dinitrophenylhydrazine derivative of acetyl ferrocene; 1-pyrrolidinyl methyl ferrocene; di-*t*-butyl ferrocene; ferrocene dicarboxylic acid diesters, acylaziridinyl ferrocene etc. have been reported [270–273]. Based on their various properties 1,3-diferrocenyl-1-butene (DFB) is considered better for improving burn rates at par with Fe_2O_3. This being a liquid, has an edge over Fe_2O_3 and facilitates further increase in solids loading thereby improving the performance of composite propellants [274]. Some ferrocene derivatives have also been reported as crosslinking agents and plasticizers in addition to their role as burn-rate accelerators. Because of their tendency to migrate and susceptibility to oxidation, ferrocene derivatives have not found widespread use in solid propellants. To obviate migration problems, multi-ferrocenyl compounds (molecules) were synthesized on the presumption that the large molecules would entangle with binder molecules and thus be prevented from migration. However, the use of large molecules also has not solved the migration problems because large amounts of iron (in the form of ferrocenyl compounds) appear on the surface of solid propellant grains a short time after preparation, even when large molecules are used. The migration and oxidation problems associated with ferrocene derivatives can be largely eliminated with the use of two newly reported ferrocene derivatives: 4,4′-diferrocenyl-1-pentanol and 3,3′-diferrocenylbutyl isocyanate. These ferrocene derivatives are either directly chemically bound to HTPB or chemically bound through a curing agent. This prevents migration. Also the ferrocene derivatives used do not exhibit high vulnerability to oxidation because they have no hydrogen on the α-carbon atom adjacent to the ferrocene group in these ferrocene derivatives which can be oxidized readily [275].

Butacene SNPE, France has also developed a Butacene 800 [HTPB chemically reacted and grafted with a ferrocene derivative in the chain: Structure (4.34)] binder which is free from such drawbacks (Figure 4.10). Some details of Butacene 800 are as under:

1) **Synthesis:** This is done as in Scheme 4.8.
2) **Attributes:**
   - Butacene 800 is a liquid resin based on HTPB grafted with a ferrocene derivative in the chain.
   - It is used in conjunction with HTPB as a binder in high burn rate AP-based composite propellants.

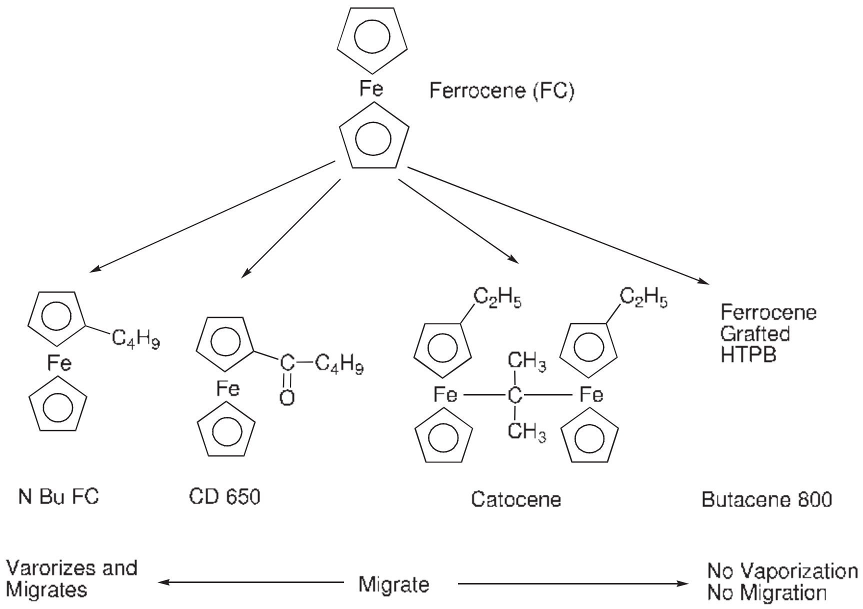


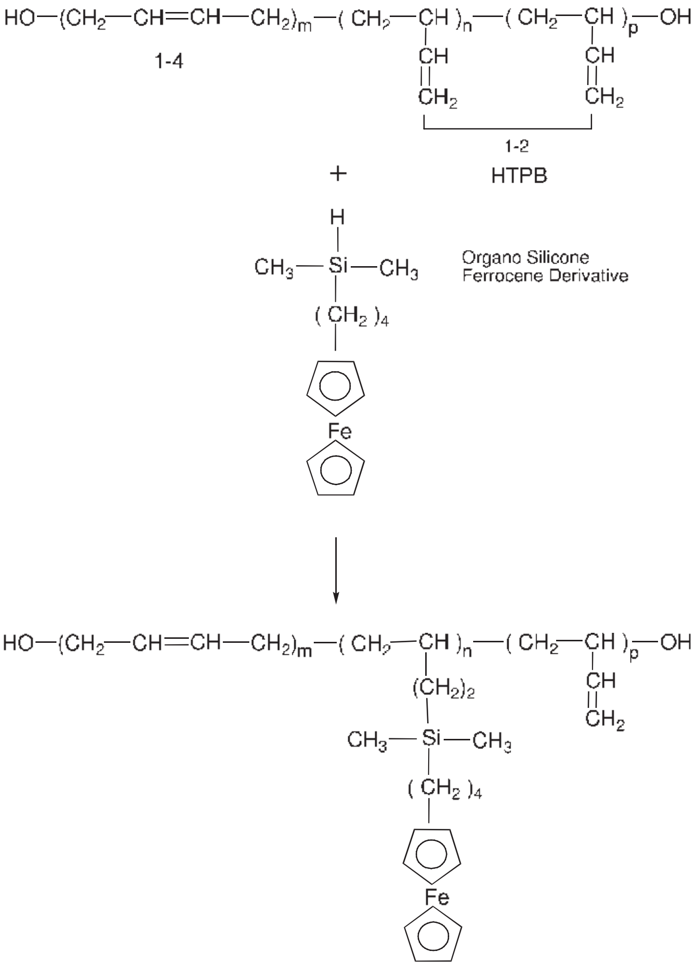
Figure 4.10 Ferrocene derivatives and their important characteristics.

- Butacene-based propellants are formulated, processed and cured like conventional HTPB-based propellants.
- The use of Butacene leads to high burn rates for AP-based propellants ($BR > 20\,mm\,s^{-1}$ at $7\,MP_a$), low pressure exponents ($n < 0.5$) and no ferrocene migration during storage and ageing.
- At present the production capacity is more than 5 tons per year by SNPE as per the specification [276] given in Table 4.12.

3) **Advantages:**
   - Maintains the properties of HTPB (R45M or HT) and ferrocene.
   - Dilutes and distributes the ferrocene derivative in the HTPB binder due to low iron content (iron content in Butacene ≈ 8% and Catocene ≈ 25%).
   - Suppresses any migration and vaporization.

A comparison of the efficacy of iron oxide and Butacene in HTPB-based composite propellants in terms of burn rate (r) and pressure exponent (n) is given in Table 4.13. More BRMs for composite propellants are given in Table 4.14.

In addition, a few other publications also address this issue of ballistic modification of composite propellants. The cobalt, nickel and zinc hexammine perchlorates have been studied by Gurdip Singh and coworkers for this purpose. The generated data indicate that cobalt complex accelerates burn rate three-fold when used at 2% level in HTPB-AP-based composite propellant [277]. Another study on transition metals (copper, iron, cobalt and nickel) salts of NTO as BRMs for HTPB-AP-based



Structure (4.34) : Butacene 800

Scheme 4.8 Synthesis of butacene 800.

composite propellants reveals that Fe-NTO salt imparts best catalytic effect and increases burn rate to the extent of 80% (pressure range: 2.0–9.0 MPa), as claimed by the authors. At the same time, pressure index (n) comes down to 0.18 which results in more flexibility to rocket designers [278].

4.10
Inhibition of Rocket Propellants

Rocket Propellant Technologists choose a propellant for any particular mission depending on the requirements. They also choose the propellant to burn in a definite pattern keeping in view the overall functional requirements of the mission. This definite pattern of burning is achieved by applying polymeric materials (which do not readily burn) over the propellant surface. These polymeric materials are called 'inhibiting materials' or 'inhibitors' and the process of their application is known as 'inhibition'. The performance of a rocket or missile depends not only on the propellant but to a large extent on the inhibition system also. There are three main types of pressure–time (*P*–*t*) profiles: (i) neutral, (ii) regressive, and (iii) progressive. The modes of inhibition along with respective *P*–*t* profiles are depicted in Figure 4.11. Thus the mode of inhibition is mainly governed by the type of *P*–*t* profile that the rocket propellant technologists desire.

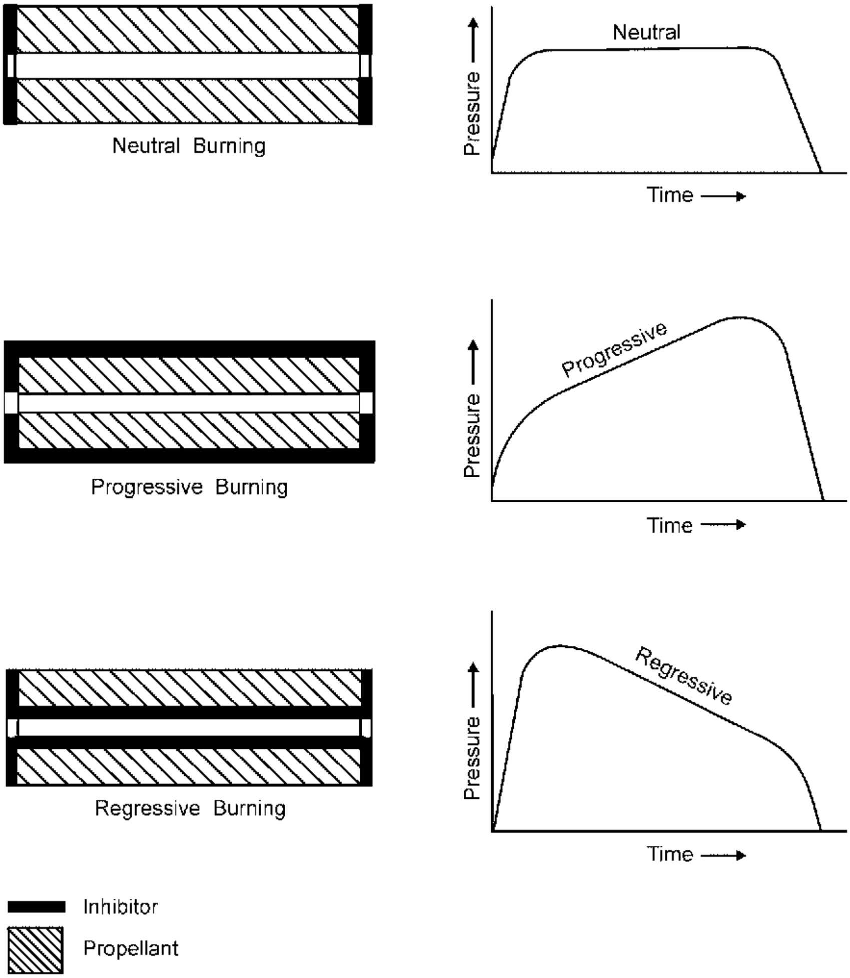


Figure 4.11 Inhibition modes with corresponding pressure-time profiles.

4.10.1
Characteristics of Inhibitors

Inert polymeric materials to be suitable for inhibition of rocket propellants must fulfill a number of requirements [279–281] and the important ones are given below:

1) Chemical compatibility with rocket propellant, that is, not promoting its deterioration.
2) Ability to form and maintain strong bond with propellant, resist any delamination, cracking or interface separation due to self-stressing. The ability to bond itself with the propellant directly on application by 'casting technique' without any barrier coat is considered an added attribute.
3) Inhibitor's mechanical and physical properties should closely match with those of propellant in order to minimize differential expansion.
4) Absorption or migration of nitroglycerine (NG), stabilizer and plasticizer from propellant to inhibitor should be as less as possible so that the physical properties and ballistic performance of the propellant during its storage are not adversely affected to the extent of vitiating their serviceability.
5) Should have a low density, low volatile content, effective ablative and thermal insulating characteristics.
6) Should not exhibit 'corrosivity' characteristics when placed in intimate contact with steel and aluminum alloy motors.
7) Ability to produce a sufficient degree of translucent finish is desirable in order to facilitate visual inspection after inhibition.
8) The inhibited propellants after conditioning at ambient, cold (–40 °C) and hot (+60 °C) temperatures, should give successful performance during static evaluation. This is the most important test and even if a polymer meets all the requirements but fails in this test, it cannot be used for inhibition of rocket propellants [282].

It is, in fact, a combination of properties such as compatibility, tensile strength (TS), % elongation (E), bond strength (BS) with propellant and explosive plasticizer (NG)/non-explosive plasticizer (TA,DEP,DOA,DOP etc.) migration or absorption, heat resistance and flame retardance which makes a polymer suitable for inhibition of solid propellants. A compromise among these properties is made in such a way that the performance of inhibited propellants after conditioning at ambient, cold (–40 °C) and hot (+60 °C) temperatures is satisfactory during static evaluation.

4.10.2
Testing of Inhibitors

The properties such as gel time and exotherm peak temperature, mechanical properties, that is, tensile strength and percent elongation, bond strength with propellant, nitroglycerine or plasticizer migration or absorption, heat resistance, flame retardance and satisfactory ballistic evaluation of inhibited propellants after conditioning over a wide range of temperatures constitute an important criteria to evaluate the suitability of a polymer as an inhibitor. These properties are assessed by the methods already reported in the literature [279–284]. The details of static evaluation of inhibited propellants, not available in the literature, are described here.

4.10.3
Ballistic Evaluation of Inhibited Propellants

This is a functional test and it is generally carried out with a 'sustainer' propellant having combustion duration ≈10–12 s. It is believed that if the inhibition system functions successfully in sustainer mode, it will function similarly in other modes as well.

The propellant sustainer is machined to the dimensions, that is, 148 mm dia. and 150–160 mm length and kept on a bottom plate. It is then fixed to the bottom plate by means of a fast curing resin. The propellant grain is wetted with the resin containing accelerator and catalyst. The assembly is then made and the resin, containing curing agents, is poured around the propellant grain and the resin is allowed to cure. The propellant grain is removed after 24 h, machined to the dimensions: 153.0 mm dia. and 160–170 mm length and X-rayed. Propellant sustainer grains (total 9 in number) are inhibited, machined, X-rayed and statically evaluated as under:

- Three grains at ambient temperature (+27 °C)
- Three grains after conditioning at –40 °C for 24 h
- Three grains after conditioning at +60 °C for 18 h.

The model pressure-time profiles are shown in Figure 4.12.

If the pressure-time profiles are smooth and flat in all cases, the inhibition system is inferred to function satisfactorily and meets the requirement. Further, the expected pressure is theoretically calculated based on Equation 4.24,and should be comparable to the pressure level determined experimentally.

$$P_c = \left[\frac{a.\rho.K_N}{C_D}\right]^{\left(\frac{1}{1-n}\right)} \tag{4.24}$$

where P_c = chamber pressure
a = constant
ρ = density of the propellant
K_N = (A_b/A_t), the ratio of burning area to throat area
C_D = discharge coefficient
n = pressure index or exponent of propellant used for ballistic evaluation.

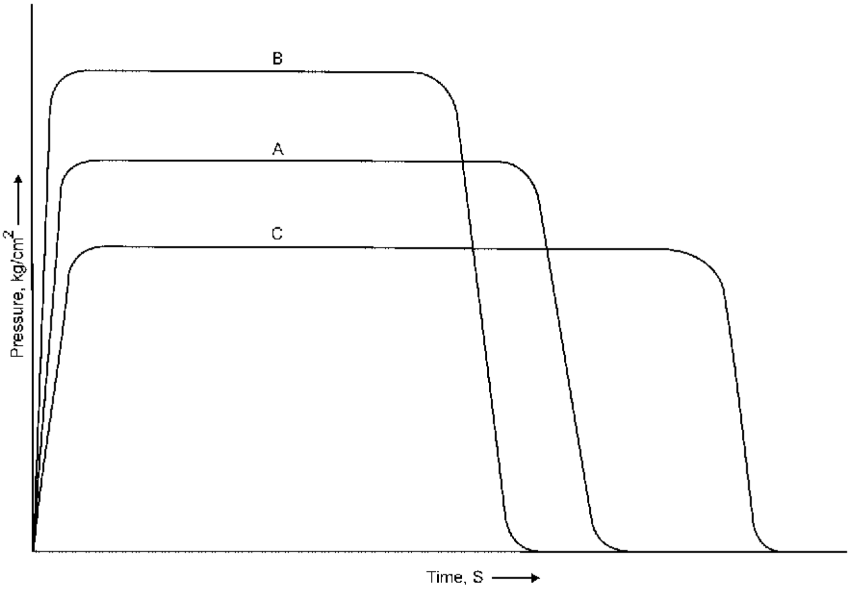


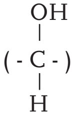
Figure 4.12 Model pressure-time profiles for sustainer propellants at different temperatures. [A: Ambient (+27 °C); B: Hot (+50 °C) and C: Cold (–40 °C)].

4.10.4
Materials for Inhibition

The choice of material for use as inhibitor depends mainly upon the type of propellant, that is, DB, CMDB, Composite and Fuel-rich and also on the ingredients in their formulations. For double-base propellants, cellulosic materials such a cellulose acetate, ethyl cellulose and different filled or unfilled flexible polyesters are used while fuel or binder material filled with inert substances such as asbestos, mica, silica, etc. in fine powder form is used for composite propellants. Since nitroglycerine is present in CMDB propellants also as in DB propellants, the materials used for DB propellants may also be used with minor modifications for the inhibition of CMDB propellants.

The major ingredients of DB propellants are nitrocellulose (NC) and nitroglycerine (NG) in addition to other minor ingredients such as stabilizer, non-explosive plasticizer, coolant, lubricant, opacifier and BRM. As the major ingredients NC and NG are esters, it is logical to use polyesters which have excellent bond with DB propellants for inhibition of DB propellants. The use of polyurethane-based inhibitors for inhibition of DB propellants is preferred in European countries and USA. This is due to the fact that these inhibitors do not produce smoke or gases which are likely to interfere with the guidance system of guided missiles.

The major ingredients of composite propellants are ammonium perchlorate (AP-68%), metal powder (≈16%) and polymeric binders like CTPB, HTPB and Thiokol. As total solids loading in composite propellants is ≈85–88%, polyesters which are commonly used for inhibition of DB propellants, have a relatively weak bond with composite propellants. This problem is further aggravated because of higher shrinkage in the case of polyesters.

The fuel binder with or without inert fillers is generally used for inhibition of composite propellants using casting technique. The epoxy resins are regarded as most universal resins for bonding applications. This is because of the good handling characteristics, toughness, low shrinkage and chemical inertness. The bonding of these resins with other surfaces arises from the polarity of aliphatic hydroxyl  $(- \overset{\overset{\text{OH}}{|}}{\underset{\underset{\text{H}}{|}}{\text{C}}} -)$ and ether (–C–O–C–) groups present in the initial resin chains and in cured systems. The polarity of these groups serves to create electromagnetic bonding forces between epoxy resins and the adjacent surfaces. In addition, epoxy groups react with active hydrogen which is generally found on metal powders (an important ingredient of composite propellants) and thus establish chemical bonds also with them. Further, since epoxy resins pass relatively undisturbed, that is, with slight shrinkage from liquid state to solid state, the bond initially established is preserved. The net result of all these factors, that is, electromagnetic bonding forces, chemical reaction and relatively less shrinkage leads to strong bonds between epoxy resins and composite propellants and that is why, epoxy resins are preferred for inhibition of composite propellants.

Similar to composite propellants, flexibilized epoxy or novolac epoxy resins reinforced with fillers or fibers are used for inhibition of fuel-rich propellants.

4.10.5
Techniques of Inhibition

The techniques generally used for inhibition of rocket propellants are sleeve technique, tape winding technique and casting technique and their salient features are as follows:

4.10.5.1 Sleeve Technique

In this technique, the material, say ethyl cellulose, is first plasticized and then a sleeve of a definite size and shape is extruded. This sleeve is applied to the grain by a special technique using ethyl cellulose cement which is prepared by dissolving ethyl cellulose in cellosolve-diethyl phthalate (1 : 1) mixture or ethyl lactate-butyl acetate (1 : 4) mixture.

4.10.5.2 Tape-Winding Technique

While using ethyl cellulose in this technique, plasticized ethyl cellulose is extruded into tapes of uniform thickness and width. This tape is wound to the propellant grain with the help of a suitable cement either manually or on a lathe machine.

4.10.5.3 **Casting Technique**

The sleeve and tape winding techniques are not suitable for large sized grains and also grains with complicated geometry. For such propellant grains, 'casting technique' is used for inhibition. The propellant surface for inhibition is prepared either by rubbing with an emery paper or by giving a light cut on a lathe machine, the dust being removed with a brush. This propellant grain is then kept in a mold and the inhibitor containing catalyst and accelerator, is poured around the grain and thereafter the inhibitor is allowed to cure. The inhibited propellant grain is extracted the next day and machined on a lathe machine in the light of dimensional requirements.

Depending upon the dimensions and geometry of solid propellant, one of the techniques described above, is selected for inhibition. The inhibition thickness is invariably high if 'casting technique' is used for inhibition. In order to bring down the dead weight of inhibitor, an inhibition technique based on 'rayon thread reinforced novolac epoxy resin' and termed 'thread winding technique' has been developed for inhibition of hydroxy-terminated polybutadiene (HTPB)-based composite propellants [285]. Some salient features of 'thread winding technique' are given below.

4.10.5.4 **Thread-Winding Technique**

The assembly for inhibition by 'thread-winding technique' is shown in Figure 4.13 except that a propellant grain is used in place of a collapsible mandrel.

First of all, a machined composite propellant is mounted on a lathe machine. Then a formulation of the inhibitor (CNSL-based novolac epoxy resin with polyamide hardener) is thoroughly mixed and is taken in an aluminum tray mounted on a lathe machine. The dried rayon thread on a spool is passed through the resin and is wound on to the propellant. The pitch is selected in such a way that there is no gap between the adjacent circular thread windings. The speed of the lathe machine is ≈80 revolutions per minute (rpm) to ensure proper wetting of the rayon thread. The number of windings is decided in the light of specified diameter of the inhibited propellant. The inhibited propellant is allowed to rotate till the resin cures. After about 24 h, the inhibited propellant is machined to the specified dimensions. The inhibition thickness [286, 287] is usually 2.5–3.0 mm. Further, to make this inhibition system successful over a wide range of temperatures, that is, from −40 °C to +60 °C (desired temperature range for rocket and missile propellants for defense applications), the formulation was modified with a novolac plasticizer [288, 289] and inhibited propellants were evaluated at ambient and extreme temperatures. The composite propellants thus inhibited were successfully evaluated for a combustion duration of ≈25 s. This mode of inhibition was found to be very successful for composite propellants which are being used for several rockets and missiles. However, this technique is not considered production oriented by ordnance factories for bulk production as it is considerably time consuming. The technique also requires creation of infrastructure in terms of lathe machines and allied facilities in addition to several steps involved such as cutting of propellant to length, machining of propellant, application of barrier coat and inhibition and machining after inhibition as per the required dimensions.

In order to reduce the steps involved during inhibition and make this technique more acceptable to ordnance factories for bulk production, 'inhibitor sleeve technique' wherein most of these steps are eliminated, has been developed by Agrawal *et al.* [290, 291].

4.10.5.5 **Inhibitor Sleeve Technique**

The assembly for fabrication of a sleeve is shown in Figure 4.13.

A collapsible mandrel is prepared by applying a very thin coat of silicone grease on it followed by application of aluminum foil of suitable thickness. This prepared mandrel is then held in the lathe machine. A thin uniform coat of resin (novolac epoxy resin plus hardener) is applied to the prepared collapsible mandrel revolving at a speed of 40 rpm and is allowed to cure partially. Then the dried rayon thread on a spool is passed through the resin formulation and is wound on to the mandrel

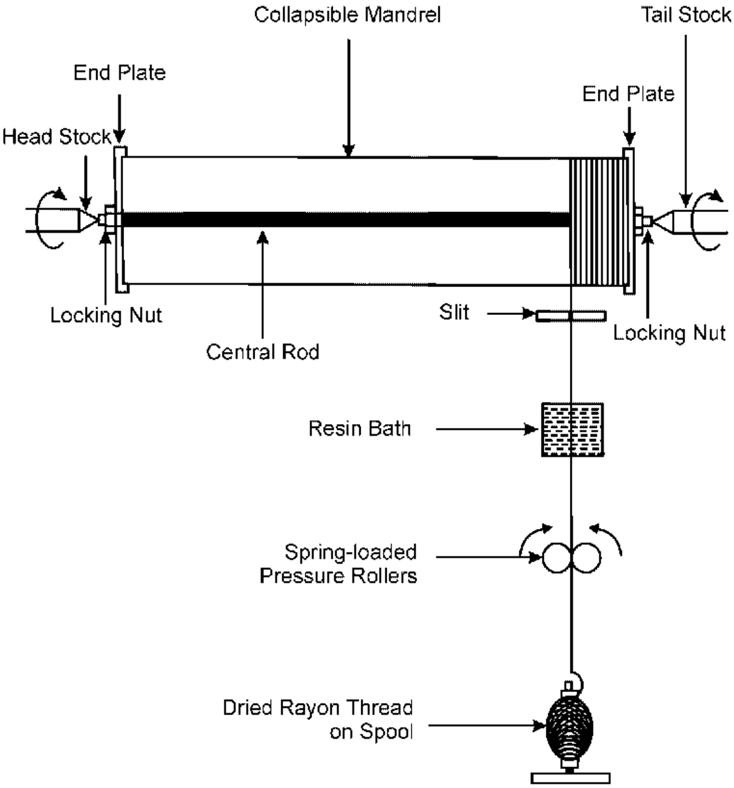


Figure 4.13 Assembly for fabrication of inhibitor sleeve.

with a careful pitch selection to ensure that there is no gap between the adjacent circular windings. This is continued till a thickness of 2.5–3.0 mm is achieved. The sleeve on mandrel is first cured at ambient temperature followed by post-curing at 70 °C. The sleeve is later removed from the collapsible mandrel. The inner surface of the sleeve is made rough by rubbing with an emery paper followed by application of a pre-polymer coat before casting of composite propellant.

This technique is universal and the inhibitor sleeve with the use of polyurethane (Formulation: HTPB : TDI : BD: 1 : 3.2 : 2) as a matrix and rayon thread as a reinforcement may also be similarly made for this purpose [292].

These techniques of inhibition, that is, 'thread winding technique' and 'inhibitor sleeve technique' are based on the concept of fabrication of fiber-reinforced plastics (FRP) which possess high strength-to-weight ratio. The use of these techniques reduces the dead weight of inhibitor resulting in increase in the 'weight of propellant' leading to increase in the range or the payload of the rocket or missile. Thus these techniques of inhibition are considered strategically important from military angle.

The propellant grains inhibited by these techniques are then loaded into, or assembled into the rocket motors. The rocket motors with such inhibited propellant grains are known as cartridge-loaded or free-standing rocket motors. A typical cartridge-loaded or free-standing grain in a motor or case is shown in Figure 4.14. It is easier to replace free-standing grains if found defective on X-ray examination or if the propellant grain has aged excessively. Cartridge-loaded grains are used in some small tactical missiles and a few medium-sized rocket motors. It is easier to inspect them and their cost of production is also lower.

The inhibitor, in addition to restricting the burning of propellant surface, also provides protection to the rocket motor from high temperatures generated during the combustion of propellant.

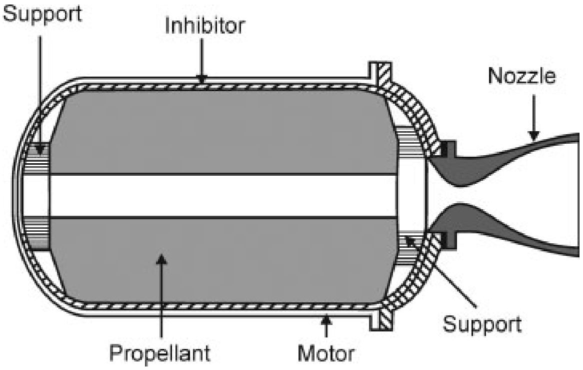


Figure 4.14 Schematic of a cartridge-loaded/free-standing propellant. Reprinted from G.P.Sutton, *Rocket Propulsion Elements: An Introduction to the Engineering of Rockets*, 1992; © 1992, John Wiley and Sons, Chichester, UK.

The choice of an inhibiting material or inhibitor depends upon several factors such as the type of propellant, cost-effectiveness, and physical and mechanical properties of an inhibitor with special reference to ballistic requirements. The inhibition of propellants is therefore discussed by category of propellant.

4.10.6
Inhibition of Double-Base Propellants

The inhibition of DB/CMDB propellants has always been a difficult problem because of the presence of NG in them and its subsequent migration from propellant toward inhibitor. Slight migration of plasticizer/NG from propellant toward inhibitor is generally beneficial to the adhesive bond but any large migration leads to several problems mentioned earlier. Further, the migration of NG results in several ballistic anomalies including coning of the burning propellants especially in end-burning rocket motors. This coning arises from an increased burn rate at the side walls of the propellant. The nature of inhibitor plays an important role in this regard. The findings are based on static evaluation of small scale motors. These ballistic anomalies may be avoided by using a plasticizer equilibrated insulator or inhibitor as reported by Proebster and Schmucker [293].

The inhibition of DB propellants is usually done by:

1) Interpositioning of barrier coats resistant to NG migration, before application of flexible polymerics as main inhibitor and
2) Without applying any barrier coat.

Unsaturated polyesters have been used extensively for inhibition of solid DB propellants. These unsaturated polyesters are generally produced as a result of condensation of a glycol, dibasic acid, unsaturated acid followed by blending with a crosslinking monomer. A large number of glycols, dibasic acids, unsaturated acids and crosslinking monomers are reported in the literature and depending on the desired properties in an unsaturated polyester, a formulation based on glycol, dibasic acid and unsaturated acid (mostly maleic acid or anhydride) is formulated and the synthesis is done either by a 1-step or 2-step polyesterification process followed by blending with a crosslinking monomer [294–296].

Agrawal *et al*. [297–300] have formulated and synthesized a wide range of unsaturated polyesters: rigid, semi-rigid, flexible, semi-flexible and very flexible and characterized them for gel time (G_t), exotherm peak temperature (E_{PT}), tensile strength (TS), % elongation (E), bond strength (BS) with propellants, NG absorption or migration, heat resistance and flame retardance etc. The data generated on such polyesters indicate that the elongation depends upon chain length of glycol or dibasic acid and if high E is required, a glycol or dibasic acid of high chain length is used. As % E and TS are interrelated, polyesters with high % E have low TS. For high TS, a glycol like propylene glycol (PG) alone or in combination with diethylene glycol (DEG) is invariably used. It is the author's observation that if TS is high, BS of polyesters with propellants is also high. At the same time, it is also proved that if TS (indicative of extent of crosslink density) is high, NG absorption is low. If TS decreases, NG absorption increases in a given series of unsaturated polyesters. The gel time (G_t) and exotherm peak temperature (E_{PT}) data for unsaturated polyesters are equally important and a compromise between them is worked out in such a way that the auto-ignition temperature of the propellant is not reached during gelling and at the same time, G_t is not unduly high [301]. The gel time of an unsaturated polyester suitable as a barrier coat is 8–10 min whereas it is ≈30 to 40 min for the main inhibitor.

EP-4 developed by ERDL is a very flexible polyester based on polyethylene glycol with molecular weight-200 (PEG-200), isophthalic acid (IPA) and maleic anhydride (MAn). Before its use, it is blended with styrene monomer (1 : 1) and cured at room temperature using cobalt naphthenate (as an accelerator) and methyl ethyl ketone (MEK) peroxide (as a catalyst). This meets the requirements of the main inhibitor and is used for inhibition of DB and CMDB propellants after the application of a barrier coat (generally a rigid polyester such as PR-3). However, it is observed during manufacture of EP-4 that there is a lot of batch-to-batch variation in properties in spite of the strict quality control measures adopted during its manufacture. This is perhaps attributed to variation in molecular weight (mol.wt.) of PEG-200 as, most of the time, mol.wt. of 200 is achieved by blending PEGs of different molecular weights. In view of this, an unsaturated polyester based on triethylene glycol (TEG), IPA and MAn was developed and this meets the requirements [302]. The properties of three typical batches of TEG-based polyester are given in Table 4.15.

Table 4.15 Various properties of TEG-based polyester resin.

Properties	**Batch-I**	**Batch-II**	**Batch-III**
Visual Observation	Reddish brown clear viscous liquid	Reddish brown clear viscous liquid	Reddish brown clear viscous liquid
Moisture content, % Max	0.34	0.41	0.46
Specific gravity at 27 °C	1.263	1.218	1.221
Refractive index at 27 °C	1.519	1.524	1.518
Acid value (mg of KOH/g)	30.25	28.18	30.50
No. average mol. wt. ($\overline{M}_n$)	1430	1494	1400
Viscosity of virgin resin (cPs) at 40 °C	35 500	37 440	36 000
Viscosity with 50% styrene (cPs) at 40 °C	250	274	268
Gel time at 40 °C, min	21.5	20.4	19.2
Tensile strength, kg cm^{-2}	76–86	82–90	76–86
Elongation, %	62–69	61–67	60–68
NG absorption, % (after 5 days)	6.5	7.0	6.3

It is evident from the data that the batch-to-batch variation is within the specification limits. It is, therefore, considered a better substitute of EP-4 and is likely to substitute ERDL, EP-4 for inhibition of DB and CMDB rocket propellants in future.

4.10.6.1 Tailoring of Properties of Unsaturated Polyesters

A study of essential requirements for a polymeric material to be suitable as an inhibitor for rocket propellants suggests that it should possess good tensile strength, high elongation, high bond strength with propellants, low NG/plasticizer absorption or migration and high flame retardance. Unsaturated polyesters have proved their potential for inhibition of DB/CMDB rocket propellants but usually suffer from two minor drawbacks – slightly higher NG absorption or migration and low flame retardance. The tailoring of properties of unsaturated polyesters in order to make them better for inhibition of DB/CMDB rocket propellants is usually done through

1) formulation;
2) method of polyesterification;
3) use of different crosslinking monomers;
4) addition of fillers.

The details are given in the literature [303–314] and the important conclusions of this comprehensive study are:

1) If TS increases ⟶
    * BS with rocket propellants increases
    * NG/Plasticizer migration decreases
    * Heat resistance increases
2) If E increases ⟶
    * BS with rocket propellant decreases
    * NG/Plasticizer migration increases
    * Heat resistance decreases
3) 'Formulation' and 'method of polyesterification' impart considerable changes in properties whereas variation of 'crosslinking monomers' and 'fillers' impart only minor changes.
4) Addition of fillers such as alumina trihydrate, antimony trioxide, molybdenum oxide [315], zinc borate and zinc borate complex [316] leads to increase in TS but decrease in elongation and NG migration/absorption. Addition of inorganic fillers also leads to increase in flame retardance.

Unsaturated polyesters usually possess slightly higher NG absorption. If tetrachlorophthalic anhydride (TCPAn) or tetrabromophthalic anhydride (TBPAn) is used in the place of IPA, NG absorption reduces considerably. Several halopolyesters based on TCPAn/TBPAn, MAn and different glycols have been formulated, synthesized by a 2-step process and studied for the above mentioned characteristics. CPB-4,a blend of chloropolyester-1 (CP-1) and chloropolyester-2 (CP-2), 40 : 60 and CPM-9S (chloropolyester based on mixed glycols) were selected for inhibition without any barrier coat and their static evaluations yielded expected Pressure-time profiles right from −40 °C to +50 °C. Another flexible chloropolyester based on mixed glycols and designated as FCPM-90 also possesses an excellent combination of various properties coupled with lower NG absorption and is expected to be better than unsaturated polyesters, chloropolyesters and bromopolyesters reported earlier [317–321].

The mechanism of reduction of NG absorption in halopolyesters (chloropolyesters and bromopolyesters) and filled unsaturated polyesters and halopolyesters (after addition of fillers) has already been proposed by us [322] and accordingly, techniques for reduction of NG migration have been suggested [323–325].

4.10.6.2 **Recent Trends**

In Europe, the main area for development of inhibitors for DB and CMDB propellants is polyurethane-based inhibitors because these inhibitors do not produce smoke or gases which are likely to interfere with vision for remote guidance of guided tactical rockets.

Société Nationale des Poudres et Explosifs (SNPE), France has suggested preparation of combustion inhibiting coatings in the form of aliphatic polyurethanes from polyisocyanate with a mixture containing ≥ one polyfunctional polyether glycol having ≥ three OH groups/mol and ≥ bifunctional polymer having two OH groups/mol, a low mol. wt. glycol or diamine chain-extender and heat resistant fibers [326]. SNPE has also developed 'preformed inhibitor technology' and a new device for inhibition of end faces of a block of propellant [327]. In the 'preformed inhibitor technology', polyurethane binder-based composite propellant mix is directly cast in the preformed sleeve of EPDM or butyl rubber vulcanized with peroxide or sulfur compounds respectively and allowed to cure as per the optimized curing cycle. This is similar to 'inhibitor sleeve technique' developed by Agrawal *et al.* [290–292].

Proebster *et al.* [328] have outlined the principles of development of smokeless combustible inhibitors and have done considerable work on inhibition systems based on polyurethane for inhibition of double-base and composite propellants. The polyurethanes are prepared by mixing sequentially polyhydroxy compounds having ≥2 reactive –OH groups with Desmodur-N (a triisocyanate), organometallic catalyst (lead octoate) and an amide containing filler (oxamide). They claimed this inhibitor to be a low-smoke castable inhibitor [329]. The optical attenuation is reported to be −21.35 db compared with 0 for crosslinked styrene-polyester containing lithopone as a filler. The inhibitor becomes extremely low-smoking if oxamide is substituted by succinimide or 2,5-diketopiperazine, crotylidene urea or melamine isocyanurate [330, 331]. Anhydrous salts preferably borates, carbonates, bicarbonates, phosphates and biuret etc., have also been used in the place of an amide without adversely affecting low-smoking characteristics of inhibitors [332]. The polyurethane-based inhibitors have already been reported to be compatible with propellants and therefore, these systems have a bright future. In an attempt to make polyurethane-based inhibitor cost-effective, filler containing amide group is replaced by dolomite which makes the inhibitor highly resistant to burning without adversely affecting its mechanical properties as encountered with calcite and magnesite [333]. Similarly, a water dispersible inhibitor based on polyurethane (mol. wt. 200–6000) prepared from an aliphatic isocyanate and caprolactone polyester, is applied to DB propellants with a pneumatic atomizer. This gives an adherent film of thickness 270–360 μm with sufficient combustion inhibiting effect [334].

4.10.7
Inhibition of Composite Propellants

The inhibition of composite propellants is somewhat easier than that of DB propellants. The binders used for composite propellants (with or without fillers) have been reported for inhibition of composite propellants. Such inhibition systems possess stronger bonds with composite propellants and prove to be more compatible coupled with better shelf-life of the inhibited propellants. However, epoxy or novolac epoxy resin with or without inert fillers is generally preferred for the inhibition of composite propellants due to a combination of properties possessed by them. The inhibition is usually done by 'casting technique' and inhibition thickness is usually required on higher side in order to make the missions successful. In India, 'thread winding technique' or 'inhibitor sleeve technique' is preferred where 2.5–3.0 mm inhibition thickness is sufficient as against 3.5–4.0 mm in case of inhibition by 'casting technique'.

Considering thermodynamics of adhesion, epoxy/novolac epoxy resins play a vital role for bonding applications especially for inhibition of composite propellants. In view of this fact, it is considered worthwhile to discuss the chemistry of epoxy/novolac epoxy resins in this section before we discuss other systems for this purpose.

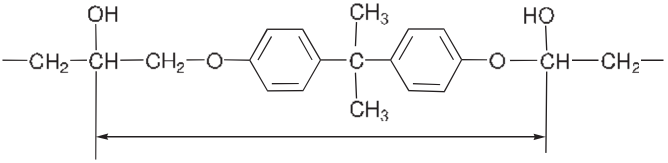
4.10.7.1 Chemistry of Epoxy Resins

Kay and Fust postulated the use of epoxy resin for inhibition of composite propellants [335] and as a consequence, epoxy resins were tried for the first time for the inhibition of HTPB-based composite propellants at Thiokol Corporation, USA. Subsequently, use of the amido-amine hardened modified bisphenol-A-based epoxy resin was reported as inhibitor for fluorocarbon-based composite propellants [336]. Epoxy resins are the most versatile resins for bonding applications for a variety of substrates. This is because of the following characteristics.

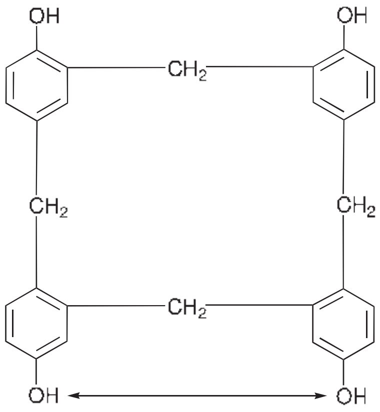
- **Inertness** The cured epoxy resins are chemically inert. The ether groups and benzene rings are virtually non-vulnerable to caustic attack and are extremely resistant to acids. Chemical inertness of an epoxy resin is enhanced by the dense and closely packed structure which is extremely resistant to solvent action.

- **Good handling properties** A most widely used epoxy resin is in liquid form and possesses viscosity in the range of 800–20 000 cPs and therefore, their handling is convenient. These resins have long shelf-life before curing agent is incorporated provided they are properly made and stored. The curing agent and resin ratio (especially in case of polyamide hardener) is not as critical as with some other thermosetting resins. It should be, however, fairly close to the empirically determined optimum amount if best results are desirable.

- **Superior toughness and mechanical properties** The strength of properly formulated epoxy resins usually surpasses other types of casting resins. The cured epoxy resins [Structure (4.35)] are seven times tougher than the cured phenolic resins [Structure (4.36)] as is evident from Figure 4.15. The relative toughness is attributed to the distance between the crosslinking sites and presence of internal aliphatic chains.
- **Low shrinkage** The epoxy resins, highly associated in the liquid state, differ from many other thermosetting resins and give off no by-products during curing. The curing is by direct addition and shrinkage is ≈2% for an unmodified epoxy resin indicating little internal rearrangement. The condensation and crosslinking of phenolic and polyester resins on the other hand, yield a significantly higher shrinkage.



Strucure (4.35) : Cured Epoxy Resin



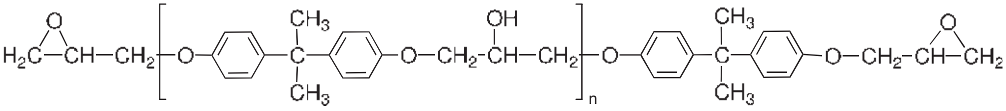
Strucure (4.36) : Cured Phenolic Resin

Figure 4.15 Cured epoxy and phenolic resins.

- **High adhesive properties** As explained earlier, electromagnetic bonding forces, chemical reaction and relatively less shrinkage lead to strong bonds between epoxy resins and composite propellants and that is why epoxy resins are preferred for inhibition of composite propellants [337–339].
- **Easy cure and versatility** Epoxy resins cure quickly and easily at practically any temperature from ambient temperature 25 °C to 150 °C depending upon the curing agent. The basic properties may be modified in many ways: (i) by blending different types of resins (ii) by using different curing agents (iii) by the use of modifiers and fillers.

In other words, epoxies are the most versatile of contemporary plastics and it is considered necessary to briefly describe their chemistry.

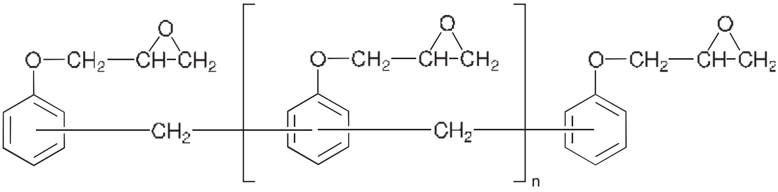
Epoxy Resins The term epoxy refers to an epoxide group which is a three-membered oxide ring. An epoxy resin is defined as a molecule containing more than one epoxy group capable of being converted into a thermoset (cured) form. The simple structure of epoxy resin [Structure (4.37)] is:



Structure (4.37): Epoxy resin

where n stands for degree of polymerization, if $n = 0$, the resin is a viscous liquid or low m.p. solid and if $n = 1,2,3$ … etc. resins are solids with increasing m.p.

Novolac Epoxy Resins The novolac epoxy resins have a high crosslinking density, high functionality and epoxy content greater than two. The novolac epoxy resins maintain their properties at a high temperature and possess high deflection temperature (HDT) and high glass transition temperature (T_g). The presence of a phenolic resin backbone provides a short term high thermal stability together with the chemical versatility of epoxide group leading to their manifold newer applications. The simple structure of a novolac epoxy resin [Structure (4.38)] is:



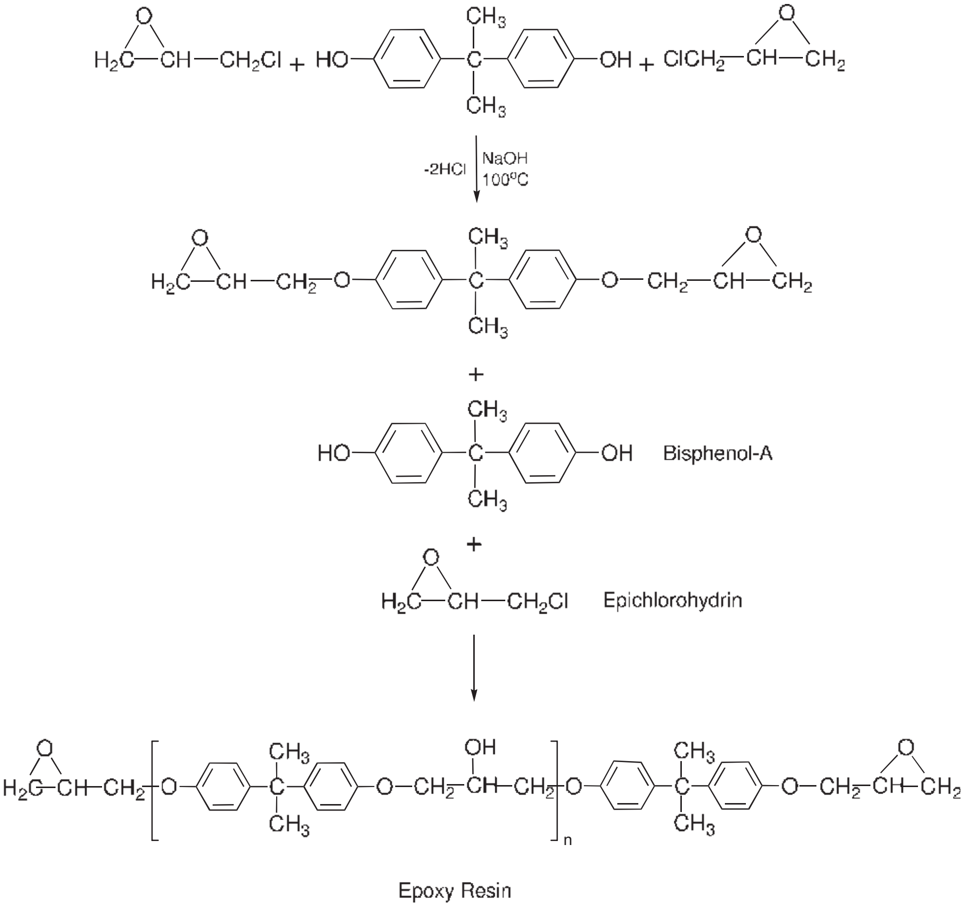
Structure (4.38): Novolac epoxy resin

The most commonly used novolac epoxy resin has $n \approx 1.6$. Novolac epoxy resins with functionalities of 2.5 to 6.0 are also available commercially [340, 341].

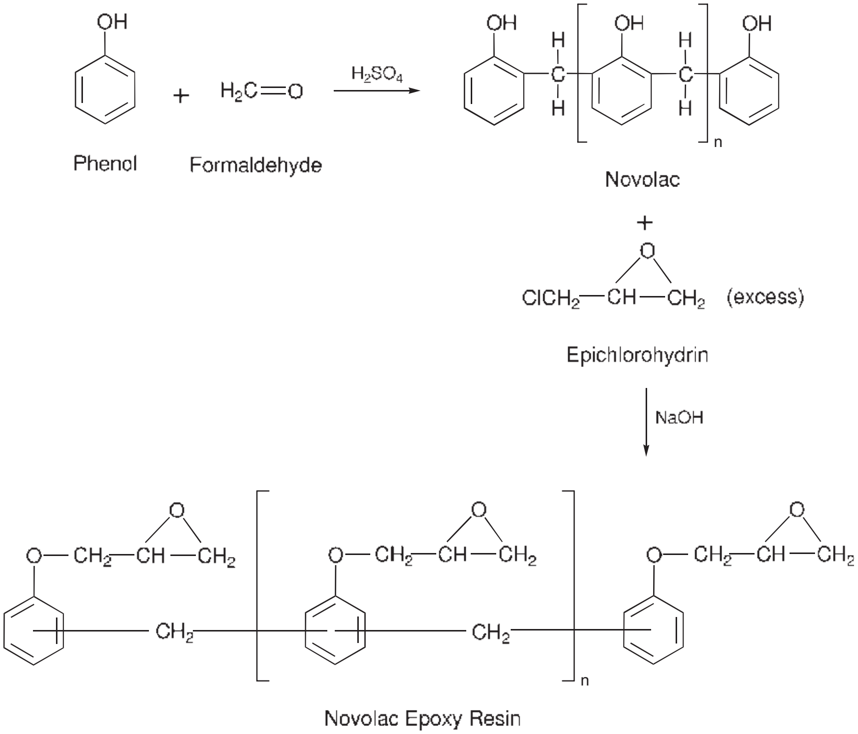
Synthesis Epoxy resins consisting of glycidyl ether, ester and amines are generally prepared by the condensation reaction between diol, dibasic acid or amine and epichlorohydrin in the presence of sodium hydroxide with the elimination of hydrochloric acid. The commercially available epoxy resins are, however, made by the reaction of epichlorohydrin and bisphenol-A. Cashew nut shell liquid (CNSL)-based novolac epoxy resins have also been reported [342].

An outline of the general method of synthesis of epoxy resin and novolac epoxy resin are shown in Schemes 4.9 and 4.10 respectively.

Novolac resins are condensation products of phenol and formaldehyde made in the presence of an acid catalyst such as hydrochloric acid, sulfuric acid or oxalic acid. For novolac resins, mole ratios of phenol to formaldehyde vary from 1:0.5



Scheme 4.9 Synthesis of epoxy resin.



Scheme 4.10 Synthesis of novolac epoxy resin.

to 1 : 0.9. novolac epoxy resins are prepared similar to that of bisphenol-A-based epoxy resins. The synthesis consists of condensation of the phenolic hydroxyl groups of novolac resin with epichlorohydrin in the presence of an alkaline catalyst. Instead of novolac resins, resol type of phenolic resins have also been used for making epoxy resins which are viscous liquids and are used for production of laminated boards. A number of phenolic compounds such as *p*-*t*-butyl phenol, *o*- and *p*-cresol have been used for making novolac resins which are finally used for the preparation of novolac epoxy resins.

Curing Agents for Epoxy Resins The most valuable property of epoxy resins is their ability to transform readily from liquid to tough and hard solid. The conversion normally occurs without the formation of by-products. This conversion is achieved by the addition of chemically reactive compounds such as polyamines, polyamides, acid anhydrides, acids (drying oil fatty acids), urea–formaldehyde and phenol–formaldehyde resins which are called curing agents. Curing agents are considered broadly in the following categories.

1) **Primary and secondary aliphatic polyamines:** These are low viscosity and low cost materials. In general, linear and branched primary and secondary aliphatic

amines cure epoxy resins fast at room temperature. The cyclic aliphatic amines require high temperature for curing of epoxy resins. Some important primary and secondary aliphatic polyamines are: diethylene triamine (DTA), triethylene tetramine (TET) and diethyl aminopropylamine (DEAPA) etc.

2) **Aromatic amines:** The aromatic amines have medium viscosity and act in the same manner as aliphatic polyamines. The most important aromatic amines used as curing agents are: m-phenylenediamine (MPD), 4,4′-diaminodiphenyl methane (DDM) and 4,4′-diaminodiphenyl sulfone (DDS). Aromatic polyamines impart better thermal and chemical resistance to castings and glass cloth laminates compared with aliphatic polyamines. In addition, products cured by aromatic amines retain their properties better at elevated temperatures. At room temperature, aromatic amines react sluggishly with epoxy resins. The lower basicity of the aromatic amines together with the relative lack of mobility of the growing polymer network, all contribute to the difference in reactivity between aromatic and aliphatic amines. Aromatic amines react faster than aliphatic amines with cycloaliphatic epoxides.

3) **Polyamides:** These are aminopolyamides produced from the reaction of dimerized and trimerized vegetable oil fatty acids with polyamines. The polyamides available commercially are complex mixtures of substances containing additionally free carboxyl groups and ring structures of imidazoline type. Polyamides are regarded as flexibilizers as well as curing agents. This is being achieved by the flexible nature of the molecules between the reactive points. From the structure of polyamide, it is seen that it contains not only amide but also primary and secondary amino groups which are responsible for the curing reactions. The commercial polyamides are amber-colored resins with molecular weights up to 10 000 (at room temperature). The viscosity of polyamides is high for this reason. The polyamides are versatile curing agents and their mixing ratios are not critical. Polyamides provide fairly long pot life, good impact strength and excellent adhesion. At the same time, curing is possible at room temperature also.

4) **Acid anhydrides:** A large number of anhydrides including polymeric anhydrides, dianhydrides and various compounds in combination with acid anhydrides act as curing agents but the most important are based on a cycloaliphatic structure. When cycloaliphatic anhydrides are used as curing agents, the cured products have good mechanical and electrical properties and high temperature stability than the amine-cured systems. The resin-liquid anhydride mixture has a low viscosity, long pot life and low volatility. Acid anhydrides are also the main curing agents for crosslinking cycloaliphatic and epoxidized olefin resins which react more rapidly with anhydrides than with amines. Anhydrides do not react very readily with epoxide rings whereas carboxyl groups do so and therefore, a catalyst is incorporated with anhydrides. They serve to speed up gelling and reduce duration and temperature of cure.

Cure Mechanism Epoxy resins are converted by means of crosslinking reactions into three dimensional infusible networks held together by covalent bonds. This conversion of a liquid or friable brittle solid into a tough crosslinked polymer is called curing or hardening and is achieved by the addition of curing agents which serve as initiators for resin homopolymerization. The polyfunctional curing agents function as reactants or co-monomers in the polymerization leading mainly to the formation of three dimensional networks composed of resin molecules crosslinked via curing agents.

4.10.7.2 Novel Systems

Laird and Becker [343, 344] have reported that the uncontrolled burning of composite propellant strands is inhibited by applying a partially cured phenolic resin, RESINOX R737 (Monsanto) in a solvent like polyethylene glycol or acetone and subsequently, volatilizing the solvent. The coating provides improved high speed photographic analysis of deflagrating surface with very little flashing, charring etc. Novolac epoxy–liquid polysulfide blends have also been reported for the inhibition of composite propellants [345].

4.10.7.3 Plasticizer Migration in Composite Propellants

Plasticizer migration is generally referred to in the context of double-base (DB) and CMDB propellants as it is not significant in the case of composite propellants. However, it is likely to be the main thrust area in the near future as migration of plasticizers, curing agents and ballistic modifiers and their adverse effects on the performance of composite propellants have recently been reported in literature [293, 346–350]. The kinetics of migration of diethyl phthalate (DEP) through novolac epoxy resin formulations have been reported as a model study [351]. The most important conclusion is that polyamide-based formulations which are invariably preferred for inhibition of composite propellants, possess higher diffusion coefficients (D) as well as plasticizer migration at infinite time ($M\infty$) compared with epoxy formulations cured with polyamines. Consequently, the extent of migration of non-explosive plasticizer DEP (used for manufacture of composite propellants) is also more for polyamide cured inhibition systems. Hence, plasticizer migration is not considered desirable because it adversely affects the mechanical properties and performance of inhibitors and composite propellants during storage.

4.10.8
Inhibition of CMDB Propellants

The combustion temperatures are much higher in CMDB propellants than that of DB and composite propellants and therefore, inhibition systems for CMDB propellants should have better BS and ablative properties. As major ingredients of CMDB propellants are NC and NG similar to DB propellants, it is logical to use polyesters which have already proved their potential for DB propellants for inhibition of CMDB propellants. However, the unsaturated polyesters which function successfully as inhibitors for DB propellants do not work similarly in the case of CMDB propellants due to the presence of aluminum and ammonium perchlorate powders. This is probably due to the fact that the presence of AP and Al in CMDB propellants lower bond strength between polyesters and these propellants. A number of inhibition systems for CMDB propellants have been reported in the literature but the most important system is based on the mixture of epoxy resin and (butadiene-acrylic acid) copolymer filled with zinc chromate which was originally patented for the inhibition of DB propellants. This system has also been evaluated for CMDB propellants with successful performance. Such inhibited propellants, after 16 cycles at –40° to +60°C for 24h, does not show any deterioration of the propellant-inhibitor bond [352]. The inhibition of these propellants has also been developed by the author using acropol resin (a rigid polyester) containing antimony trioxide as a barrier layer and lithopone filled flexible polyester resin (EP-4) as a main inhibitor. The bond strength between the propellant and barrier layer is enhanced by using Desmodur-R in some organic solvent [353].

Polyesterification between a diol and dibasic acid is usually done by (i) a 1-step process, (ii) a 2-step process and (iii) a 3-step process [163]. The commercially available unsaturated polyesters are generally manufactured by 1-step polyesterification process and as a result, possess poor flexibility and inferior heat resistance. At the same time, higher temperature of reaction in the 1-step process converts maleic configuration to fumaric configuration. On the contrary, unsaturated polyesters and chloropolyesters for inhibition of DB and CMDB propellants are synthesized by 2-step polyesterification process which imparts more regular structure, better flexibility and greater heat resistance to the resulting polyesters.

The effect of method of polyesterification on various properties is depicted in Table. 4.16.

It is seen from the data that the order for G_t is NUP (I) < NUP (II) < NUP (III) whereas the order for tensile strength is NUP (I) > NUP (II) > NUP (III). Further, % elongation gradually increases from NUP (I) to NUP (III). However, there is no specific trend for NG migration, that is, first it increases from NUP (I) to NUP (II) and then decreases from NUP (II) to NUP (III). A detailed study of structural aspects of virgin NUP (I) [Structure (4.39)], NUP (II) [Structure (4.40)] and NUP

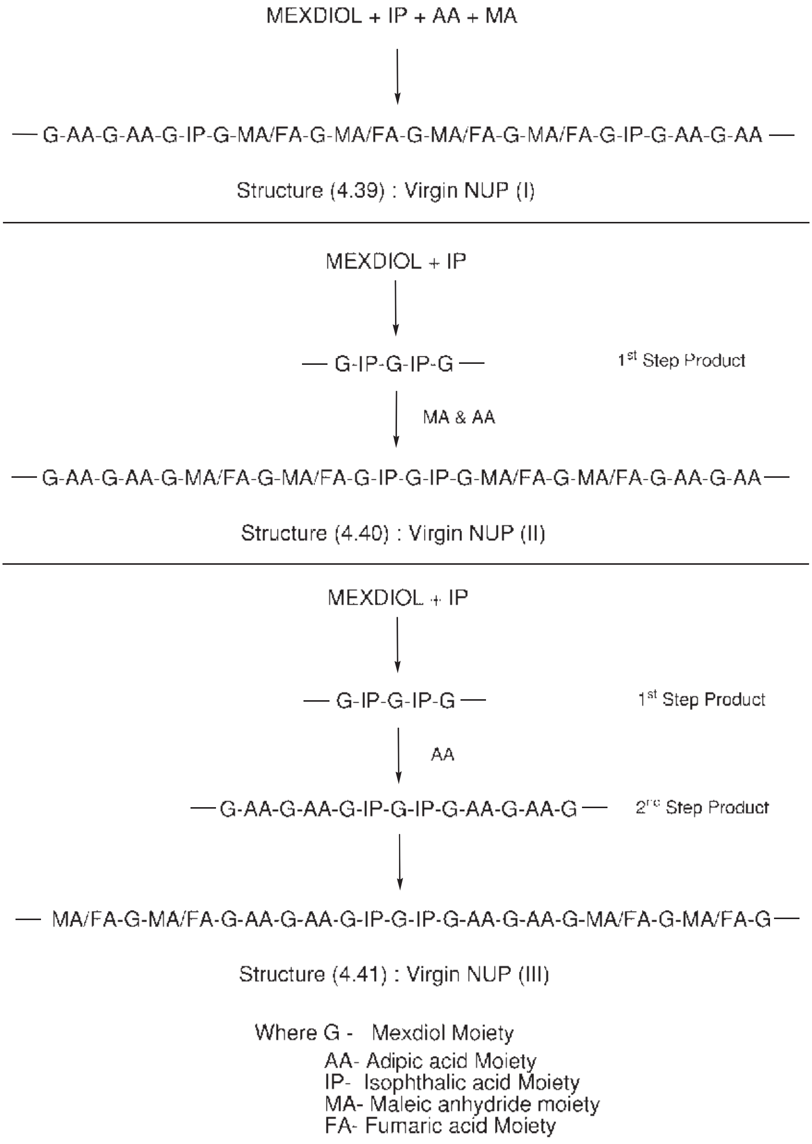
Table 4.16 Effect of methods of polyesterification on some DEG-based NUPs.

Resin	Formulation[a]				Method	Properties			
	DEG	IPA	AA	MAn		G_t/Min	TS/kg cm^{-2}	E/%	NG Absorption (after 8 days)/%
NUP (I)	12.0	2.0	5.0	5.0	1-Step	11.0	41.0	26.0	23.98
NUP (II)	12.0	2.0	5.0	5.0	2-Step	12.5	30.0	30.0	32.05
NUP (III)	12.0	2.0	5.0	5.0	3-Step	23.3	5.1	36.0	26.93

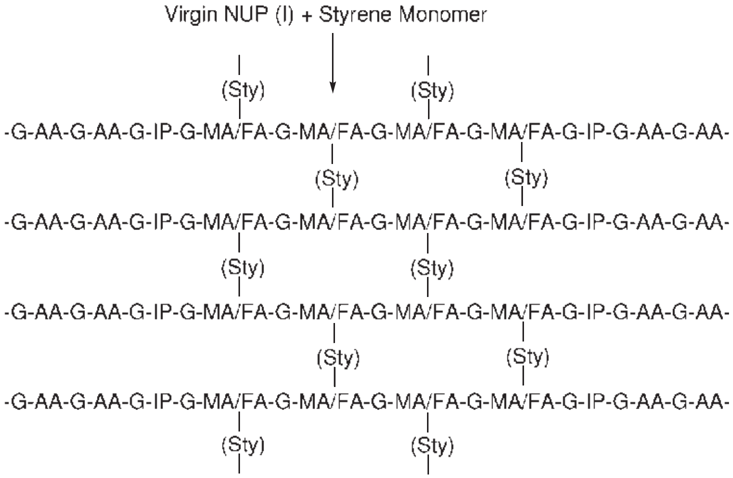
[a] Acid values at the end of all steps are 50 ± 2.

(III) [Structure (4.41)] with the help of IR, NMR, dissociation constants of acids and method of preparation suggests the structures [303, 304, 354] as shown in Scheme 4.11.

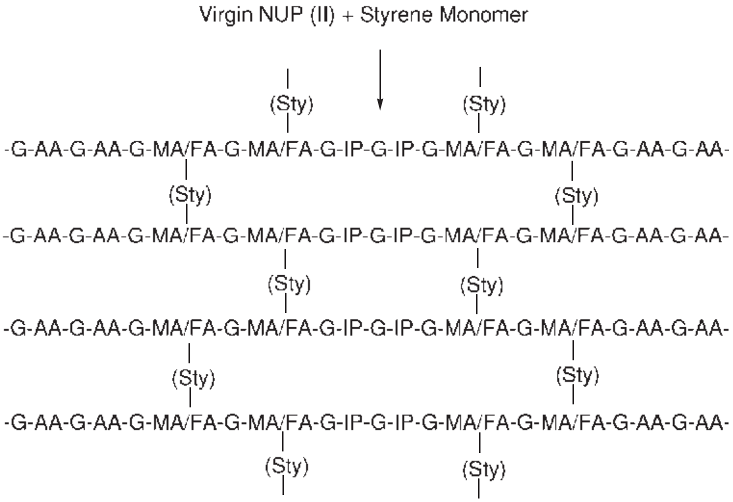
The model structures of cross-linked unsaturated polyesters (on curing with styrene monomer) are depicted in Figure 4.16 A [Structures (4.42) and (4.43)] and Figure 4.16 B. [Structure (4.44)].



Scheme 4.11 Structures of Virgin NUP (I), NUP (II) and NUP (III).



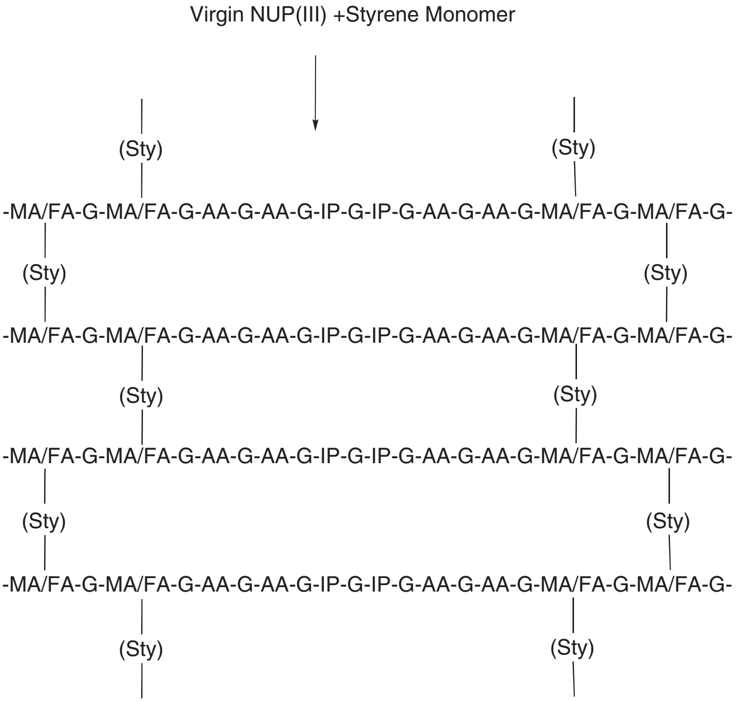
Structure (4.42): Crosslinked NUP (I)



Structure (4.43): Crosslinked NUP (II)

Figure 4.16 (A) Model structures of crosslinked NUP (I) and NUP(II).

It is evident from the structures that the distance between the crosslinking sites increases from NUP (I) to NUP (III) leading to increase in elongation [303, 304, 354] which is in accordance with the data given in Table 4.16. The lower value of NG absorption or migration of NUP (III) compared with NUP (II) may be explained on the basis of the presence of double-bonds in the polyester backbones of NUP (III) which are terminal and provide crosslinking sites for styrene monomer. This



Structure 4.44: Crosslinked NUP (III)

Figure 4.16 (**B**) Model structure of crosslinked NUP(III).

3-dimensional network because of crosslinking of terminal double bonds with styrene, offers more hindrance or resistance to the seepage of NG molecules through it and the net result is a decrease in NG absorption in case of NUP (III). This is also in agreement with the data reported in the literature [305, 355] which suggests that if crosslinking sites are available on the terminal of a polyester backbone, chemical resistance of the 3-dimentional network is better after curing.

It is well established as a result of exhaustive study that if elongation of a polymer is higher, migration or absorption of plasticizer is also higher. The elongation and NG migration data for NUP (III) reveal that it possesses a unique combination of elongation and NG migration, that is, higher elongation and lower NG migration or absorption. As inhibition of propellants demands higher elongation and lower migration or absorption of explosive or non-explosive plasticizers (NG/TA or DEP) – a combination of two contradictory properties, NUP (III) is considered better than other unsaturated polyesters for inhibition of CMDB propellants [281]. The CMDB propellants (tubular and sustainer) grains inhibited with NUP (III) give expected *P–t* profiles during their static evaluation at ambient, cold (–30 °C) and hot (+50 °C) temperatures suggesting that NUP (III) is a potential inhibitor for inhibition of CMDB propellants [356].

The PU system based on HTPB–MDI–TMP and filled with carbon black and antimony trioxide was also evaluated for inhibition of CMDB propellants. Due to superior mechanical properties, thermal properties and low NG migration, this PU system holds a potential for inhibition of CMDB propellants [357].

4.11
Insulation of Rocket Motors

The other way of providing protection to a motor is to apply a polymeric material or rubber to its inner surface and cast propellant directly into the insulated motor. Before casting propellant mix, a liner material is also applied to the motor insulation in order to ensure a strong bond between them. Such propellant grain in known as case-bonded grain which is shown in Figure 4.17.

Such polymeric materials or rubbers are known as insulating materials or insulators and the process of their application is known as insulation. The motor insulation not only provides protection to motor but also functions as an inhibitor. The case-bonded motors have a little less inert mass and as a result, give slightly better performance. However, they are more stressed and more difficult and expensive to manufacture. Many tactical missiles and almost all larger rockets or missiles for defense and space applications use case-bonded motors.

4.11.1
Characteristics of Insulators or Insulating Materials

The insulating material or insulator must possess a number of properties [358] and the most important are:

1) Chemical compatibility with the components of the motor, that is, it should not upset the chemistry of propellant and other components of the motor.

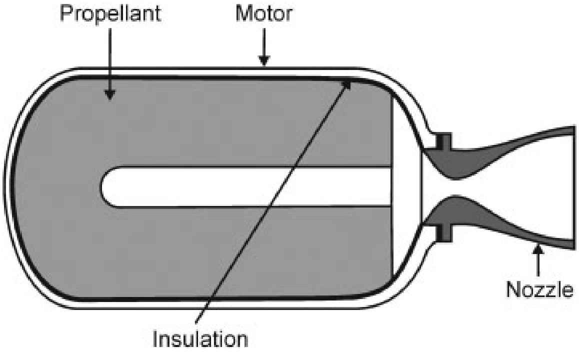


Figure 4.17 Schematic of a case-bonded propellant. Reprinted from G.P.Sutton, *Rocket Propulsion Elements: An Introduction to the Engineering of Rockets*, 1992; © 1992, John Wiley and Sons, Chichester, UK.

2) Excellent bond with motor, liner and propellant over a wide range of temperatures, that is, −40 °C to +60 °C. It should also be sustainable in this temperature range throughout the Service life of insulated motors.

3) Good mechanical properties such as tensile strength, elongation, compressive strength etc. at all temperatures encountered during the Service life of insulated motors. This prevents deformation of the grain or separation of the insulator from propellant grain, liner and motor during various manufacturing and storage and handling phases.

4) Low ablation rate and low density in order to minimize the inert mass on board. Also, the resulting char must remain porous and the resulting gases must be of low molecular mass. At the same time, pyrolysis of the insulating material must not lead to emission of smoke or flashes.

5) Low thermal conductivity and high specific heat.

6) Low moisture absorption and superior thermal resistance.

7) Good ageing characteristics so that the case-bonded motor has a minimum 10–12 years of Service life.

8) There should be no migration of its ingredients to adjacent interfacial surfaces or vice versa.

The most important requirement is that the case-bonded motor must give expected performance throughout propellant combustion at all temperatures including extreme temperatures. This is the most important functional requirement and even if the insulating material meets all other requirements but fails in this test, it cannot be used for the insulation of motor.

4.11.2
Materials for Insulation

Filled nitrile rubber, polydimethyl siloxane (PDMS) and polyisoprene etc. are a few of the various elastomers which have found application as insulator in solid rocket motors [359, 360]. Nitrile rubber-based insulation system is being currently used by the Indian Space Research organization [361]. The same insulation system has also been established in the Defence R&D Organisation for experimental motors [362, 363]. However, nitrile rubber-based insulation suffers from a number of disadvantages: higher density, inferior low temperature characteristics and limited shelf-life (critical defect from defense application point of view) etc. In an attempt to improve upon these defects of nitrile rubber-based insulation system, use of ethylene–propylene–diene monomer [EPDM – a terpolymer made of ethylene, propylene and a diene (1,4-hexadiene, ethylidene norbornene or dicyclopentadiene in varying ratios)] rubber was patented by Herring [364]. Skolnik and coworkers also made efforts to replace nitrile rubber-based insulation system by EPDM rubber-based insulation system for 'Tomahawk' booster motor [365]. The evaluation of EPDM in order to replace nitrile rubber in Indian Space and Missile

Programs is in advanced stage of development [366–369]. EPDM being a material with a low specific gravity, outstanding resistance to oxidation, ozonization and weathering effects [370, 371], it is considered a novel material for manifold applications including insulation of solid rocket motors. The most important attributes of EPDM which make it attractive for defense applications are its excellent low temperature properties and long shelf-life. Kakade *et al.* have recently reviewed the use of EPDM rubber for insulation of rocket motors [363].

4.11.3
Process for Insulation of Motors

Neoprene and nitrile rubbers (gum stocks) filled with silica are generally used for insulation of rocket motors and the general process consists of (i) sand blasting of rocket motor followed by cleaning with petrol or organic solvent and drying, (ii) application of unvulcanized rubber sheet (2.0–2.5 mm thick) on the inner side of rocket motor with the help of bonding agents like Chemlok 220 (MS motors) or Chemlok 205 (Al motors), (iii) application of optimized pressure to the inner side of rubber surface by an inflated balloon for 24 h (iv) partial vulcanization of rubber sheet applied to rocket motor by keeping it in air oven at elevated temperature after removal of rubber balloon, (v) Application of liner composition to insulated motor and its partial curing (vi) casting of propellant mix in the lined motor under vacuum (vii) Application of vibration in order to remove entrapped air, (viii) curing of propellant mix in the insulated motor by keeping it in a water-jacketed oven and finally (ix) trimming of propellant ends and inhibition. The procedure seems to be simple but it is quite complex and utmost care is required at each and every stage in order to get defect-free case-bonded rocket motor.

In case of insulation by EPDM rubber, the method is slightly modified as it does not possess strong bond with metal surfaces. The formulation for insulation invariably consists of EPDM rubber as primary and secondary polymer to enhance the bonding properties [372, 373]. Various additives such as plasticizer, propellant bonding agent, anti-oxidant, flame retardant filler (particulate and fibrous), activator, accelerator and curative are normally included in the rubber-based insulation formulation. A typical formulation for EPDM rubber insulation is reported in the literature [374]. The details of ingredients of EPDM formulation and general procedure for its bonding with rocket motor and casting of propellant mix are also described by Kakade *et al.* [363].

4.11.4
Future Materials for Insulation

Another rubber which appears to be of interest for insulation of rocket motors is hydrogenated hydroxy-terminated polybutadiene (HHTPB). As this rubber is derived from HTPB, it is more compatible and would also have strong bond with the HTPB-based propellants. Further, as the quantum of unsaturation is considerably reduced in HHTPB, the life of rocket motors insulated with HHTPB will also be more. In a nutshell, the use of HHTPB results in an increased stability to thermal and oxidative degradation, improvement in tensile strength, elongation, stiffness, hardness and better adhesion to metals and other materials or polymers.

A lot of work has already been done by the Japanese on HHTPB – synthesis, characterization and application for electrical insulation, lubricating oil additives, catalyst support for ethylene polymerization and also as a plasticizer in synthetic and natural rubbers. HHTPB was synthesized by hydrogenation of HTPB using Raney Nickel as a catalyst and isopropyl alcohol as a reaction medium in SS autoclave at optimized temperature, pressure and reaction time [375–377] and characterized for residual unsaturation or extent of hydrogenation, any loss of hydroxyl group during hydrogenation, extent of any side reaction (dehydration, crosslinking, cyclization etc.), iodine number, hydroxyl value, number average molecular weight ($\overline{M}_n$) by VPO and polydispersity ($\overline{M}_w / \overline{M}_n$) by size exclusion chromatography [378, 379]. The data for a typical batch of HHTPB is: unsaturation ≈3.0%, OH value 41–46, $\overline{M}_n$ (by VPO) ≈ 3500 and $\overline{M}_w / \overline{M}_n \approx 1.7$. The polyurethanes derived from HHTPB possess improved flexibility, adhesion, resistance to hydrolysis, oils, heat and improved weathering [380, 381] and mechanical properties [382].These polyurethanes with such outstanding properties and remarkable electrical properties (volume resistivity and resistance to arc and tracking) are of high industrial value [383, 384]. The HHTPB-based formulations consisting of optimum proportions of alumina hydrate and magnesium hydroxide possess very good insulation property, resistance to arc, tracking, water and heat besides possessing desirable mechanical properties (tensile strength and elongation). As a result, the formulations disclosed in these patents hold a tremendous potential for use as insulating materials for rocket motors and need further exploration [385, 386].

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5
Pyrotechnics

5.1
Introduction

The origin of pyrotechnics is obscure and the Chinese are usually credited with the invention of pyrotechnics (gunpowder – a pyrotechnic mixture of charcoal, potassium nitrate and sulfur). Pyrotechnics are among the oldest explosive devices known to man and have been used from very early times to display fireworks for celebrating important occasions or to express victory. Fireworks are believed to be similar to pyrotechnics with minor differences.

The term ‘pyrotechnics’ is derived from two Greek words ‘pyr’ (fire) and ‘techne’ (an art) and hence pyrotechnics may be defined as the art of creating fire. In recent times, this definition has undergone transformation and pyrotechnics, originally considered as an art of making and using fire, has now emerged as an independent science and technology. In principle, pyrotechnics are very similar to explosive and propellant formulations. Explosives function at the highest speed of reaction producing gaseous products whereas propellants function at a slower speed than explosives. On the other hand, pyrotechnics function at visibly observable rates with the formation of solid residues or a lot of gases or both [1–5]. There are two special features of pyrotechnics:

1) Pyrotechnic formulations are mixtures of different chemicals, mostly inorganic chemicals. These formulations generally burn and do not detonate. However, some formulations are capable of detonation if confined heavily or incorrectly initiated by overstimulus.

2) Pyrotechnics are employed to produce special effects other than those produced by high explosives and propellants. There are several special effects produced by pyrotechnics which are classified according to their nature. A brief on their nomenclature, special effects and applications is given in Table 5.1.

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Table 5.1 Pyrotechnics: special effects, nomenclature/devices and applications.

Special effect	Nomenclature/device	Purpose/application
Light	(a) Illuminants (i) Flares (ii) Photoflashes (b) Signals (c) Tracers	(a) (i) A single source of illumination for observation, identification, location of targets etc. (ii) A single flash of light for photographic purposes. (b) For giving various types of signals. (c) For observing the trajectories of shells and missiles in flight.
Heat	(a) Incendiary devices (Flame thrower fuels, Napalm bombs) (b) Igniters	(a) For setting fire to combustible targets. (b) For producing intense heat for ignition of subsequent train of formulations and propellants.
Time	Delays (a) Gas-producing (b) Gasless	For producing a time interval between two successive explosive events.
Smoke	(a) Signals (b) Screening	(a) For signaling and observation. (b) For screening/masking.
Sound	Simulators	For imitating actual battle sounds and flashes of light produced by a typical weapon. These are generally designed for use in training.

5.2
General Features of Pyrotechnics

Pyrotechnics are invariably intimate mixtures of finely powdered fuels and oxidizers together with other additives in order to impart special effects depending on the requirement. Pyrotechnic formulations burn very rapidly when ignited as a loose powder. However, there are some applications where controlled steady burning is required for a definite time and this is achieved by compressing the mixture into columns surrounded by a relatively non-combustible material so that combustion proceeds from one end to other, layer by layer for a long duration.

Pyrotechnic formulations which are intended to produce gases, are generally based on a carbonaceous fuel and an oxidizer and these burn to form carbon oxide. On the contrary, 'gasless' pyrotechnic formulations are more likely to contain metal powders or metal oxides. The most important attribute of 'gasless' pyrotechnic formulations is that their burning rate remains largely unaffected by changes in pressure. Such formulations are suitable for use at high altitudes or under confinement.

Pyrotechnics are rarely composed of a single substance; the examples are titanium tetrachloride ($TiCl_4$), red phosphorus (RP) and white phosphorus (WP). $TiCl_4$

reacts with moisture in the air to produce smoke which gives a screening effect, not by combustion but by hydrolysis. On the other hand, WP and RP burn in air to give a screening effect. Since these materials react with atmospheric air or moisture to give special pyrotechnic effects, these materials are classified under pyrotechnics. These are the examples of a 'fuel only' formulation.

The chemical reactivity of the ingredients and their particle size have considerable influence on the ignition characteristics and burning rates of pyrotechnics. Finer particles are easier to ignite, leading to a faster reaction rate because of greater degree of contact between fuel and oxidizer particles.

5.3
Ingredients of Pyrotechnic Formulations

Pyrotechnic formulations in general consist of physically intimate mixtures of various combinations of fuels and oxidizers, of which many are in use. The tailoring of the formulation is done by changing the proportions of fuel, oxidizer and other ingredients and also by changing their particle sizes. In addition, additives are used in order to impart special effects to the formulations.

5.3.1
Fuels

Charcoal and sulfur were the earliest pyrotechnic fuels. The choice of fuels is very wide, ranging from metallic to non-metallic elements and binary compounds to various types of carbonaceous materials, both natural and synthetic. The main fuels are aluminum and magnesium powders, their alloy, sulfur, lactose, carbon and carbonaceous fuels etc. The fuels listed below are usually powdered materials, which when oxidized provide heat energy.

- **Metals:** aluminum (Al), chromium (Cr), iron (Fe), magnesium (Mg), titanium (Ti), tungsten (W) and zirconium (Zr) etc.
- **Non-metals:** boron (B), carbon (C), silicon (Si), sulfur (S) and phosphorus (P) etc.

Fuel is the main burning ingredient in pyrotechnic formulations. Magnesium powder is used most frequently to produce light and heat. Aluminum, antimony, boron and other metals are used to a smaller extent. Magnesium powder generates more light than any other fuel. Formulations with Al are more stable and have better storage life than Mg. Magnesium produces a heat and temperature continuum for intense white light.

In a nutshell, Mg and Al are the most commonly used pyrotechnic fuels to create heat and light. Both have been used in the development of radiation effect. While Mg is the fuel of choice for most illuminating and tracer formulations, Al is still the main ingredient of photoflash and thermite formulations. The pyrotechnic behavior of Mg is due to its low melting and boiling points in comparison to most other metals and hence it is easily vaporized. Aluminum also has low melting point (m.p.) but its boiling point is comparatively high. Sometimes it is difficult to ignite Al-based formulations. Titanium has also been used in pyrotechnic formulations for first fires, igniters and heat sources. It has low ignition and initiation temperatures and also forms hot white sparks. It is also an ingredient for gasless and millisecond-delay formulations.

5.3.2
Oxidizers

The oxidizer is the source of oxygen. The choice of oxidizer is restricted and is confined to metallic and some non-metallic oxides, oxygenated salts and some halides. These oxidizers are chlorates, perchlorates, peroxides, chromates and nitrates. Oxidizers commonly used for pyrotechnic formulations are the nitrates of sodium and potassium. To a lesser extent, barium and strontium peroxides are also used. Halocarbons may also act as oxidizing agents in the true chemical sense; fluorine is the most energetic oxidizer; Teflon, Viton-A and Kel-F800 are some important examples. Oxidizers may be selected from chlorates ($KClO_3$), chromates ($BaCrO_4$), dichromates ($K_2Cr_2O_7$), halocarbons (C_2Cl_6, PTFE), iodates ($AgIO_3$), nitrates (KNO_3), oxides/peroxides (ZnO/BaO_2) and perchlorates ($KClO_4$). Oxidizers such as barium peroxide supply a spectral band system and general thermal continuum that contribute mainly to provide white light. Potassium salts have lower temperatures of melting and decomposition than those of barium. The violet color of the potassium flame neutralizes the greenish tinge of the barium flame. Sodium nitrate produces sodium ions in the flame on complete reduction and therefore, the sodium continuum makes the light yellowish-white.

In addition to fuel and oxidizer, other additives are as important to the final formulation as the fuel–oxidizer system, and their role, along with some important examples, is as follows.

5.3.3
Binders

Binders increase cohesion between the particles of fuel and oxidizer, facilitating better consolidation and resulting in better mechanical properties of the end products. In addition, an equally important function is to coat and protect metallic or non-metallic fuels (such as metal or non-metal powders) which may otherwise react with moisture and oxygen. They also modify the burning rate and hence the performance, and at the same time reduce sensitivity to impact or friction. A comprehensive list of binders, natural to synthetic resins used for pyrotechnic formulations follows.

1) **Natural binders:** Paraffin wax, beeswax, carnauba wax, Chinese wax, boiled linseed oil, lithographic varnish, shellac and gum arabic etc.

2) **Man-made binders:** Bakelite resin, polyester resin, chlorinated rubber, polyvinyl chloride, Thiokol rubber, epoxy resin, Thiokol–epoxy blends, vinyl acetate alcohol resin (VAAR), Viton-A, Teflon and Kel-F800 etc.

Shellac, boiled linseed oil, resins, paraffin wax, beeswax, lithographic varnish and acaroid resin are used in various pyrotechnic formulations. Similarly chlorinated rubber powder has also been used successfully as a binder. Some of the waxes and resins which are of natural origin are still popular and are in use. In order to improve quality and avoid batch-to-batch variation, manufacturers of pyrotechnics are moving from natural binders to man-made binders.

5.3.4
Coolants

Coolants are used in various pyrotechnic formulations to decrease the temperature during their burning; important examples are carbonates of Mg , sodium and other metals.

5.3.5
Retardants

Oxalates are most commonly employed to retard the rates of burning of these formulations. Formates and citrates are some of the organic salts used for this purpose. Calcium carbonate has also been reported for this purpose.

5.3.6
Dyes

Dyes are used to produce colored smokes. 1-methylamino anthraquinone is used to produce red color whereas auramine hydrochloride is used to produce yellow color.

5.3.7
Color Intensifiers

Some substances are used to intensify the color of pyrotechnic formulations. For example, polyvinyl chloride, hexachlorobenzene (HCB) or other organic chlorides mixed with barium and copper salts are used to produce green color whereas strontium salts produce red color.

5.3.8
Moderators

Moderators are used to modify the color of the flame or to improve the smoothness and efficiency of combustion. Important examples of moderators employed to modify the color of the flame are (i) sodium nitrate or oxalate for yellow color; (ii) barium nitrate, chlorate or oxalate for green color; (iii) strontium nitrate, oxalate or carbonate for red color and (iv) copper oxychloride or basic carbonate for blue color.

5.4
Important Characteristics of Ingredients for Pyrotechnic Formulations

The knowledge of the important properties of commonly employed oxidizers, fuels, organic and polymeric additives is essential in order to understand their roles in pyrotechnic formulations [5]. The properties of some commonly employed ingredients: fuels, oxidizers and organic and polymeric additives are given in Tables 5.2–5.4 respectively.

Some of the important properties which are considered when choosing the ingredients for pyrotechnic formulations are: density, hygroscopicity, melting and boiling points and decomposition temperatures, oxygen content of oxidizers, thermal conductivity of fuels and containers, nature of combustion products and toxicity etc.

5.4.1
Density

Densities of the fuel, oxidizer and other ingredients decide the densities of formulations. Density of the formulation determines its weight that can be accommodated in a particular volume. The density becomes one of the important criteria in ammunition where specified performance in terms of burning time, delay or luminous output is required in a limited space or column.

Table 5.2 Some common fuels and their properties[a].

Fuel	Density/ gcm^{-3}	Melting Point/°C	Boiling Point/°C	Heat of combustion/ k cal g^{-1}	Main combustion product	M.P. of oxide/°C	B.P. of oxide/°C
Aluminum (Al)	2.70	660	2467	7.4	Al_2O_3	2072	2980
Magnesium (Mg)	1.74	649	1107	5.9	MgO	2852	3600
Titanium (Ti)	4.51	1660	3287	4.7	TiO_2	1830–1850	2500–3000
Tungsten (W)	19.30	3410	5660	1.1	WO_3	–	1800
Zinc (Zn)	7.14	420	907	1.3	ZnO	1800	1950
Zirconium (Zr)	6.51	1852	4377	2.9	ZrO_2	2700	5000
Boron (B)	2.35	2300	2550	14.0	B_2O_3	450	1860
Carbon (C)	2.26	Decomposes	–	7.8	CO_2	–	–
Silicon (Si)	2.33	1410	2355	7.4	SiO_2	1610	2230

a) Reference [5].

Table 5.3 Some common oxidizers and their properties[a].

Oxidizer	Density/ gcm^{-3}	Mol. wt	Melting Point/°C	Heat of Decomposition/ $kcal\ mol^{-1}$	Grams of O_2 released per g of oxidizer	Remarks
Sodium nitrate $NaNO_3$	2.26	85.0	307	60.5	0.47	Imparts yellow color
Barium chlorate $Ba(ClO_3)_2$	3.86	322.3	414	–28.0	0.32	Impart green color to flame
Barium chromate $BaCrO_4$	4.50	253.3	Decomposes	–	0.095	
Barium nitrate $Ba(NO_3)_2$	3.24	261.4	592	104	0.31	
Barium peroxide BaO_2	4.96	169.3	450	17	0.09	
Lead chromate $PbCrO_4$	6.30	323.2	844	–	0.074	–
Lead oxide PbO	9.53	223.2	886	–	0.72	–
Potassium chlorate $KClO_3$	2.32	122.6	356	–10.6	0.39	Imparts violet color
Potassium nitrate KNO_3	2.11	101.1	334	75.5	0.40	
Potassium perchlorate $KClO_4$	2.52	138.6	610	–0.68	0.46	
Strontium nitrate $Sr(NO_3)_2$	2.99	211.6	570	92	0.38	Imparts red color

a) Reference [5].

5.4.2
Hygroscopicity

Hygroscopicity of the ingredients is also an important factor which should be taken into consideration while considering their use in pyrotechnic formulations. Oxidizers absorb moisture and some oxidizers are more hygroscopic than the others. Moisture also reacts with metal surface to form a layer of metal oxide or metal hydroxide. Formation of such non-reactive layers changes the ignition and propagative characteristics of the formulation leading to malfunctioning. Therefore, it is necessary to have a knowledge of the moisture absorption characteristics of the ingredients before their selection. Yet, on many occasions the use of an ingredient in pyrotechnic formulations cannot be avoided despite the fact that it is prone to moisture absorption.

Table 5.4 Some common organic and polymeric additives and their properties[a].

Additive	Melting point/°C	Grams of fuel consumed per gram of oxygen	Heat of combustion/ k cal mol^{-1}
Lactose	202	0.94	1351
Naphthalene	80.5	0.33	1232
Shellac	120	0.44	–
Sucrose	188 (decomposition.)	0.89	1351
Laminac	200 (decomposition.)	–	–
Nitrocellulose	200 (decomposition.)	–	–
Polyvinyl chloride	80 (softens)	0.78	4375
Starch	Decomposition	0.84	4179
PTFE (Teflon)	327 (softens)	–	–
Hexachloroethane	185	–	–
Anthracene	217	–	1700.4

a) Reference [5].

5.4.3
Melting and Boiling Points and Decomposition Temperatures

The ease of ignition and burning rate of a pyrotechnic formulation are considered important combustion parameters which depend on melting and boiling points and decomposition temperatures. It is reported in the literature that the fuels with low m.p.s generally lower the ignition temperature of pyrotechnic formulations. Sulfur and organic compounds with lower m.p.s impart lower ignition temperatures and thus facilitate combustion while the fuels with higher m.p.s confer higher ignition temperatures. The m.p. of a fuel is not the only parameter which decides ignition temperature of the formulation but the endothermic or exothermic nature of decomposition of the oxidizer is also a crucial factor. This is evident on comparison of the ignition temperatures of the formulations $KClO_3$ + S and KNO_3 + S The ignition temperature of the first formulation is 150 °C because decomposition of $KClO_3$ is exothermic. On the other hand, ignition temperature of formulation KNO_3 + S is 340 °C because the decomposition of KNO_3 is endothermic. Accordingly, low ignition temperatures are obtained in pyrotechnic formulations containing fuels: sulfur, lactose, Mg and oxidizer $KClO_3$ whereas higher ignition temperatures are obtained on replacement of $KClO_3$ by KNO_3 in these formulations (Table 5.5).

In fact, the burning rate of a formulation depends on the fuel as well as the oxidizer. However, the rate-determining step mostly depends on the oxidizer in question. In general, higher decomposition temperature and endothermic nature of decomposition of oxidizer bring down the burning rate. Similarly, exothermic metal fuels increase the burning rate while higher ignition temperature of fuel decreases burning rate.

Table 5.5 Ignition temperatures of some pyrotechnic formulations.

Formulation	Melting point/°C	Ignition Temperature/°C
$KClO_3$	356	150
Sulfur	119	
$KClO_3$	356	195
Lactose	202	
$KClO_3$	356	540
Magnesium	649	
KNO_3	334	340
Sulfur	119	
KNO_3	334	390
Lactose	202	
KNO_3	334	565
Magnesium	649	

5.4.4
Oxygen Content of Oxidizers

The oxidizers which have higher oxygen content and also, which give off oxygen easily are preferred. Nitrate oxidizers release about 0.4 to 0.5 g oxygen per gram of oxidizer while oxides release comparatively less oxygen. Therefore, nitrates result in formulations with higher burning rates and flame temperatures compared with oxides.

5.4.5
Thermal Conductivity of Fuels and Containers

The thermal conductivity of the fuels as well as the containers affects the burning rate of the formulations. Fuels with high thermal conductivity are considered useful in the case of gasless formulations where the heat transfer from layer to layer is by conduction.

5.4.6
Nature of Combustion Products

The nature of combustion products required from a formulation depends on the end use or effects desired. The gaseous combustion products should be greater where the pressure generated by combustion is supposed to do the specified work. On the contrary, gasless formulations are required where there is no vent in the ammunition or where ammunition has to work at high attitudes. Some priming formulations also require slag to be formed so that hot spots are formed and transfer of heat is facilitated. BaO_2 is generally used with Mg as a fuel where a hot slag of BaO + MgO is produced. The combustion products also influence the color of light and infrared (IR) intensity of the flares designed for these end effects, for example, $NaNO_3$ in illuminating formulations gives yellow color (Na^+ gives yellow color) whereas $Sr(NO_3)_2$ and SrC_2O_4 give red color (due to Sr^{2+} and SrO) and $Ba(NO_3)_2$ and $(BaClO_3)_2$ give green color (due to Ba^{2+} and BaO). These salts have dual role that is, they function as oxidizers as well as color-imparting agents in these formulations. Similarly, melting and boiling points of the decomposition products and also their heat of fusion and vaporization become limiting factors for the flame temperature of the formulations.

5.4.7
Toxicity of Ingredients

The toxicity of the ingredients used is a very important parameter which is concerned with the health of the workers. It is essential that the personnel handling these chemicals are aware of their toxic effects and the management provides the necessary facilities in terms of personnel protective equipment and infrastructure. The chemicals handled manually during various operations involved in the preparation of a formulation are likely to enter the human system through inhalation and oral and dermal routes. Research is in progress to replace some toxic chemicals like $BaCrO_4$, colored dyes and hexachloroethane (HCE) etc. But sometimes it is not possible to replace some chemicals in the absence of non-toxic chemicals giving the same effects. Therefore, it is imperative to take all necessary precautions against occupational hazards while handling such toxic chemicals. Chapter 6 on 'Explosive and Chemical Safety' may be referred for more details in this regard.

Polymers are generally used in order to protect the formulations against moisture ingress. In addition, polymers help in binding the ingredients together and imparting mechanical strength to the formulations. Polymers or resins are chosen very carefully as they also take part in combustion and influence the burning rate. Besides fuel, oxidizer and binder, some ingredients are introduced in the formulations to impart special characteristics. For example, burning rate modifiers: $CaCO_3$, $MgCO_3$, CaC_2O_4, clay etc.; and color intensifiers (for flame): PVC, chlorinated rubber and HCE etc.

Further, the ingredients employed should be stable and compatible with each other. They should also be readily available and inexpensive. At the same time, the pyrotechnic formulations should possess good storage properties under widely varying climatic conditions.

To summarize, the quality and performance of pyrotechnic formulations depend on a number of important factors [6]:

- Chemical nature of the ingredients, their purity, proportion, particle size and physical form.
- Density of the consolidated formulation.
- Moisture absorbed during manufacture of the formulation.
- Uniformity of blending of the mixture.

- Loading pressure that is, degree of consolidation.
- Material and properties of the body(container).
- Physical properties of the combustion products.
- Ambient temperature and pressure during combustion.
- Effect of spin on combustion.

5.5
Types of Pyrotechnic Formulations

Pyrotechnic formulations are classified depending on their end use [6]:

- illuminating formulations;
- delay formulations;
- smoke formulations;
- incendiary formulations.

5.5.1
Illuminating Formulations

Darkness has always been considered a supreme hindrance to military operations during the night. Therefore, the first requirement for effective military operations is an efficient illumination that dispels the darkness. The illuminating formulations have proved their effectiveness in this regard. In other words, illuminating formulations filled in illuminating candles are used to illuminate the area of enemy territory during night warfare giving a strong light output, and permitting a clear view of the targets. In order to provide powerful illumination, end-burning candles suspended by parachutes in air are ejected from tubular containers or special dispensers. The light effect of illuminating formulations is also used in photoflash cartridges, tracer and signal flares. Long duration white light is used for illumination whereas short duration intense white light is suitable for night time aerial photography. Further, colored light is used for tracer and signal flares.

Basically, an illuminating formulation is a mixture of a metallic fuel and an oxidizer besides some additives in order to modify the burning rate and radiation output and to enhance safety in handling. The Mg–sodium nitrate binder system appears to be a universal choice for illuminating formulations. The main reaction of the Mg–sodium nitrate binary system is (Equation 5.1):

$$6\,\mathrm{Mg} + 2\,\mathrm{NaNO_3}\ (47/53\ \mathrm{Mg/NaNO_3}) \rightarrow 6\,\mathrm{MgO} + 2\,\mathrm{Na} + \mathrm{N_2} + 2\,\mathrm{k\,cal\,g^{-1}} \quad (5.1)$$

In the presence of excess oxygen, the following reaction (Equation 5.2) also takes place:

$$12\,\mathrm{Mg} + 6\,\mathrm{O_2} \rightarrow 12\,\mathrm{MgO} + 5.9\,\mathrm{k\,cal\,g^{-1}} \quad (5.2)$$

It has been practically observed that the best luminous efficiency is obtained with the formulations which contain excess fuel. This is attributed to the fact that atmospheric oxygen also takes part during combustion and consumes the excess fuel, giving better performance. The light emission from the Mg–sodium nitrate system is due to both background radiation from magnesium oxide and the atomic emission of sodium vapor in the flame. Magnesium oxide acts as a gray body and emits radiation throughout the visible range producing a white light.

To produce atomic emission in a pyrotechnic formulation, sufficient heat must be produced in order to generate atomic vapors in the flame and then excite the atoms from ground level to various excited electronic states. As more and more atoms are vaporized and excited with increase in the flame temperature, the net result is an increase in the emission intensity. The luminosity of illuminating flares is expressed in 'candela' which is related to the burning rate. To some extent, the luminosity of the formulations can be increased by increasing their burning rates. Luminous efficiency is a product of luminosity and burning time per gram of the formulation and is used to compare the performance of different illuminating formulations. To get high efficiency, luminosity should be high but the burning rate should be slow, which is contradictory and it is not possible to achieve both simultaneously.

The performance of an illuminating formulation mainly depends on the factors: (i) chemical nature of the main ingredients – fuel and oxidizer; (ii) their proportions and particle sizes; (iii) type and proportion of binder; (iv) nature and proportion of additives; (v) consolidation pressure; (vi) diameter of candle; (vii) nature of liner material and (viii) ambient conditions at the time of test.

5.5.1.1 Chemical Nature of Fuel and Oxidizer, Their Proportions and Particle Size

(i) Fuels The metal powders which readily undergo an exothermic oxidation with the formation of corresponding oxides coupled with the evolution of heat and light are used as fuels in illuminating formulations. Fuels which emit white light are preferred for these formulations. The common white light-producing metals are Mg, Al, Ti, Zr and W. However, Mg is preferred because (i) its high calorific value increases the flame temperature; (ii) its low boiling point allows excess Mg in the mixture to vaporize and burn with oxygen in air providing additional heat to the flare formulation; (iii) Mg vaporizes in the reaction zone producing MgO, a colloidal oxide present in the gaseous state and considered an excellent white light emitter; (iv) it has good volatility at 2000 °C and (v) it is easily available and cheap compared with other metals.

Some studies demonstrate the advantage of using bimodal Mg and its use is already in practice in some formulations. Aluminum has high calorific value and high boiling point but most of the heat is used to vaporize Al powder instead of to produce the special effect. Kott observed that the luminous efficiency of Al/$NaNO_3$/epoxy resin-based formulations is about 1/3 to 1/2 of Mg fuel-based formulations. It was also found that small particle size, atomized Al yields the highest efficiency, and high oxygen content in the binder generally improves the flare performance [7]. The studies conducted with alternate fuels like aluminum, boron, titanium etc. have not been fruitful so far, besides their higher costs.

(ii) Oxidizers The oxidizers which release high oxygen easily are preferred. Nitrates release about 0.4 to 0.5 grams of oxygen per gram of oxidizer and are the most commonly employed oxidizers. Sodium nitrate is used as an oxidizer in the illuminating formulations despite its hygroscopic nature. The reaction with Mg leads to the formation of magnesium oxide. The heat of the reaction per gram of ingredient is high because of the high oxygen content of the nitrates and low equivalent weight of the sodium. Because the complete reduction of $NaNO_3$ produces sodium ions (Na^+ ions) in the flame, sodium continuum makes the flame yellowish-white. Also, sodium exhibits luminescent properties that add significantly to the production of useful light.

(iii) Proportions It has been reported in the literature that as the Mg content increases from 20–80% in the formulations based on $Mg/NaNO_3$/lithographic varnish, linear burning rate and mass burning rate increase continuously. Further, the intensity and efficiency attain maximum values at 65% Mg and subsequently decrease sharply as the % of Mg powder increases. Similarly, it is reported that the luminosity increases with increase in the % of Mg powder up to 70–75% in a binary system and a further increase in Mg% results in a reduction in luminosity. The burning rate is maximum at 75–80% Mg.

(iv) Particle size of the ingredients The rate of reaction of a pyrotechnic formulation is related to the specific surface of the ingredients and therefore, their particle size, shape, distribution and surface area are likely to affect the burning properties. It is observed that a decrease in particle size of Mg powder increases the linear burning rate and luminous intensity but it has little effect on its luminous efficiency. On comparison of ground and atomized Mg powders having same sieve size, it is observed that the ground Mg powder gives higher luminosity and faster burning rate because of its greater specific surface.

(v) Type and proportion of binders A large number of resins, waxes, plastics, oils and rubbers have been employed as binders which fill interstices between particles and bind them together, and as a result impart mechanical integrity to the pyrotechnic formulations. This facilitates the achievement of maximum density and efficiency in burning. Some binders also desensitize the formulation and hence increase safety in processing as well as subsequent operations. They also protect Mg powder from corrosion by moisture, modify the burning rate and enhance the luminous intensity of flare.

Many investigators have studied the effect of binders and their percentages on the efficiency of illuminating formulations. In general, the luminosity and luminous efficiency increase to a maximum at ≈4–6% of the binder and thereafter decrease. It has also been reported that binders with high oxygen content, such as unsaturated polyesters and epoxy resins, improve the efficiency of the flare formulations. Polyesters and epoxy resins are therefore considered to be the most suitable binders for such formulations. A typical illuminating formulation consists of Mg powder (50%, 200 μ), sodium nitrate (43%, 30–50 μ) and binder (7%). US Army formulations currently use VAAR or epoxy resin–polysulfide (PS) binder systems [8]. Some important aspects of liquid PS, epoxy–PS blends and VAAR are given toward the end of this section.

(vi) Nature and proportion of additives Some compounds are added to the illuminating formulations to produce specific effects such as cooling of the flame and retarding the burning rate by slowing down the reaction between oxidizer and fuel. Oxalates are most commonly used as moderators because of the dilution effect of CO_2 produced during their thermal decomposition and oxide slag formation which modifies the nature of burning surface without affecting the luminosity. For example, calcium oxalate brings down the burning rate due to the formation of CO_2 gas. The gases evolved also tend to expand the flame and at the same time, calcium oxide acts as incandescent oxide which increases luminous intensity.

(vii) Liner materials Both the physical and chemical characteristics of the materials used for a pyrotechnic device container and its associated coating affect the luminous output of the flare. In a steel case, loading is simplified due to its rigid nature but direct contact of the formulation with its wall leads to erratic burning due to its thermal conductivity (loss of heat from the formulation through the walls of the container to the surroundings). The possibility of friction between the formulation and container while consolidating the formulation also exists. Thus a lining of insulating material to the metal case of the device is essential. Various materials such as card board, paper, thermosetting resin etc. are used as device case materials for illuminating flares. The conductivity of the liner material also plays a major role in modifying burning characteristics of the flare. The application of thermal insulation to a metal container decreases the heat loss and thereby increases burning rate of flare formulation.

(viii) Diameter of flares The luminous intensity of the formulation is directly related to the diameter of the flare (i.e., burning area of the flare). For a particular formulation pressed in containers of various diameters at a given consolidation pressure, the flare of higher diameter gives more luminous intensity. It is also possible that more area of burning surface will give a longer flame. If the density of the formulation is kept constant, the linear burning rate and efficiency will remain unaffected for a particular formulation. Dillehay has reported that increasing the diameter of a candle does not result in corresponding increase in the output. Figure 5.1 shows a typical trend of candela for a fixed formulation as the diameter of the flare increases. He further established experimentally that the plume length increases as a function of diameter and fuel richness [9].

(ix) Consolidation pressure Illuminating formulations are consolidated into containers so that they burn in a cigarette-like manner from one end to the

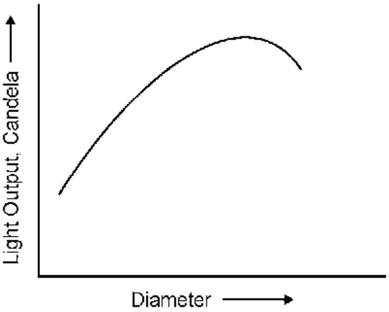


Figure 5.1 Variation of light output vs diameter. Reprinted with permission from D.R. Dillehay, *J. Pyrotech.*, (19) (Summer 2004) 1–9; © 2004, J. Pyrotechnics Inc, USA.

other at a steady rate. The degree of consolidation has a varying effect on the burning rate and luminous intensity of a pyrotechnic mixture. The effect of loading pressure on the performance of an $Mg/NaNO_3$ flare was studied and it was observed that the linear burning rate slightly decreased while the mass burning rate and luminous intensity increased with the increase in loading pressure.

(x) Ambient conditions of the test The performance of the candle also depends on the ambient conditions of the test. In most of the cases, higher light output is observed in an oxygen-rich atmosphere than in an oxygen-deficient atmosphere. Dillehay studied the luminous output of illuminating candles in air, argon and nitrogen atmospheres and reported a decrease in candle power in both nitrogen and argon atmospheres. However, the burning rate was not significantly affected but the flames were longer in air than the flames in nitrogen and argon [8]. Further, the flare plumes in a nitrogen atmosphere are much shorter than the plumes in an argon atmosphere because nitrogen is more effective in collisional de-excitation of excited sodium atoms. Douda [10] and Dillehay have done pioneering research on various aspects of illuminating formulations. As a result of their extensive study, Dillehay proposed the involved thermochemistry by Equations 5.3:

$$\begin{array}{lll}
2\,NaNO_3(s) & \xrightarrow{\Delta} 2\,NaNO_3(l) \xrightarrow{\Delta} 2\,NaNO_2 + O_2 & \\
3.5\,O_2 + C_5H_5O \rightarrow & 4\,CO + CO_2 + 2\,H_2O + 0.5\,H_2 + Heat & \\
2\,NaNO_2 \quad \rightarrow & Na_2(g) + 2\,O_2 + N_2(g) & (5.3) \\
O_2 + 2\,Mg \quad \rightarrow & 2\,MgO(s) + Heat & \\
Na_2 \quad \rightarrow & 2\,Na &
\end{array}$$

To process formulations, thermoplastic and thermosetting resins are used. For thermoplastic resins such as VAAR, the binder is dissolved in a solvent and then mixed with Mg and sodium nitrate until the solvent is evaporated. This formulation can then be stored and used whenever needed. No curing is required after consolidation. On the other hand, the epoxy–PS blend is mixed with an amine curing agent followed by mixing with Mg and sodium nitrate. This mixture has a pot life and is consolidated before the onset of curing process. After consolidation, the candles are cured at an elevated temperature to complete the curing process. This binder gives some flexibility to the formulation to prevent shrinkage and separation from the case.

The performance of the illuminating formulations is assessed by various parameters such as burning rate, luminosity and luminous efficiency. In addition to performance, some other important characteristics such as sensitivity to impact and friction, ignition temperature, mechanical properties and luminosity are also assessed as discussed in Section 5.6.

5.5.1.2 Formulations of Tracers

Tracers are used to indicate the trajectory of projectiles, rockets and missiles. They are attached at the rear end of the ammunition for this purpose. Sometimes they are also used to determine the range during proof by observing the point of impact of the projectile. A tracer is regarded as a very small flare pressed into a cavity at the base of small arms or artillery projectiles or into a separate assembly fitted into the base of the projectiles. The tracer makes it possible to observe the flight trajectory of the bullet, shell and projectile during day or night and to adjust the firings. In other words, tracers facilitate more accurate aim at fast-moving targets.

The chief requirement of a tracer is that it should be clearly visible under field conditions. For this purpose, a red color has most often been chosen since it is most visible during the day and night under all conditions. The duration of the tracer depends on the tactical use of the ammunition with which it is used.

Tracer formulation is basically a mixture of an oxidizer and a metal fuel together with other additives, included to modify the burning rate, color, radiant output, mechanical integrity and sensitivity. Since tracer formulations are relatively difficult to ignite, a more readily ignitable formulation is pressed on the top of the tracer formulation.

All tracer formulations are based on magnesium–strontium nitrate–binder because this system gives a distinct red color which is most suitable for tracing purposes, because of the maximum sensitivity of the human eye to red light. The proportions of ingredients, their particle size, binder etc are optimized to get the required performance with respect to color and luminosity. A study on a number of synthetic binders such as polyester, epoxies, silicones, Thiokols etc. in the place of natural binders concludes that polyesters give higher luminosity [11]. Also, the fluorine-rich rubbers such as Viton-A and Kynar make the best binders in terms of specific luminous efficiency. An investigation conducted by Agrawal *et al.* for the use of unsaturated non-halo polyester (NHP) and halo-polyesters (HP) as binders for tracer formulation [containing magnesium, strontium nitrate and sodium nitrate] suggests that chloropolyester (CP) is better than NHP as chloro groups enhance the intensity of red color of the flame. Further, CP-based tracer formulation has better mechanical strength than the NHP-based formulation. In view of higher mechanical strength coupled with more intense color of CP-based tracer formulation, CP is a better choice for use as a binder in tracer formulations [12].

5.5.1.3 Photoflash Formulations

Some pyrotechnic formulations are used for photographic purposes and the main requirement of such formulations is that they should produce a very powerful illumination for a short duration. Such pyrotechnic formulations are known as photoflash formulations and are used in photoflash cartridges, photoflash bombs and dust bombs.

Many fuel–oxidizer mixtures are of smooth burning nature and can be made to react instantaneously with a suitable explosive device leading to self-acceleration of the reaction. Such devices liberate energy in the form of very high illumination within a very short duration and this very high light output during such a short duration is adequate for aerial photography during night time. A typical flash formulation is: atomized Al ($20 \pm 5\,\mu$), 40%, potassium perchlorate ($24\,\mu$), 30% and barium nitrate ($150\,\mu$), 30%. This photoflash formulation contains potassium perchlorate ($KClO_4$) which is fairly sensitive to impact. Bombs containing such photoflash formulations, positioned in the airplane are likely to explode by bullet or shell fragments. Therefore, a sensitive oxidizer, such as $KClO_4$, is not used for bombs. Bombs that contain metal powders and mild oxidizers are used for such applications and are called ‘dust bombs’. Photoflash bomb, M-122 contains Mg–Al alloy (65:35) which is finely divided. Al and Mg powders provide the brightest white flash. Magnesium is used either as a finely divided powder or as an atomized powder while Al is used as a flake. The oxygen for combustion is supplied by the atmosphere where metal particles are scattered or by oxidizers which are present in the formulation. The products of combustion are mainly solid oxide products of high reflectivity. A typical formulation available in the literature is: aluminum, 30%, TNT, 50% and RDX, 20%. Such formulations are normally made by thoroughly mixing the ingredients followed by filling the mixture in loose form in the containers or cartridges. Binders are not generally used.

Aluminum powder is used in photoflash formulations with barium nitrate or potassium perchlorate as oxidizers. Further, it is never used with sodium nitrate because of their chemical incompatibility in the presence of moisture. However, potassium and calcium nitrates have been used for this purpose.

The main reactions involved in the photoflash formulations are as follows (Equations 5.4–5.6):

$$5\,Mg + 2\,NaNO_3 \quad 5\,MgO + Na_2O + N_2 + 584\,kcals \tag{5.4}$$

$$10\,Al + 3\,Ba(NO_3)_2 \quad 5\,Al_2O_3 + 3\,BaO + 3\,N_2 + 1588\,kcals \tag{5.5}$$

$$6\,Al + 3\,KClO_3 \quad 3\,Al_2O_3 + 3\,KCl + 1495\,kcals \tag{5.6}$$

5.5.1.4 Signal Formulations

Communication between units is considered of vital importance in modern warfare. Wireless and line communications are generally used for this purpose but in circumstances where they cannot be used, use of code signals by pyrotechnics is resorted to. Signals can be classified into three types:

- aircraft signals;
- ground signals;
- marine signals.

Signals contain candles filled with the pyrotechnic formulations which produce: red light, green light and yellow light. Strontium nitrate, barium nitrate and sodium oxalate are the ingredients mainly responsible for producing high intensity red, green and yellow color respectively. Magnesium is a common fuel to all such formulations. As the use of too much Mg displays white light, its proportion ranges only from 15–30% in the signal formulations.

5.5.1.5 Infrared Flare Formulations

Infrared radiation is used for both civil and military applications. The military applications are target acquisition, surveillance, homing and tracking. IR flares are used in military applications mainly for two purposes: tracking a missile and decoying enemy missiles [13, 14]. Depending on their applications, IR flares are classified into three different classes.

(i) IR Tracking flares These flares are mounted at the tail end of the missile and used for tracking or tracing the path of a wire-guided missile. This method of tracking missiles is very useful especially in bad weather and under adverse flight conditions.

(ii) IR Decoy flares for training These IR flares are used for training the aircrew members for accurate firing of combat missiles.

(iii) IR Decoy flares for defense Infrared decoy flares are used by aircraft for defense against IR-guided missile threats.

Infrared flares are pyrotechnic devices which emit radiation of sufficient intensity in the IR region of the electromagnetic spectrum in addition to visible radiation. When ejected from an aircraft, Airborne Infrared Countermeasure (AIRCM) flares present a more attractive IR signature than that of the target and thus decoy the missile seeker away from the aircraft. The decoy flare emission should be larger than that of the aircraft in the spectral waveband of operation of the IR missile seeker so that the decoy is a prominent target for a missile. The target aircraft can protect itself from an IR missile attack by ejecting an IR decoy flare.

There are currently two types of pyrotechnic flares: (i) magnesium, Teflon, Viton (MTV) decoy flares first used in the Vietnam war and (ii) dual-spectral flares which are of recent origin and are now entering operational service. MTV flares are still effective against the older generation of missiles. They come in a variety of shapes, formats and sizes. The level of performance depends on the country of origin and the aircraft type. UK and US flares are similar in size, form and specification whereas the French and Russians have designed their own flares which can only be fired from aircraft of French and Russian origin respectively. Over the years, improvements have been made in terms of performance and safety of the MTV decoy flares, which are still the most widely used flares.

An IR flare is a compressed pellet of fuel and oxidizer with suitable additives. The shape is generally similar to the shape of a storage canister or dispenser from which the decoy flare is ejected by the aircraft upon command of the pilot. The decoy body generally has a circular or rectangular cross-section because of the cost considerations and ease of manufacture. The shaped flare is covered with a priming coat that facilitates ignition when the decoy is released from the aircraft. The effective wavebands of heat-seeking missiles are 1.5–2.5 μm, 3.0–5.0 μm and 8.0–14.0 μm.

The decoy flares which emit IR radiation similar to or more than the targets, are generally filled with magnesium–Teflon-based formulations. The detection or tracking type flares generally contain metal fuels (Mg, Si, Zr) or alloys (Fe–Si, Mg–Al), oxidizers (BaO_2, Fe_2O_3), additives (charcoal, graphite) in addition to polymeric binders. These formulations emit radiant energy partly in the IR range and partly in the visible range with a minimum amount of smoke. The performance of the flares invariably depends upon both the design and chemical nature of the IR-producing formulations. In short, the parameters such as shape, size, weight, burning characteristics and IR output play an important role at the time of selection of a suitable formulation for a specific purpose.

The IR output of a pyrotechnic formulation depends on the nature of combustion products, their concentration in the flame, their emissivity and flame temperature and mass burning rate. As carbon black behaves like a black body (emissivity assumed to be close to unity), pyrotechnic formulations generating a large amount of heat and carbon black particles are required in order to get better IR output. The flame temperature of the IR formulation should be less than an illuminating formulation because the emission maximum shifts to short wavelength, that is, toward the visible range with increase in temperature. The IR output increases with the increase in burning rate for a system because of the high concentration of combustion products in the flame.

The MTV formulation is the most common pyrotechnic formulation used for IR flares. The main reaction on combustion of Mg with Teflon is as shown in Equation 5.7:

$$2n\,\mathrm{Mg} + -(\mathrm{C_2F_4})_n - \longrightarrow 2n\mathrm{MgF_2} + 2n\mathrm{C} + 23\,\mathrm{kcal\,g^{-1}} \tag{5.7}$$

The heat generated heats up carbon black to a temperature ≈2200 K, yielding radiant emittance values comparable to a black body. Magnesium-rich formulations yield some extra energy by atmospheric oxidation or vaporized Mg in the gas phase. In addition, carbon oxidized to carbon dioxide provides additional radiant energy. Thus MTV spectral distribution displays the peak maximum at 2.0 μ and strong emission bands at 4.3 μ due to carbon dioxide.

Some information on IR flares is available in the literature. Two pyrotechnic formulations consisting of Mg–Teflon–rosin and Mg–$Ba(NO_3)_2$–rosin were formulated and studied for radiant intensity, mass flow rate, effect of combustion temperature by Gongpei and coworkers [15] and the gist of their findings is as follows:

1) Teflon-based formulations emit a high order of IR intensity compared with $Ba(NO_3)_2$-based formulations in the wavebands 3.0–5.0 μ and 8.0–14.0 μ regions because of the presence of fluorine therein.
2) The increase in combustion temperature increases the radiant intensity in 3.0–5.0 μm region only.
3) The radiant intensity increases with increase in the mass flow rate up to a certain limit and decreases subsequently.
4) The radiant intensity also increases with the addition of metals like Fe, Al, Cu, Ti and Si in both the formulations in the wavebands of 3.0–5.0 μ and 8.0–14.0 μ. However, Cu and Al show the highest radiant intensity.

The salient features of some IR flares and decoy flares: burning time, IR output along with end use, are given in Table 5.6.

The IR intensity of formulations based on Mg/KNO_3/hydrocarbons are equally high and are used in new decoy flares. These formulations are good for decoy

Table 5.6 Salient features of some infrared flares/decoy flares.

Flare	Formulation %	IR Output		Burning time/s	End use
		Wave band/μm	Powerw/str		
IR Flare for SS11B1 (French Missile)	Mg(Grade IV) – 45 BaO_2 – 20 Fe_2O_3 – 31 PVC – 1 Charcoal – 1 NC/EC – 2	1.5–2.5	490–540	21–22	Missile tracking
IR Flare for MILAN (French Missile)	Mg (Grade V) – 45 Fe_2O_3 – 35 ZrO_2 – 3 Si – 6 Teflon – 8.5 Phenolic Resin – 2.5	2.0–2.4	120	10	Missile tracking
IR Flare for RM3B (Russian Missile)	Mg(Grade V) – 22 $Ba(NO_3)_2$ – 52 Zirconium – 18 Charcoal – 2 Phenolic Resin – 6	1.5–2.5	95–180	34	Missile tracking
IR Decoy Flare for Pied Piper (UK Missile)	Mg(Grade V) – 60 Teflon – 35 Naphthalene/ Anthracene – 5	1.5–2.5	10 000	10	Decoying

purposes but the formulations containing iron oxide have been found to be better for tracking purposes.

Modern missiles employ counter-counter measures. Their advanced seeker heads use two or more spectral bands in an attempt to distinguish between the flare and the target. Trajectory discrimination may also be used by some seeker heads. The physical size of the heat source is more important as imaging seekers that can discriminate a spot target of IR flares, have been developed. Depending on their application, IR decoy flares can be further classified into:

- spectrally adapted flares;
- kinematic flares;
- spatially and spectraly adapted flares.

These are specialized flares which are of recent origin. The readers may consult books exclusively devoted to flares in order to get more details on the formulations, performance parameters and mechanism of operation.

5.5.1.6 **Some Resins for Illuminating Formulations**

With the advancement of polymer chemistry, a wide range of polymers are now available for use as binders for HEMs. The extensive use of polymers such as unsaturated polyesters, epoxy resins, epoxy–PS blends and VAARs as binders for illuminating formulations has been reported in the literature. The chemistry of unsaturated polyesters and epoxy resins has already been discussed in Chapter 4 on propellants. Some salient features of liquid PS and its blends with epoxy resin and VAARs are given in this section.

Liquid Polysulfides Liquid polysulfides are thiol (–SH)-terminated liquid polymers and are prepared as suspensions by the polycondensation of dihalide monomer with inorganic polysulfides in an aqueous solution. Bis-2-chloroethyl formal is the monomer usually used and 0.1–4.0% of trichloropropane is added as a crosslinking agent. The high molecular weight dispersions are reacted with sodium hydrosulfide and sodium sulfide to give the desired low molecular weight branched mercaptan-terminated products. The range of molecular weights of mercaptan-terminated products varies from 500 to 100 000 containing various amounts of branching depending on the proportion of trichloropropane added to monomer and carrying mercaptan-terminated groups [16, 17]. The structure of the resulting liquid PS [Structure (5.1)] may be represented as:

$$HS\left[CH_2-CH_2-O-CH_2-O-CH_2-CH_2-S-S\right]_n CH_2-CH_2-O-CH_2-O-CH_2-CH_2-SH$$

Structure (5.1): Liquid polysulfide (PS).

where *n* varies from 2–26 for commercially available liquid polymers. The commercially available liquid polysulfide polymers are marketed in three viscosity ranges and their physical properties are shown in Table 5.7.

Table 5.7 Properties of some commercial polysulfide liquid polymers.

Property	LP-2	LP-3	LP-8	LP-32	LP-33
Crosslinking agent, wt %	2.0	2.0	2.0	0.5	0.5
No. Average Mol. Wt	4 000	1000	500–700	4 000	1000
Viscosity, cPs	35 000–45 000	700–1200	250–350	35 000–45 000	700–1200
Specific gravity	1.27	1.27	1.27	1.27	1.27
No. of Separating Segment	23	6	3–4	23	6

The liquid polymer is converted to the rubbery state by reagents that react with mercaptan (–SH) and side groups of the polymer segments by oxidation, addition or condensation to effect sulfide (–S–S–) bond formation. The oxidation reactions are exothermic and accelerated by an alkaline environment. The most commonly employed oxidizing agents which are suitable for curing liquid polymers are cobalt or manganese or lead octoate, *p*-quinonedioxime and di- or tri-nitrobenzene. Epoxy resin also reacts with liquid polysulfide polymers by addition in the presence of an aliphatic or aromatic amine and polyamide activator as shown in Equation 5.8:

(5.8)

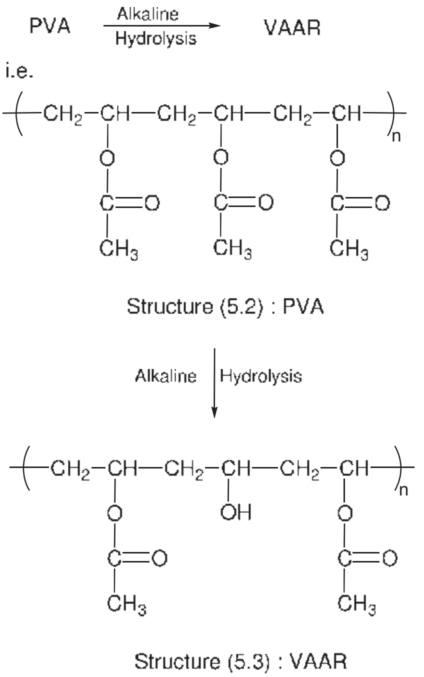
The reaction of the epoxy group with the mercaptan (–SH) group is not so vigorous as with an amine or amide group.

Epoxy–Liquid Polysulfide Blends Epoxy resins in combination with liquid PSs appear to possess many added advantages as the elastomeric PS segments in epoxy chains impart permanent flexibility [18]. Epoxy–liquid PS blends have been reported as binders for Army illuminating formulations [8]. Similarly, novolac epoxy-liquid PS blends have been reported for inhibition of composite propellants [19].

Vinyl Acetate Alcohol Resins These may be considered as a vinyl acetate/vinyl alcohol copolymers consisting of 82% vinyl acetate and 18% vinyl alcohol and is supplied as a solid dissolved in methyl alcohol (18%) and methyl acetate (82%) or technical grade methyl acetate. It is popularly known as VAAR. Military specification MIL–V–50433 (MU), July 1969 governs the quality of its solution for use in ammunition.

It is prepared by the alkaline hydrolysis (saponification) or alcoholysis (ester interchange) of polyvinyl acetate [Structure (5.2)] as shown in Scheme 5.1.

VAAR [Structure (5.3)] contains oxygen, through its alcohol and ester functional groups, which can react with ingredients in the pyrotechnic formulations to produce additional energy. In addition, it has many other highly desirable characteristics as a pyrotechnic binder: (i) it comes in the liquid form and thus it is simply



Scheme 5.1 Synthesis of vinyl acetate alcohol resin (VAAR).

added to the formulation during blending; (ii) it yields a product having high tensile strength; (iii) only 1–2 parts of VAAR are required to strongly bond the pyrotechnic ingredients. In fact, only 1% of VAAR (by wt) gives a strength equivalent to that using 4–5% of Laminac 4116 (an unsaturated polyester) or epoxy resin. Since only small quantities are required, it produces minimal gaseous products on burning making it ideal for obstructed delay systems.

VAAR has been extensively used since the 1960s, especially for delay and illuminating formulations in US Army munitions. According to Taylor and Jackson, it is no longer commercially available in the USA [20]. The scientists of the Royal Military College of Science, UK, also investigated VAAR (or partially hydrolyzed polyvinyl acetate) as a binder for HMX-based PBXs and pyrotechnic formulations. These polymers are often referred to as polyvinyl alcohols but they are copolymers of vinyl acetate and vinyl alcohol. The distribution of the hydroxyl groups may be either random or in blocks. It is available in two grades: Alcotex 47P (a 47% hydrolyzed poly[vinyl acetate, vinyl alcohol] supplied as a solution consisting of 40% solids, 49% methanol, 9% methyl acetate and 2% water) and Alcotex 20–009 (a 20% hydrolyzed poly[vinyl acetate, vinyl alcohol] with a molecular weight ≈50 000 supplied as a solution consisting of 40% solids, 49% methanol, 9% methyl acetate and 2% water) and is manufactured by Harlow Chemical Company Ltd., UK. Based on the data generated by these two grades in several pyrotechnic formulations, Langston suggested Alcotex 20–009 as a good replacement for VAAR used by Americans [21]. VAAR has also been used as a binder for pyrotechnic smoke formulations based on potassium chlorate, sugar and organic dyes as well as first fire formulations. Carrazza and Kaye studied the long-term and high temperature storage stability of VAAR-based colored flare formulations and concluded that it was a suitable binder for pyrotechnics with a long storage life [22]. Further, it is non-toxic, physiologically inert and its wash waters are biodegradable. As VAAR is thermoplastic, pyrotechnic formulations containing VAAR as a binder from life-expired munitions or devices have potential for recycling. In summary, VAAR is non-toxic, biodegradable and an excellent binder for pyrotechnic formulations.

5.5.2
Delay Formulations

It is often essential to have an interval of time between two successive explosive events while using military ammunition. This interval of time is called a ‘delay’ and may vary from a few milliseconds to a few seconds and is achieved by using a pyrotechnic delay device. The delay is normally produced by incorporating the pyrotechnic delay device suitably into the design of an ammunition. The specified time is achieved by the steady and regular burning of a train of pyrotechnic delay formulation ignited by the first event and which, after burning for a specified time, initiates the second event. For example, consider the use of a hand grenade. When a soldier throws a hand grenade, the ignition system functions, which is the first event. Then the delay formulation burns for a few seconds (a period during which the grenade covers a certain distance in its path) and finally the grenade explodes which is the second event.

The purpose of incorporating a delay device in ammunition is: (i) to cover the time of flight; (ii) to provide safety of persons using the ammunition; (iii) to ensure safety of carrier aircraft; (iv) to ensure self-destruction and; (v) to enhance post impact effects.

Delays ranging from a few milliseconds to one minute duration are common in military use and are widely used in different types of ammunition [23]. Accordingly, a variety of delay formulations have been reported in the literature in order to achieve delays ranging from a few milliseconds to a few seconds.

Depending on the nature of the products of combustion, delay formulations can be broadly classified as gasless and slagless and the delay formulation is chosen according to the geometry of main ammunition (see Section 5.5.2.3). Gasless delays are preferred where venting of the hot gases is not possible in the ammunition. Since the combustion of the slagless (gas producing) delay formulations invariably results in the production of a large amount of gas, it is imperative to provide a suitable vent for their escape. If such a provision is not made, burning becomes faster due to the pressure of the gases and the delays obtained are erratic. The production of large amount of gas is not desirable, particularly when filled in fuses.

5.5.2.1 **Requirements of an Ideal Delay Formulation**

Some of the most important requirements of an ideal delay formulation with reproducible results are:

1) The formulation should be free flowing and should also be capable of being blended, filled and loaded in the delay device.
2) The burning rate of the formulation must be uniform and reproducible. At the same time, its burning rate should not change with small variations in the proportions of ingredients.
3) It should be readily ignitable.
4) Its performance characteristics should not be affected significantly by changes in pressure and temperature.

The linear burning rate of a delay formulation which is generally expressed in $\mathrm{cm\,s^{-1}}$ is its most important characteristic. This decides the choice of a delay formulation for end use because delay time is directly proportional to the length of the delay column. In order to study the effect of ingredient proportions on the burning rate of a formulation, several delay formulations are prepared in which the fuel/oxidizer ratio is varied around the stoichiometric ratio (between the fuel deficient and the fuel rich). A number of delay columns of set length are then prepared and ignited under ambient conditions of temperature and pressure. The inverse burning rate (IBR) of the columns is then measured for each formulation. These are then plotted against fuel content as shown in Figure 5.2.

The formulations falling in the zone ‘AA’ only are selected for actual Service use as these formulations satisfy one of the most important requirements of an ideal delay formulation that is, ‘any minor change in the proportion of ingredients should not affect the burning rate adversely’. The delay formulations are categorized in terms of IBR as shown in Table 5.8.

5.5.2.2 **Factors Affecting the Performance of Delay Formulations**

In order to have burning time within the specified limits, the formulation must burn uniformly throughout the length of the filled column (also called the delay

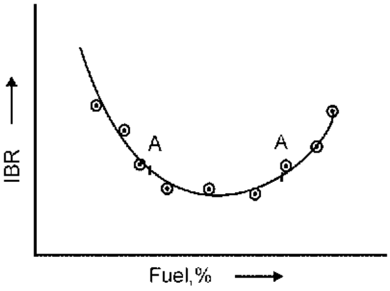


Figure 5.2 Variation of IBR against fuel.

Table 5.8 Classification of delay formulations and their applications.

Formulation	IBR/ s cm^{-1}	Application
Very fast	>0.04	Millisecond delay applications
Fast	0.4	As priming formulation that is, to initiate the delay train
Medium	2.0	These formulations are selected depending on availability
Slow	4.0	of length for delay filling, time required and the
Very slow	>12.0	environmental forces acting on them.

column). A uniform burning rate of the formulations depends upon a number of factors which have been described in the literature by Conkling [24] and Ellern [25]. The important factors are:

- Free space into which the products of combustion may vent.
- Dimensions of the delay column.
- Size and number of increments.
- Method of initiation and ease of ignition of the surface of increments in addition to the factors already described in Section 5.5.1.

In order to achieve the goals of pyrotechnic delay formulation, ingredients are chosen and formulated in an elegant way. The ingredients of a pyrotechnic delay formulation are: (i) fuel (carbonaceous materials or inorganic substances); (ii) oxidizer; (iii) binder; and (iv) retardant, if required.

The fuel and oxidizer are the principal constituents of a delay formulation. In certain mixtures of oxidizers and fuels, exothermic reaction after ignition is very fast which is not always desirable. Therefore, it becomes mandatory to control the reaction by the addition of a third ingredient called a retardant which is an inert material and does not take part in the exothermic reaction.

5.5.2.3 Types of Delay Formulations

There are two types of delay formulation:

Gas-producing (Slagless) Delay Formulations These formulations are used in a system where a vent is provided for the generated gases to escape. The types of fuels used for these formulations can be classified into the following groups:

i) Naturally occurring substances such as starch, sugar, charcoal, resins and gums etc.
ii) Potassium salts of organic acids such as salicylic acid, sulfonic acid, nitrated phenols, cresols and their derivatives etc.
iii) Chlorinated materials such as poly (vinyl chloride) (PVC) and chlorinated rubber (chloroprene) etc.
iv) Polynitro organic derivatives such as tetranitro carbazole (TNC) and tetranitro oxanilide (TNO) etc.

The formulations which are based on barium nitrate as oxidizer are generally slow burning. The fuels are used according to the choice of fast- or slow-burning formulation. The reactions taking place are normally very complex. These formulations have a tendency to burn slower on higher consolidation as the pores for propagation of flame and hot gases into the unburned mass are restricted.

Gasless Delay Formulations Gasless delay formulations were introduced around 1929 to replace the old fuse formulation based on gunpowder which used to give erratic results under conditions of low ambient pressure at higher altitudes.

The basic reaction underlying the combustion of many gasless delay formulations is the Goldschmidt or thermite reaction where a metal powder and a metallic oxide interact in an oxidation–reduction reaction manner with the evolution of a large amount of heat but very little or no gas. Consequently, these formulations are used where no vent or very little vent is provided in the ammunition. Gasless delay formulations tend to burn faster under higher consolidation as the points of contact of fuel and oxidizer increase. This is because the reaction in this case is a solid state reaction by diffusion.

The fuels are finely powdered metals (2.0–10.0 μ) among which titanium, zirconium, manganese, tungsten, molybdenum and antimony are very common. Sometimes, non-metal powders such as boron and silicon (for fast burning delays), binary alloy powders such as ferrosilicon, zirconium–nickel, aluminum–palladium and metal compounds such as antimony sulfide, calcium silicide etc. are also used.

The oxidizers include heavy metal oxides such as red lead (Pb_3O_4), lead dioxide (PbO_2), iron oxide (Fe_2O_3), bismuth oxide (Bi_2O_3), lead and barium chromates etc., peroxides (barium peroxide) and various oxysalts of potassium and barium.

As a delay formulation is a mixture of fine powders of fuel and oxidizer, there is a tendency to segregation of the ingredients because of their varying densities. Also this mixture does not have free-flowing properties and it sticks to the tools, containers and scoops etc. Further, such mixtures are susceptible to the absorption of moisture from the surroundings when the ingredients are hygroscopic. These drawbacks of simple mechanical mixture are overcome by granulating the mixture with the use of a suitable binder.

The most important characteristic of a delay formulation is its IBR. In addition, other important characteristics are: sensitivity to impact, friction and electric spark, ignition temperature, heat output and gas output. Therefore, before static evaluation of delays, the delay formulation must be characterized thoroughly for these properties.

Some ingredients such as sulfur have an inherent characteristic of changing the burning rate considerably when used in a small proportion that is, 1–2 parts in 100. In general, the delay systems subjected to higher temperatures realize lower values compared with ambient temperature. Therefore, all these facts should be kept in view when developing delay systems. The chromates of barium, lead etc. are used in many of the delay formulations but these ingredients are carcinogenic in nature and search for non-toxic replacements is currently pursued all over the globe. Some important gasless delay formulations are:

1) **Silicon and lead oxide:** Mixtures of powdered silicon and lead oxide/lead dioxide/red lead burn fiercely and rapidly with the formation of metallic lead and fusible lead silicate. The reactions may be shown in Equation 5.9:

$$2\,Si + Pb_3O_4 \rightarrow 3\,Pb + 2\,SiO_2 \rightarrow 3\,Pb\,2\,SiO_2 \qquad (5.9)$$

   Reactions with other oxides are similar in nature. The rate of burning varies from one second to ten seconds depending upon the proportions of the fuel and oxidizer.

2) **Amorphous boron and bismuth oxide:** Amorphous boron reacts vigorously with bismuth oxide to form fusible metallic bismuth and volatile boric oxide (Equation 5.10):

$$2\,B + Bi_2O_3 \rightarrow B_2O_3 + 2\,Bi \text{ (stoichiometric mixture contains 4.4\% B)} \qquad (5.10)$$

   The burning rates from 0.68–0.24 seconds per cm can be obtained by varying the proportion of boron from 8% to 3%.

A formulation based on antimony trisulfide (Sb_2S_3) – 20%, potassium perchlorate ($KClO_4$) – 8% and barium chromate($BaCrO_4$) – 72% (with NC as binder) is a well-known slow-burning delay formulation with a burning rate of $0.43\,cm\,s^{-1}$. The burning rate decreases to $0.23\,cm\,s^{-1}$ on substitution of barium chromate by bismuth chromate. These formulations are safe to handle as revealed by the sensitivity data [26].

A number of formulations based on alternate oxidizers (barium permanganate, barium manganate, rubidium permanganate, manganese dioxide, bismuth oxide and molybdenum trioxide together with several metals as fuels(Ti, W, Ta, Nb, Mn, B and Al) have been formulated and evaluated. At the end of the investigation, it was concluded that the systems: barium manganate/W and manganese dioxide/W/$KClO_4$ are very attractive for this purpose. However, before these systems are brought into operation, further research is necessary on the criteria of low gas and long-term storage capability [27].

5.5.3
Smoke Formulations

In the broad family of pyrotechnics, smoke formulations constitute an important and indispensable class. The military use of smoke for screening and/or signaling is probably as old as warfare itself. Before the availability of gunpowder and other pyrotechnic mixtures, smoke was generated by burning natural materials such as grass. The first recorded use of screening smoke occurred in 1701, when Charles XII of Sweden burned damp straw to produce a smoke screen to cover a river crossing.

Pyrotechnic smoke is basically an aerosol, that is, a suspension of small solid or liquid particles in a gaseous medium. The small particles of smoke are formed due to the heat of chemical reaction between oxidizer and fuel (exothermic oxidation–reduction chemical reaction) to vaporize volatile ingredients or products from the pyrotechnic reaction, followed by condensation of the volatile ingredients in air, creating smoke. The particles suspended in the gaseous medium scatter, reflect and absorb radiation depending upon the nature, size and shape of the particles and wavelength of the incident radiation. Therefore, these are the factors which determine the effectiveness of the smoke for screening. The formation of the cloud depends upon the smoke agent, particular munition and the method of release. The density, persistency and subsequent behavior of the smoke cloud also depend on meteorological conditions such as humidity, wind speed, wind direction and air stability etc. [28].

5.5.3.1 **Requirements for Smokes**

The smoke may be produced from a large number of chemicals in a variety of ways. However, only a few meet the specific requirements for a military smoke. The ideal military smoke or smoke material should be:

- effective at a low concentration of material;
- available in sufficient quantities for large scale production at a relatively low cost;
- disseminated easily and efficiently without the use of elaborate equipment;
- able to persist when disseminated that is, should not evaporate, fall out or coagulate rapidly;
- substantially non-toxic, non-irritating to the eyes, throat and skin and at the same time non-corrosive to equipment;
- suitable for large scale manufacture, storage and transportation without hazard or deterioration.

5.5.3.2 **Classification of Smokes**

Smokes may be classified in the following categories:

(i) Screening smokes Screening smokes are usually white and are used to conceal military movements, equipment and installations from ground and air observations or attacks.

(ii) Signaling smokes These smokes are mostly colored as they are clearly distinguishable from other smokes and are used for signaling and communication. Thus use of white and gray smokes is very limited for such purposes.

(iii) Lachrymatory smokes Lachrymatory smokes for riot control are produced by pyrotechnic reactions, a vaporization process that is followed by a condensation process. The physiological effectiveness of disseminated smoke depends strongly on the particle size. The visibility of such smokes is not considered very important.

(iv) Tracking and acquisition smokes Such smokes are used for tracking the path of space vehicles and tracer projectiles at high altitude. A tracer bullet is a light-producing device for improved aim and fire control for automatic weapons.

(v) Marker smokes Sea water is allowed to react with calcium phosphide/magnesium phosphide/aluminum phosphide to produce phosphine gas which is spontaneously ignitable. Naval markers based on calcium/magnesium/aluminum phosphide are used to mark the position on the sea surface.

(vi) Training smokes Such smokes are generally non-toxic and eco-friendly because of increased awareness regarding the need to have clean environment and less harmful effects on troops.

5.5.3.3 Types of Smoke Agents

Smokes are produced with the use of the following chemicals or formulations:

(i) Use of phosphorus for smoke The simplest screening smoke produced by pyrotechnic formulation is obtained by using WP in air to form phosphorus pentoxide. The oxide, which is very hygroscopic, immediately absorbs moisture from the atmosphere and forms a cloud (aerosol) of hydrated phosphoric acid. It is particularly useful for filling bombs, shells and grenades, producing bursts of screening smokes since it is readily melted, scattered and ignited by detonating explosives. The main reactions involved are shown in Equation 5.11:

$$\begin{aligned} &4\,P + 5\,O_2 \rightarrow 2\,P_2O_5 \\ &P_2O_5 + 3\,H_2O \rightarrow 2\,H_3PO_4 \\ &H_3PO_4 + nH_2O \rightarrow H_3PO_4.nH_2O \end{aligned} \tag{5.11}$$

The screening properties of WP smoke depend on the relative humidity of the atmosphere. In small concentration the smoke is non-toxic but irritating to eyes, skin and respiratory tract. In addition, it produces an incendiary effect and causes flesh burns. Because of the large amount of heat generated, there is a pillaring effect which causes the smoke to rise up fast, reducing the duration of its utility. To overcome this problem plasticized white phosphorus (PWP: 75% WP and 25% rubber) which is useful to effect controlled fragmenting, slow burning and reduced pillaring, is used. PWP is a plastic mass with low shattering characteristics.

(ii) Chlorinated hydrocarbons for smoke The UK developed smoke formulations in which HCE, ZnO, $CaSi_2$ and KNO_3 were used, whereas USA used Al powder in the place of $CaSi_2$, which was difficult to ignite. There are in general two types of formulation, in which the use of chlorinated hydrocarbons is made.

Type 1 (Formulation):

Carbon tetrachloride, %	....	45
Zinc powder, %	....	20
Zinc oxide, %	....	28
Kieselguhr, %	....	7

In this formulation, carbon tetrachloride is absorbed on the kieselguhr (a silicious earthy material). The reactions that take place during the combustion are complex. However, the main reaction, which is exothermic can be represented by Equation 5.12:

$$2\,\mathrm{Zn} + \mathrm{CCl_4} \rightarrow 2\,\mathrm{ZnCl_2} + \mathrm{C} + 160\,\mathrm{k\,cals} \tag{5.12}$$

Zinc chloride (and not carbon) is the main smoke-producing material.

In the initial stages of development of smoke formulations, HCE–Zn dust-based formulations were in use for screening purposes. But as this formulation is very sensitive to moisture and accidents were reported, zinc dust was replaced by zinc oxide.

Type 2 (Formulation SR 264)

Calcium silicide, %	10
Hexachloroethane (HCE), %	45
Zinc oxide, %	45

The main reaction is exothermic (Equation 5.13):

$$3\,\mathrm{CaSi_2} + \mathrm{C_2Cl_6} \rightarrow 3\,\mathrm{CaCl_2} + 2\,\mathrm{C} + 6\,\mathrm{Si} + \text{Large amount of heat} \tag{5.13}$$

The most important point is that this reaction does not contribute to smoke formation. However, smoke is formed due to the presence of $ZnCl_2$ which is formed during the secondary reactions, as shown in Equation 5.14:

$$\begin{array}{ll} \mathrm{C_2Cl_6} & \rightarrow \mathrm{C_2Cl_4} + \mathrm{Cl_2} \\ \mathrm{ZnO} + \mathrm{C} + \mathrm{Cl_2} & \rightarrow \mathrm{ZnCl_2} + \mathrm{CO} \\ 3\,\mathrm{ZnO} + \mathrm{C_2Cl_6} & \rightarrow 3\,\mathrm{ZnCl_2} + \mathrm{CO} + \mathrm{CO_2} \\ 2\,\mathrm{ZnO} + \mathrm{C_2Cl_4} & \rightarrow 2\,\mathrm{ZnCl_2} + 2\mathrm{CO} \end{array} \tag{5.14}$$

The screening smoke formulations based on HCE–ZnO have some drawbacks like poor screening property at low relative humidity (RH) as the metal halide smoke particles need atmospheric moisture to react and form a smoke screen. However, such smokes are well known for screening purposes and have been found to have IR characteristics also which make them useful in modern day warfare.

(iii) Metal chlorides for smoke Metal chloride (liquid or solid) once disseminated in air, reacts with water vapor in air resulting in the formation of hydrated oxides or hydroxides and hydrochloric acid which result in screening.

a) FM smoke $TiCl_4$ is extremely reactive with atmospheric moisture resulting in the formation of $Ti(OH)_4$ and HCl (Equation 5.15):

$$\mathrm{TiCl_4} + 4\,\mathrm{H_2O} \rightarrow \mathrm{Ti(OH)_4} + 4\,\mathrm{HCl} \tag{5.15}$$

The reaction of $SiCl_4$ is similar but it is less reactive and less corrosive than $TiCl_4$.

b) FS smoke ($ClSO_3H/SO_3$–45/55): Large smoke screens are also created without undesirable fire hazards (Equation 5.16):

$$\begin{aligned}&SO_3 + H_2O \rightarrow H_2SO_4\\&ClSO_3H + H_2O \rightarrow H_2SO_4 + HCl\end{aligned} \tag{5.16}$$

This smoke can be generated by mechanical atomization or thermal vaporization but it is very corrosive to skin and metals. This is a cheap and effective method of screening though its screening efficacy is about half or less than that of P.

c) ***Solid metal chlorides smoke*** They are vaporized by pyrotechnic reaction followed by hydrolysis with atmospheric moisture resulting in the formation of smokes (Equation 5.17):

$$CuCl_2 + 2\,H_2O \rightarrow Cu(OH)_2 + 2\,HCl \tag{5.17}$$

Chlorides of iron, zinc, cadmium and mercury also behave in a similar manner.

d) ***Organic chloro compounds smoke*** These are known as Berger mixtures. They burn in the presence of zinc, aluminum, calcium silicide etc. and produce metallic chlorides which form smoke as shown above.

5.5.3.4 **Colored Smokes**

Colored smokes are produced by one of two methods:

1) Detonation of an explosive leading to scattering of colored material.
2) Vaporization and condensation of a colored material.

These methods both of which involve vaporization and condensation of a colored material, have been found suitable only when volatile organic dyes are used as coloring materials. The choice of a suitable dye for colored smoke depends on the following:

- Heat of fusion, vaporization, sublimation and decomposition of the dye.
- Equilibrium vapor pressure.
- Rate of vaporization.
- Temperature at which the vaporization takes place.

The low vapor pressure of the dye requires a high temperature, which necessitates the use of a large quantity of fuel and oxidizer leading to inferior quality of color. Also, if the difference between the vaporization temperature and the decomposition temperature of the dye is not large, then probably decomposition increases resulting in poor quality of color.

Five colors are normally used that is, red, orange, yellow, green and blue. The colors are due to the organic dyes, which are strong absorbers of visible light. The light that is reflected from these particles lacks the absorbed wavelengths and accordingly the complementary color is seen by observers. The colored smoke formulation consists of mixture of oxidizer, fuel and dye. The oxidizer is generally KClO3 while the fuel is lactose/sucrose and the chemical reactions involved are as shown in Equation 5.18:

$$\begin{aligned} 8KClO_3 + C_{12}H_{22}O_{11}{\cdot}H_2O &\longrightarrow 8KCl + 12CO_2 + 12H_2O + 1.06\ \text{k cal g}^{-1} \\ 4KClO_3 + C_{12}H_{22}O_{11}{\cdot}H_2O &\longrightarrow 4KCl + 12CO + 12H_2O + 0.6\ \text{k cal g}^{-1} \end{aligned} \tag{5.18}$$

The amount of heat or duration of smoke can be controlled by varying $KClO_3$ and sugar/lactose ratios. The $KClO_3$ and lactose react to produce heat which vaporizes the dye and the gaseous products help in the dispersion of dye. The dye then condenses to give colored smoke. For production of good smoke, approximately equal proportions of dye and vaporizer are generally used. Some important dyes and their resulting colors are:

• 1-Methylamino anthraquinone	Red
• 1-Amino anthraquinone	Orange
• Quinoline yellow/Auramine hydrochloride	Yellow
• 1,4-Di-p-toluidino anthraquinone	Green
• 1,4-Dimethylamino anthraquinone	Blue

$NaHCO_3$ and $KHCO_3$ are used as cooling agents to prevent excessive decomposition of the dye. Ammonium chloride, bromide, oxalate, carbonate, sulfate and tartrate have disadvantages of forming white smoke on condensation, which reduces the color intensity. Inert diluents like calcium carbonate, kaolin etc. reduce burning rate and flaming. Various binders are also used to provide mechanical strength to the smoke pellet and control the burning rate.

One problem which has frequently been encountered especially in the case of orange smokes, is the tendency to inflame. This problem is overcome by the addition of cooling agents and proper design of smoke emission nozzles. A typical heating mixture which is considered most efficient is: potassium chlorate/ lactose, 50%/50% and combustion takes place according to Equation 5.18. Accordingly, a typical formulation is as follows:

Lactose, parts	25
Potassium chlorate, parts	25
Dye, parts	50

Sometimes dyes are mixed with PETN in order to produce instantaneous smoke of a very short duration. White smoke which can be produced from many chemicals in a variety of ways, is in general more efficient on a weight basis than colored smokes.

India has developed a number of colored smoke formulations for various applications and important among them are: smoke formulation for aircraft or helicopter landing (formulation producing orange smoke for 120 s); smoke formulation for training of anti-aircraft gunners and air-to-air weapon engagement (high density red smoke for 65–70 s); and smoke formulation for recovery of training torpedoes (high density orange smoke for 60 s).

5.5.3.5 Lachrymatory Smokes

Smokes for riot control are generated using sensory agents like ω-chloroacetophenone (CN), dibenz(b,f)-1,4-oxazepine (CR), *o*-chloro benzylidene malononitrile (CS). They are disseminated using evaporating formulations. The formulation consists of a fuel and oxidizer. It is formulated in such a way that it delivers just sufficient heat to evaporate the agent in the atmosphere without decomposition. In such smokes, visibility of smoke is not that important but the volume and duration of smoke are very important to make them effective. HEMRL, Pune has recently developed a non-lethal sensory irritant formulation based on oleoresin (extract of red pepper) which is less toxic than the existing sensory irritants [29]. In order to make riot control more effective, an altogether different approach was suggested and some formulations capable of inducing temporary blindness in a human or animal have been proposed. A typical formulation of this class consists of an incapacitant mixture comprising of less than 5% pelargonic acid vanillylamide (PAVA) and a solvent [30].

5.5.3.6 Non-toxic and Eco-friendly Smokes

The toxicity of many of the smoke ingredients has been realized and consequently research is being carried out to develop non-toxic and environmentally acceptable smokes. Such smokes are mostly used for training purposes because of increased awareness regarding the need to have a clean environment and less harmful effects on troops. Non-toxic and eco-friendly smoke formulations for training purposes are similar to colored smoke formulations and consist of a fuel, oxidizer and binder. After much experimentation, $KClO_3$ has been accepted as a universal oxidizer and sugar/sucrose as a fuel. The main ingredient responsible for smoke varies from formulation to formulation. Several formulations have been patented and are available in the literature and the gist of some important formulations is given below:

1) **Ammonium chloride smoke:** A smoke formulation containing NH_4Cl – 56%, white sugar – 15%, Rosin – 9.5% and $KClO_3$ – 19.5% is described in a Dutch patent. The smoke is claimed to be long lasting and milky white and has been suggested for use in training as well as in testing of the leakage in pressure vessels. The smoke is formed due to the emission of ammonium chloride particulates, which are non-toxic in nature [31]. Another smoke formulation containing NH_4Cl – 50%, naphthalene/anthracene – 20%, $KClO_3$: 20–30% and wood charcoal: 0–10% has been reported by Shidlovskiy [2]. This formulation produces non-toxic smoke and is used for training purpose. HEMRL, Pune has developed a smoke generator with a smoke formulation (ammonium chloride – 45%, potassium chlorate – 40%, anthracene – 15% and a binder) which emits non-toxic smoke and is being used for fire fighting purposes on ships and also for practical demonstration to graduate trainees.

2) **NaCl, KCl type smoke:** NICO Pyrotechnik, Germany produces a non-toxic smoke formulation called KM which contains KCl – 44%, KNO_3 – 27%, $KClO_4$ – 5%, Mg – 8% and azodicarbonamide – 16%. The aerosol contains par-

ticles of sublimed KCl, potassium compounds and MgO which are non-toxic in nature [32].

3) **Cinnamic acid and terephthalic acid-based smokes:** This formulation contains a mixture of $KClO_3$ – 29% and sucrose – 12% to volatilize cinnamic acid – 47.5% in addition to cooling agents $NaHCO_3$ – 6.5%, and SiO_2 – 5.0% with nitrocellulose as a binder. This formulation produces a good volume of smoke and can be used to stimulate fires for fire-fighting training [33]. Another formulation consisting of terephthalic acid – 57%, sucrose – 14.0%, $KClO_3$ – 23%, $MgCO_3$ – 3%, graphite – 1% and nitrocellulose – 2% as a binder also produces non-toxic smokes used for training purposes [34].

NICO Pyrotechnik, Germany claims to have developed the world's first multispectral smoke screen (designated as NG 90) which defeats millimetric wave (MMW) radar in addition to preventing detection in the visual and IR bands of the electromagnetic spectrum. The NG 90 smoke is therefore impenetrable to most reconnaissance and target homing devices. The pyrotechnic formulation used for this purpose is based on $KClO_4$, Mg and carbon which is packed in cartridges, canisters or grenades and provides a non-toxic and environment-friendly smoke. On initiation, Mg is oxidized by $KClO_4$ with simultaneous release of sufficient heat to transform the packed carbon into aerosol particles that scatter electromagnetic waves. NICO further claims that the smoke attenuated more than 99% of the energy of 35–140 GHz signals [35]. Similarly, another smoke-generating pyrotechnic formulation consisting of 50–70% anthracene/naphthalene and 30–50% (by weight) $NaClO_4$/$KClO_4$/AP has been reported and is suitable for generating a masking smoke containing carbon particles. The screening efficiency of this smoke [36] is in the IR region (especially a wavelength of 0.78–14.0 μm). An exhaustive review on such formulations has recently been published by Amarjit Singh *et al.* [37].

Though smokes play an important role in defense, their civilian uses outweigh their uses in defense. Some of the civilian uses of smokes are: testing of leakages for boilers; as an insecticide; putting out underground fires; protection of orchards from sudden temperature changes; rapid generation of gases for filling air bags in cars: creation of rain; removal of fog over airport for planes to resume operation by seeding silver iodide crystals etc.

5.5.3.7 Infrared Screening Smokes

The battlefield of the future will be characterized by a large number of highly lethal and sophisticated weapons based on electro-optical devices which use optics and/or electronics to acquire targets or guide munitions to their targets. The basis of electro-optical devices is the electromagnetic spectrum shown in Figure 5.3 which comprises energy levels ranging from gamma rays through visible light, infrared and then on to microwaves and radio waves.

But for military applications only visible, infrared and microwave bands are useful. Visible band comprises visible light (0.40–0.75 μm) which is the only part of entire spectrum that can be seen by human eye. Radiation covering the

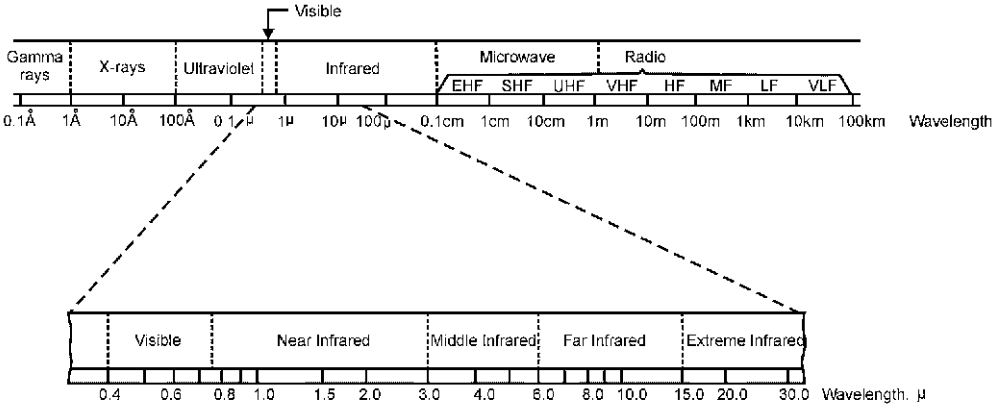


Figure 5.3 Electromagnetic spectrum.

wavelength between 0.75 μm to 1 mm is called IR radiation and is not detected by human eyes. There are specific windows in this band, where the attenuation due to atmosphere is less. The four portions of the IR band are:

1) Near IR (NIR) band lies just beyond the visible portion of the spectrum, that is, 0.75–3.0 μm.
2) Mid IR (MIR) band cannot be seen, but can be easily detected with electro-optical devices that is, 3.0–6.0 μm.
3) Far IR (FIR) band, that is, 6.0–15.0 μm is actually the real heat portion of the IR band. This is where we use extremely sensitive heat-sensing systems to pick up and contrast the subtle differences in temperatures between an object and its background.
4) Extreme IR (EIR) band, that is, 15.0 μm–1.0 mm.

All objects above absolute zero temperature (–273 °C) emit electromagnetic radiation in the IR region. Further, the emission of IR radiation is theoretically based on the concept of black body which is considered a perfect and efficient emitter. As the temperature of the object increases, wavelength of maximum emission shifts to the shorter wavelength region and therefore radiant energy is emitted in the IR and visible range.

Microwave band (millimeter portion) is the last portion. The specific segment of the microwave band which needs discussion is the millimeter wave (MMW) band portion. This part of the spectrum is not only impossible to see but also impossible to feel. So electro-optical devices are used to convert this energy into an image which can be seen. Devices that operate in the MMW region are highly complex, sophisticated and very expensive. For this reason, only a few electro-optical devices are available in the advanced countries. Electro-optical devices are designed to monitor the flow of energy through the atmosphere and this flow of energy can be disrupted by the use of some of the countermeasures such as: paint films; heat suppression and dispersion techniques; use of special material nets, mats, umbrellas; use of decoys like IR flares and chaff flares; use of IR jammers and use of IR smoke screens. This disruption can either degrade or completely defeat many electro-optical devices. While conventional smokes are effective in the visual and near IR region (0.4 to 3.0 μm), IR smokes are effective in neutralizing effects of opto-electronic equipment operating in mid-IR region (3.0–6.0 μm), far-IR region (6.0–15.0 μm) and beyond. The conventional smoke screens work by absorbing, reflecting and scattering of the visible light. On the other hand, IR screening smoke combines these effects with a high degree of absorption and emission from the smoke cloud in the IR band and provides effective screening against modern opto-electronic equipment. IR smoke is thus a potential countermeasure to modern weapon systems and is capable of degrading the effectiveness of enemy's opto-electronic devices as well as target acquisition devices.

Many smoke-generating compounds are used to camouflage the military as a protection against visual reconnaissance. A few pyrotechnic smoke formulations based on HCE and HCB along with various oxidizers, metallic fuels and other additives are readily available for use. The data reported in the literature reveal that the smoke formulations producing large amount of carbon particles from various hydrocarbons are more effective in attenuating radiation compared with the formulations which produce various inorganic particles [38–40]. The smokes generated by these formulations are effective for attenuation in the MMW region also in addition to visible and IR region. One of the promising compounds which has been reported for this purpose is RP [41]. It is a powerful material for generating screening smoke for military applications as it not only provides effective visual obscuration, but also has the capacity to provide protection in the IR region of the spectrum. Before we discuss the use of RP for visual and IR obscuration, it is worthwhile to highlight some important aspects of its chemistry.

5.5.3.8 **Chemistry of Phosphorus**

Phosphorus is the eleventh most abundant element in the crystal rocks of the earth. Elemental phosphorus does not exist in nature and all of its known terrestrial minerals are orthophosphates found in phosphate rocks which occur in vast deposits throughout the world. Phosphate rock is the starting material for the industrial manufacture of elemental phosphorus. White phosphorus is produced by heating phosphate rock with sand and coke in an electric furnace according to Equations 5.19:

$$\begin{aligned} &2\,Ca_3(PO_4)_2 + 6\,SiO_2 \rightarrow 6\,CaSiO_3 + P_4O_{10} \\ &P_4O_{10} + 10\,C \qquad\qquad \rightarrow 10\,CO + P_4 \end{aligned} \tag{5.19}$$

The gaseous WP (P_4) is distilled from the furnace by condensing with water. The WP allotrope that is formed by this process is a white waxy solid with a m.p. of 45 °C that should be kept under water to prevent its contact with air where it spontaneously ignites because of its extreme reactivity. It is also known as yellow phosphorus because most commercially-produced material exhibits yellow coloration. Red phosphorus (RP) is thermodynamically more stable than the white

Table 5.9 Properties of allotropes of phosphorus.

Characteristic	White P	Red P	Black P
Appearance	Crystalline waxy translucent	Amorphous or crystalline opaque	Crystalline resembling graphite
Stability in air	No	No	Yes
Melting point, °C	44.1	585–610	NA
Vapor pressure	High	Very low	None
Density, g cm^{-3}	1.83	2.0–2.4	2.3–2.7
Solubility in organic solvents	Yes	No	No
Toxic	Yes	No	No
Heat of sublimation, k cal mol^{-1}	13.4	30.0	NA
Chemiluminescence	Yes	No	No
Odor	Yes	No	No
Spontaneity to ignition at room temperature	Yes	Ignites at 725 °C	No
Reaction with alkali	PH_3 is formed	No	No

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form. It is a reddish brown powder with a m.p. of 590 °C. It is commercially produced from WP by thermal conversion in the presence of a catalyst. RP has WP as an impurity which is removed by treatment with sodium hydroxide. Technical grade RP contains significantly less than 200 ppm WP. The third allotrope, black phosphorus is formed by heating WP to 200 °C under a pressure of 12 500 kg cm^{-2}. Each of the allotropic modifications of phosphorus exhibits more than one form. There are two crystalline forms of WP, at least six crystalline forms of RP and two forms of black P. Some physical and chemical properties of each of the allotropes are given in Table 5.9.

There are stability problems associated with RP as it has a propensity to degrade to form various phosphorus acids and toxic gas phosphine. Various attempts have been made over the past 60 years by the addition of stabilizers such as metal hydroxides and epoxide coatings to produce a grade of RP which is stable. The fundamental chemistry of the degradation process is still not yet understood, although water and oxygen are known to contribute in the oxidation of RP. It has been postulated that the absence of water eliminates formation of phosphine, while a reduction in oxygen content reduces the rate at which it is formed. It is also believed that oxygen promotes the formation of 'active acidic groups' which then react with water [42, 43]. Another problem with RP is that it is extremely friction sensitive.

Stability of Red Phosphorus During storage, RP generally releases toxic phosphine gas and various phosphoric acids are formed. This decomposition reaction takes place in the presence of oxygen and water. In the presence of moisture, some impurities like copper and iron react with RP and cause deterioration [44]. The decomposition rate depends directly on the availability of air, moisture and temperature. In pyrotechnics and munitions, phosphine liberated by standard RP charges may diffuse through the device and can give rise to corrosion. Therefore, stabilized RP is prepared by eliminating these impurities and is used for smoke ammunition.

A systematic and methodical study to prevent or retard formation of phosphine has been carried out by Hoerold and Ratcliff of Clariant GmbH, Germany and their findings through the following approaches are reproduced here [45].

i) use of dust suppressants (oiling);
ii) use of stabilizers to inhibit phosphine formation;
iii) restricting the availability of moisture and oxygen;
iv) coating the surface of the RP (microencapsulation);
v) storage at room temperature.

(i) Use of dust suppressants Handling of RP powder can be hazardous due to the potential for dust explosions. Dust suppression or oiling prevents dust explosions, improves handling and increases its stability in air due to the reduction of the active surface of RP [46]. Typical dust suppressants are liquid organic compounds such as long chain ethoxylates rather than original transformer oils.

(ii) Use of stabilizers Various metal oxides can be used as stabilizers by precipitating them on the surface of the RP grains. Typical metal oxides are those of Al and Mg that work by buffering traces of acid formed on oxidation of RP. Freshly prepared RP in an aqueous dispersion [47] gives a nearly neutral P_H.

(iii) Use of combination of dust suppressants and stabilizers The combination of both stabilizing metal oxides and dust suppressing oils on the RP surface imparts further improvements. Such RP is used in the match industry. The MIL-P-670A specifies an Al stabilizer coupled with a basic particle size distribution requirement but no dust suppressant.

(iv) Use of microencapsulation Microencapsulation of RP reduces its active surface. It is a very thin coating on the individual grains. Various resins can be used for microencapsulation with the best results obtained with the use of some selected thermosetting resins such as epoxy resins or phenolic resins. The resin content varies from 1–8% (by weight) of RP. Microencapsulation is normally combined with stabilization and dust suppression to impart optimum performance [48, 49]. Clariant, Germany has done pioneering work on the stabilization of RP and a comparative account of PH_3 formation after stabilization of RP through these approaches is given in Table 5.10.

It is evident from the data that the stabilized and microencapsulated RP grades (HB 700 and HB 714) provide a significant improvement in stability. Similarly,

Table 5.10 Comparison of phosphine formation of various grades of red phosphorus (at 25 °C and 65% humidity).

Red phosphorus grade	**PH_3 Formation (μg/g RP)**			
	24 h	**48 h**	**14 days**	**28 days**
Non-dust suppressed Clariant grade SF	150	290	1300	2400
Dust suppressed Clariant grade HB 250	18	40	507	980
Stabilized Clariant grade NF	3	5	48	81
Stabilized and dust suppressed Clariant grade NFD	3	5	32	48
Microencapsulated Clariant grade HB 700[a]	2	3	7	8
Microencapsulated Clariant grade HB 714[b]	0.8	1.2	3	4

a) HB 700: Stabilized, dust suppressed and microencapsulated.
b) HB 714: Stabilized and microencapsulated.

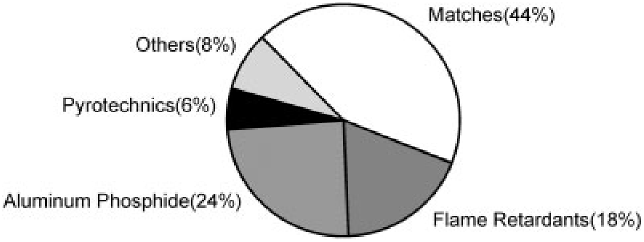

Figure 5.4 Worldwide applications tree of red phosphorus (1999). Reprinted with permission from S. Hoerold and A. Ratcliff, *J. Pyrotech.*, Issue 13 (Summer 2001) 1–8; © 2001, J. Pyrotechnics Inc, USA.

another European RP manufacturer (Italmatch of Italy) is also reported to have developed additives that reduce the oxidation reaction in RP and therefore, the formation of phosphine.

Applications for Red Phosphorus RP is commercially used in a wide variety of industrial applications: safety matches, flame retardants, phosphides and pyrotechnics. (Figure 5.4). In most applications, the red allotrope is favored over the white because of its greater stability in air and also its easier handling characteristics. RP is also not considered problematic with regard to environmental and occupational health issues. It is not soluble in water and is considered non-toxic when pure. When the content of WP is less than 0.02%, the LD_{50}-value is >15 000 mg/kg (rat).

As is evident, less than 10% of RP produced annually is used for military pyrotechnics. Its major use is in non-military applications where it is used mainly for the production of safety matches, aluminum phosphide (used for grain fumigation) and flame retardants. The use of RP as a flame retardant in the plastics industry, where it is added at the levels of a few percent to plastics such as polyamide and polyurethane, is increasing day by day. RP is an extremely versatile material and is used for many military applications throughout the world. The use of RP can be categorized as follows:

i) screening smoke;
ii) signaling smoke;
iii) IR decoys;
iv) incendiary.

The reason for this is that the form and chemical reactivity of RP can be altered depending on the particular application. For example, it can be manufactured as a slow-burning pellet resulting in long duration smoke output for signaling applications. At the same time, it can also be produced in a granular form or as a thin film which burn very rapidly to form a highly emissive IR signature. It may be mixed with metal fuel and oxidizer to accelerate its burning rate to produce a rapidly formed and dense smoke cloud.

(i) Screening smoke Similar to WP, RP burns in an excess of air to produce phosphorus pentoxide (P_2O_5) which undergoes hydration to give a mixture of phosphorus acids depending on the prevailing atmospheric conditions as shown in Equations 5.20:

$$\begin{aligned} &P\ (\text{Solid}) &&\rightarrow P_4\ (\text{Gaseous}) \\ &P_4 + 5\,O_2 &&\rightarrow 2\,P_2O_5 \\ &P_2O_5 + H_2O &&\rightarrow (HPO_3)_2 \\ &(HPO_3)_2 + H_2O &&\rightarrow H_4P_2O_7 \\ &H_4P_2O_7 + H_2O &&\rightarrow 2\,H_3PO_4 \end{aligned} \tag{5.20}$$

The acids formed are hygroscopic and absorb moisture from the atmosphere to produce submicron-sized droplets of an aqueous solution of phosphoric acid and a series of polyphosphoric acids. It is the mist of these acids which constitutes the white smoke cloud and scatters visible and near-IR electromagnetic radiation. The amount of smoke formed depends on the RH of the atmosphere. Under high humidity conditions, it is possible to achieve yield factors of four or even higher.

Some pyrotechnic formulations based on epoxy-resin-plasticized RP in combination with Mg and other additives could screen IR radiation (0.82 µm, 3.0–5.0 µm and 10.6 µm wavelengths) with high efficiency under field conditions and prove to be suitable for smoke grenades of modern construction [41].

(ii) Signaling smoke RP-based munitions are used for numerous military signaling applications. This is particularly so at sea where they are used as 'man overboard' signals, position marking devices for damaged submarines and anti-submarines, anti-mine operations and targets for bombing practice. The flame and smoke produced by burning RP formulations can be seen from a long distance by both visual and IR locating devices.

Signaling smoke applications require formulations that produce large amounts of visible flame and smoke for relatively long duration. A formulation consisting of 50–70% RP, 20–40% metal fuel/oxidizer mixture and ≈10% polymeric binder, pressed into candles, has a controlled burning rate and has been found to meet the criteria for signaling smoke applications. Another slow-burning pyrotechnic mixture based on RP for signaling purposes is:

Red phosphorus, %	....	51
Manganese dioxide, %	....	35
Magnesium, %	....	8
Zinc oxide, %	....	3
Linseed oil, %	....	3

The reactions involved during combustion of this formulation are complex. However, the combustion seems to indicate a concurrent oxidation of two fuels (Mg and P) by the oxides present. It is believed that a thermite-type reaction of the Mg provides heat to evaporate most of the phosphorus which then burns in air. The reactions involved may be shown by Equations 5.21:

$$\begin{aligned}
&2\,Mg + MnO_2 && \rightarrow 2\,MgO + Mn \\
&Mg + ZnO && \rightarrow MgO + Zn \\
&Zn + 1/2\,O_2 && \rightarrow ZnO \\
&4\,P + 5\,O_2 && \rightarrow 2\,P_2O_5 \\
&P_2O_5 + 3\,H_2O && \rightarrow 2\,H_3PO_4
\end{aligned} \tag{5.21}$$

Similarly, a formulation based on RP and calcium sulfate burns at rates exceeding $0.08\,mm\,s^{-1}$. For volatilizing RP at a sufficiently low rate to provide an acceptable signal, a heater formulation based on Mg, Al and MnO_2 is used. In this case, RP is coated with an organic binder. Linseed oil imparts the most effective coating but polyvinyl butyral (PVB) is also useful. The formulations containing PVB coated RP and calcium sulfate burn at acceptable rates providing the required signal [50].

***(iii)* IR decoys** RP-based formulations are extensively used throughout the world for the protection of relatively slow moving military platforms such as naval vessels, helicopters and transport aircrafts against modern heat seeking missiles. For such applications, RP formulation which burns very quickly and produces a large RP signature are of considerable interest. RP-based formulations with rubber as a binder are considered most suitable for this application.

***(iv)* Incendiary** The military role of RP as an incendiary is far less common than its other roles since WP is more readily ignitable and considerably cheaper. However, dry vegetation and combustible materials may be ignited and burnt by dispersing or scattering a burning RP formulation over a large area.

The most important military application of RP is in the field of pyrotechnics – smoke and obscurants. RP is an essential component in the production of energetic, multi-spectral smoke and obscurant devices. A. Singh *et al.* have reviewed the phosphorus-based smoke formulations [51] along with their applications. The radiometric studies of smoke formulations based on RP/KNO_3/binder suggest that the smoke generated serves as an effective obscurant in the 0.4–13.0 μ region [52]. The manufacture of RP-based smoke formulations is a hazardous and dirty operation and hence its encapsulation is a must before processing [53]. It is then mixed with binder, oxidizer and other additives and the resulting mixture is then processed in the desired shape.

It has been realized in the recent past that the disposal of life expired RP munitions is a major concern. Dumping at sea or burning are no longer environmentally acceptable. Efforts should be made by researchers and manufacturers to develop RP formulations that can be reprocessed to yield RP suitable for reuse.

The future research in this area would focus on development of more efficient and environmentally compatible and biodegradable WP- and RP-based smoke formulations. These formulations should also be safe to manufacture and handle and at the same time, more effective in screening in the various regions of the electromagnetic spectrum that is, visible, infrared and millimetric wave bands.

5.5.4
Incendiary Formulations

> Fire is the best of servants, but what a master!
>
> *T. Carlyle*

Fire has always been a difficult weapon to handle. One of the oldest uses of fire mentioned in the literature is the throwing of oil on an enemy and setting it alight. The ‘flame thrower’ is a modern device for streamlining this ancient practice. The systematic research and development work on incendiaries started during World War I. Subsequently, the most notable development is that of Napalm and Napalm B-based incendiaries which proved to be extremely fatal during World War II, the Korean, Vietnam and Gulf wars.

An incendiary material may be defined as a material that is readily capable of starting fires and can be used in a flame thrower, bomb, shell or warhead. It may also be defined as a material that burns with a hot flame for a long duration. Its purpose is to set fire wooden structures and other combustible targets. There are some incendiaries such as thermite which can be used for melting, cutting or welding metals.

Incendiary materials are classified as either ‘intensive’ or ‘scatter’ type.

1) **Intensive agents:** An intensive agent is one that merely ignites (does not detonate) and holds its fire in one compact mass while burning. It also burns intensively for long duration but its action is confined to a small area. It is preferred against targets of low combustibility.

2) **Scatter agents:** A material that can be dispersed or scattered over a large area in all directions from the point of burst is called a scatter agent. These agents are usually liquids with the exception of WP which is dispersed as a scatter incendiary. By scattering the incendiary, the probability of starting fires is greatly improved under situations where inflammables are present. However, their dispersal over a large area results in heat loss with corresponding

decrease in incendiary efficiency. Also the duration of burning is somewhat shorter and the intensity of heat is lower with scatter agents than with intensive agents. Scatter agents are ideal for light structures built of ignitable materials.

5.5.4.1 Characteristics of Incendiary Materials

The characteristics of incendiary materials may be considered as (i) essential and (ii) desirable.

Essential Characteristics

1) **High combustion temperature:** The task of the incendiary agent is to heat an object until it reaches its ignition temperature, which is the minimum temperature required to sustain self-combustion. In order to achieve this, the incendiary agent must develop a burning temperature that is considerably higher than the ignition temperature of the object. Before heat can reach the object being heated, some energy is lost during dissipation and in order to make up for heat losses and to ensure functioning under varied conditions, the incendiary material must generate a temperature four to five times the value of the ignition temperature. Thus a combustion temperature of not less than 800–900 °C is an essential characteristic of an effective incendiary agent.
2) **High heat of combustion:** A low mass of incendiary agent must release large amount of latent heat energy which is very important from the view point of military economy. The most important are: gaseous element: hydrogen; solid elements: Al, Mg, P and Na; and petroleum derivatives: gasoline, fuel oils and paraffins. In fact, these are the materials which constitute the arsenal of incendiary warfare for military operations.
3) **Duration of burning:** The incendiary materials must not only impart high temperatures but also maintain heat generation without replenishment of fuel. The heat must continue to radiate for an appreciable time and when the heated object is ready to burn, the fire must be present to ignite it. In fact two factors viz. intensity of heat and duration of burning are complementary to each other and must satisfy the purpose of incendiary materials.

Desirable Characteristics In addition to essential characteristics, there are some desirable characteristics which are:

1) An incendiary agent should be difficult to extinguish. However, this does not mean that an agent that resists extinguishment is always a better incendiary but it is desirable. For example, thermite that continues to burn even under water, is not satisfactory as a general purpose incendiary.
2) Good heat radiating qualities are an asset to an incendiary agent, that is, the spread of luminosity for good distances greatly increases the probability of fire raising.

3) The incendiary material should burn freely without exhausting too much oxygen from the air otherwise it will defeat its purpose as an incendiary. It must also burn completely without leaving a residue to insulate and thus prevent the surface on which it burns from catching fire.

4) The incendiary material should be inert and perfectly safe in storage and shipment. Also, it should ignite at the proper time that is, when released on hostile territory.

It is still not practicable to have an ideal incendiary material meeting all the above characteristics – essential as well as desirable. However, an incendiary material which is safe in handling and storage and meets the requirements of field use should satisfy the Services [54]. Incendiary devices are used to initiate destructive fires to cause damage to various combustible targets like fuel and ammunition dumps, base camps, tents, industrial installations, refineries, camouflages and grass or paddy fields. Incendiary devices can be delivered to the target by aircraft, artillery guns or rockets or missiles in the form of bombs, shells and warheads. The tactical use of such devices is to create psychological fear of mass fire and destruction among enemy troops during operations. The efficacy of the incendiary formulations to ignite combustible targets depends on several factors, such as total heat output, burning temperature, duration of burning and spread area. The dispersion of incendiary formulation is achieved either by bursting or by base ejection of the ammunition or shell.

In general, incendiaries are classified into the following categories [55].

Liquid incendiary	Hydrocarbons, pyrophoric liquids
Solidified liquid or gel	Hydrocarbon gels
Solid incendiary	Thermites, pyrophoric metal powders, high explosive incendiaries (HEI)

5.5.4.2 Liquid Incendiaries

(i) Hydrocarbons and pyrophoric liquids Hydrocarbons in the liquid state at room temperature like benzene, toluene, xylene, petrol, diesel, kerosene and turpentine etc. were filled in containers and were used extensively as flame throwers during World War I. The liquids were filled and tried in non-spinning projectiles but the range achieved was short. Projectiles filled with liquids pose stability-related problems under dynamic conditions restricting their use. Pyrophoric liquids have the ability to burn spontaneously in air and react explosively with water. Typical examples of this class are triethylaluminum (TEA), dimethyl magnesium, diethyl zinc, pentaborane etc. [56]. However, these are only of historical importance.

(ii) Solidified or gelled liquid incendiaries The most successful substance for thickening of incendiary liquids are rubbers (natural and synthetic), Al salts or soaps of mixed fatty acids and naphthenic acid and polyacrylates.

The mechanical strength and performance of liquid incendiaries can be improved by the addition of suitable thickening and gelling agents like rubbers, acrylic polymers, polystyrenes etc. to form semi-solid formulations. These gelled incendiaries result in comparatively longer burning duration and higher heat output. They are likely to cause serious damage to the targets due to their sticky nature. A notable development is the Napalm-based incendiary which exhibits excellent performance [57] and was found to be very effective in the Korean, Vietnam and Gulf wars. The original Napalm was a mixture of Al soaps of naphthenic and palmitic acids with gasoline [58]. When about 12% of this powder is added to gasoline, it gives a thick pourable mass which on aging becomes tough and sticky. Napalm B, a later version is a viscous liquid obtained by mixing 50% polystyrene, 25% gasoline and 25% benzene. It gives longer burning duration, higher temperature output and better sticking properties than the original Napalm. The destructive effect of gelled gasoline is increased when charcoal is added. The charcoal easily ignites and the persistent fire from charcoal outlasts the burning gasoline. The initiation system for gels is invariably WP placed in a well around the burster charge for proper initiation and dispersion of burning fragments. They can also be dispersed in one direction 'en masse' by using base ejection system. SR-425 (gelling agent Perspex) is a well-known formulation. A satisfactory thickened gasoline can also be made when 15–20% isobutyl methacrylate (IM) polymer is added to gasoline. The low temperature stability is favored by a low polymer content, polymer of low methacrylic acid content, high concentration of gelling agent, low water content and use of proper grade of gasoline.

These gels have short storage life and are suitable only for non-spinning projectiles like mortars, rockets and bombs. They are likely to cause stability-related problems similar to that of liquid filled in spinning projectiles and also during storage.

5.5.4.3 **Solid Incendiaries**

(i) Thermites Thermites are mixtures of metals and oxidizers. The metals used are Al, Mg, Mg–Al alloys and oxidizers like iron (II) oxide, iron (III) oxide and Hammer scale. Nitrates of barium, potassium and sodium are added to improve the ease of ignition and slow down the burning rate. Military thermite for incendiary purposes is composed of 2.75 parts of iron oxide scale to 1 part of granular Al [59]. Since iron oxide scale (hammer scale) is a mixture of ferrous oxide and ferric oxide in various proportions, the stoichiometric amount of Al required to react with the available oxygen present also varies. Typical reactions between Al and iron oxide may be represented as in Equations 5.22:

$$\begin{aligned} 2\,\mathrm{Al} + 3\,\mathrm{FeO} &\rightarrow \mathrm{Al_2O_3} + 3\,\mathrm{Fe} + \Delta H \\ 2\,\mathrm{Al} + \mathrm{Fe_2O_3} &\rightarrow \mathrm{Al_2O_3} + 2\,\mathrm{Fe} + \Delta H_1 \\ 8\,\mathrm{Al} + 3\,\mathrm{Fe_3O_4} &\rightarrow 4\,\mathrm{Al_2O_3} + 9\,\mathrm{Fe} + \Delta H_2 \end{aligned} \tag{5.22}$$

The amount of heat liberated is so high that it melts iron or steel with which it comes in contact. The liberated heat is readily used in thermite welding. A lower ferrous oxide (FeO) content of the hammer scale produces a considerably better flame and better propagation of burning. However, the improvement is slight for values below 22% FeO.

These are filled in devices having casings of Mg or elektron metal (an alloy of Al and Mg). The heat produced by the thermite is sufficient to ignite these casings. The Mg or elektron metal casings burn for a very long time and generate temperatures of around 3000 °C. These formulations do not ignite on bursting and a separate pyrotechnic device is needed for ignition. Sulfur may be used to bring down ignition temperatures in such formulations.

Thermite (based on magnetic iron flakes and Al powder) is very safe to handle and transport because of its high ignition temperature. It burns well in cold and windy weather. It can be easily improvised if Al powder and iron oxide particles of proper size are available. Thermites are used to attack metallic targets such as transformers, electric motors, file cabinets, gears, bearings, boilers, storage tanks and pipelines etc. Because of its high heat of combustion, ease of production and non-hazardous nature, this thermite is an important incendiary agent despite the fact that it does not rate high as a primary fire starter in comparison with Mg.

Thermite formulations give temperature ≈3000 °C at the time of burning. However, burning time and spread area are not large compared with gelled incendiaries.

(ii) High explosive-based incendiary Metal powders like aluminum, zirconium, titanium etc. can be incorporated in RDX/Wax or RDX/TNT formulations in bombs, shells, mortars etc. They produce an intense fireball for a few hundred milliseconds duration along with blast and fragment effects on initiation and are reported to be very effective against air targets.

(iii) Pyrophoric metal powders-based incendiary Many metal powders like zirconium, titanium etc. in finely divided state exhibit pyrophoric property. The pyrophoric nature of the powders is reduced by incorporating them in suitable polymeric binders. The formulation thus obtained may be filled in incendiary devices with a central HE charge. On initiation of HE charge, the formulation is dispersed as burning lumps over a wide area.

A comparison of advantages and disadvantages of different incendiaries is listed in Table 5.11.

Table 5.11 Comparison of different incendiary systems.

Property	Gel/liquid incendiaries	Solid incendiaries
Heat output/cal cm^{-3}	8000	18 100
Temperature/°C	670	2 000
Duration of burning/s	60	150
Stickiness	Sticky	Non-sticky
Storage life/yr	0.5	10
Suitability	Not suitable for spinning projectiles	Suitable for spinning and non-spinning projectiles

Gharia *et al*. formulated and studied a number of solid incendiaries based on pyrophoric metal powders (Zr/Ti) and binders such as unvulcanized natural rubber (crepe rubber), Teflon and flexible polyester (EP-4) for spread area, duration of burning and mechanical strength. The use of pyrophoric metal powders facilitates ignition of incendiary formulation on bursting. At the same time, the use of a binder provides mechanical strength to the formulation which, in turn, makes it suitable for spinning-type projectiles and also provides safety in processing of pyrophoric metal powders. Based on their data in respect of pick-up, spread area, duration of burning, mechanical strength and static as well as dynamic evaluation, a formulation Zr/rubber (93/07) was selected. Some performance parameters of this formulation are: spread diameter, 50 m, burning duration, 3.0 to 4.0 min and temperature of burning incendiary pieces, ≈2000 °C. Because of high temperature, all combustible targets in the vicinity are ignited and burn with a flame [60].

Aluminum soap manufactured from vegetable oils was a commercial thickening agent for gasoline and was used as a Napalm fill. Though Napalm possesses excellent flaming ability and proved best at that time, it, however, suffers from some disadvantages such as:

1) The gels are sensitive to changes in the pH.
2) The gels are also sensitive to moisture and deterioration takes place during storage (viscosity is reduced).
3) Preparation of gelled fuel requires a long time and vigorous mixing.

A number of formulations are reported in the literature in the form of patents which claim many improvements over Napalm. A lot of research has been carried out in India also and the erstwhile Explosives Research and Development Laboratory (ERDL, now HEMRL), Pune developed a superior gelling agent in order to improve the performance of Napalm. This gelling agent is based on a mixture of coconut oil (CO – composed of a high proportion of glycerides of C_{12}, C_{14} and C_{16} fatty acids) and groundnut oil (GO – consisting of mainly glycerides of C_{18} fatty acid [with one or two unsaturated bonds]). The CO and GO in 70:30 ratio gives a gelling agent with desirable properties. Gelling agents that use higher proportions of GO, that is, 60:40 and 50:50 ratios result in fatty acid mixtures of much higher unsaturation. As a result, these gelling agents are more susceptible to oxidation and consequently, the storage life of such soaps (gelling agents) is expected to be lower. A gelling agent with desirable properties may be prepared by the following method: a 70:30 mixture of CO and GO is hydrolyzed with NaOH to obtain a mixture of sodium salts of constituent fatty acids. These sodium salts of constituent acids are then converted into corresponding Al salts or soaps by adding aluminum sulfate solution in the presence of a polymer in emulsion form at 68–70 °C. The presence of polymer during precipitation ensures that the Al soap, as soon as it is formed, becomes coated with the polymer giving a uniform combination of the polymer and the Al soap. The gelling agent thus formed is characterized by determining its ash content, bulk density and moisture content etc. [61, 62] and is mixed with 0.10–0.15% of α-naphthol.

The superior gelling agent developed by ERDL converts gasoline into gel very quickly at room temperature and hence it has been called 'instant gel'. It is used to the extent of ≈8% and its life is 4 years for operational use but 6 years for training purpose. Some distinct advantages of instant gel are:

1) Gelling time is 2–5 min at ambient temperature and 10–15 min at 5 °C.
2) Gel is stable for a long time.
3) Short notice is sufficient for filling of bombs as the fuel can be prepared as and when required at the site.
4) Suitable for preparation of gelled fuel and its subsequent filling in bombs under field conditions.

ERDL (now HEMRL), Pune has also developed Mine Anti-Personnel Inflammable (abbreviated as MAPI) with the use of this instant gel and gasoline. MAPI can be effectively used to prevent the movement of enemy personnel across water surfaces like canal, ditch-cum-bunds (DCBs) and similar water obstacles by generating a high temperature flame that spreads and floats on water. The mine deployed under water bursts open on initiation and gelled petrol floats on the water surface. The floating gelled petrol catches fire from pieces of burning sodium metal and the flame characteristics are: circular dia. of flame: 10–12 m, height of flame: 2–3 m, burning time: 2–3 min and flame temperature: 1100–1200 °C. The assembled mines may be deployed in DCBs or canals, in a row and fired as a single mine or in a group. Six of such mines deployed in a row usually provide a frontage of 100 m. The burning and floating gelled fuel may also cling to any surface or object and thus effectively transmit fire to an object present within the flame zone. If the object is combustible, it burns vigorously under the heat flux from burning gelled fuel [63, 64].

5.5.4.4 **Chemistry of Napalm**

The name 'Napalm' is derived from the first syllables of naphthenic and palmitic acids – two fatty acids first thought to be the active ingredients of the thickener and has been used to designate either a special Al soap employed as a thickening agent or a gasoline gel produced with this agent (used as a flame thrower fuel and for filling of M-69 and M-47 bombs) or a Napalm gel-filled incendiary itself. The gelling agent actually contains soaps of all the fatty acids of coconut oil. Other acids, especially lauric acid, were found to be essential to gel the fuel. Chemically, Napalm is primarily an Al disoap corresponding to the formula $Al(OH)R_2$ derived from a mixture of two parts of commercial coconut oil, one part of oleic acid and one part of naphthenic acid. It also contains some uncombined acid, water and inorganic impurities [65]. The fundamental reactions involved are shown in Equations 5.23:

$$\begin{aligned} &6\,NaOH + 4\,HR + Al_2(SO_4)_3 \rightarrow 2\,Al(OH)R_2 + 3\,Na_2SO_4 + 4\,H_2O \\ &6\,NaOH + 2\,HR + Al_2(SO_4)_3 \rightarrow 2\,Al(OH)_2R + 3\,Na_2SO_4 + 2\,H_2O \end{aligned} \tag{5.23}$$

where HR denotes the mixture of fatty and naphthenic acids.

Aluminum soaps are generally prepared by an aqueous metathesis method where the Al soap of a fatty acid is obtained by the replacement of an alkali metal ion of an alkali soap with Al^{3+} ion in an aqueous medium. Al although trivalent, forms disoaps and monosoaps. No trivalent soaps of Al have been reported. Among them, disoaps are reported to give gels with good stability and gelling characteristics. The gelling characteristics also depend upon the length of the aliphatic acid.

Napalm is a granular solid which readily disperses in gasoline at room temperature. On its addition to gasoline, the gelling agent swells by absorbing the gasoline and rapidly gives a transparent, homogeneous and stringy jelly [66]. A viscous gel increases the burning time of gasoline and the flame is very intense because of high temperature of Al combustion. The flame also creates secondary fires, difficult to extinguish.

The consistency of Napalm gel is variable and depends on many factors. However, 2–4% of Napalm gives a definitely stringy gel whereas 10–12% gives a very elastic gel which is almost solid. Napalm, while satisfactory as a thickener, is hygroscopic and also susceptible to oxidation by atmospheric oxygen resulting in a thickened gasoline with poor characteristics. In the presence of moisture, the soap may hydrolyze as shown in Equation 5.24:

$$\begin{aligned}&\mathrm{Al(OH)R_2 + H_2O \rightarrow Al(OH)_2R + HR}\\&\mathrm{Al(OH)R_2 + H_2O \rightarrow Al(OH)_3 + HR}\end{aligned} \tag{5.24}$$

In order to retard oxidation 0.10–0.15% α-naphthol is added while preparing Napalm powder. During storage of gelled gasoline, oozing out of a thin liquid from the rest of the gel is also reported. This is eliminated by coating a polymer over the Al soap and this is achieved by carrying out metathesis in the presence of a polymer in an emulsion form. Al soap, being insoluble in water, tends to precipitate out immediately after formation and hence fine particles of Al soap are coated with the free polymer leading to a thin coating on Al soap. Further, in order to help proper distribution of the base soaps in gasoline and also to impart uniform characteristics to the gelled fuels, it is desirable to add a peptizer to the fuel before addition of gelling agent. It is reported that a peptizer reacts with the Al–O bonds of the Al soap and lowers the viscosity and gelling time of the gelled fuel. It is reported that a peptizer imparts maximum effect only when it is properly distributed in the gasoline before the gelling agent is added. In other words, the peptizer should be highly soluble in the fuel and should also be uniformly distributed in it [67]. Some studies indicate that the addition of aerosil (finely divided silica) and dicalcium phosphate stabilize the viscosity of the gels.

Phosphorus and its compounds have also been used as incendiary agents against personnel and readily combustible materials. Burning phosphorus produces serious burns and tends to demoralize enemy troops. WP is effective against most easily combustible targets because it has a low combustion temperature but it is relatively ineffective for others.

5.6
Performance Assessment of Pyrotechnic Formulations

The performance of pyrotechnic formulations is assessed by determining various properties such as

- ignition temperature;
- mechanical properties;
- moisture absorption;
- heat output;
- gas volume;
- impact sensitivity;
- friction sensitivity;
- spark sensitivity;
- burning rate;
- luminous intensity;
- IR intensity
- screening performance of smoke.

The impact, friction and spark sensitivities of pyrotechnic formulations are assessed by the methods given in Chapter 3. The outlines of methods for the determination of burning rate, luminous intensity, IR intensity, and total obscuring power of smoke are given in this section.

5.6.1
Ignition Temperature

10 mg of the sample of a formulation is taken for determination and the ignition temperature is determined on DTA instrument at a heating rate of 40 °C per min. The outline of the method is given in Chapter 3.

5.6.2
Mechanical Properties

The mechanical properties (compression strength and % compression) are determined by Instron Universal Testing Machine using a pellet of 20 mm × 20 mm pressed at a pressure of 1000 $\mathrm{kg\,cm^{-2}}$ similar to the method used for plastics [68].

5.6.3
Moisture Absorption

It is determined by exposing the formulation (2 g) at 52%, 63%, 75% and 84% RH for a period of six hours. Moisture absorption is calculated from the increase in the mass which is due to moisture absorption.

5.6.4
Heat Output and Gas Volume

The heat output is determined by a Parr adiabatic bomb calorimeter in an argon atmosphere (5 atm.). The gas volume of a sample is determined in the same set-up except that the sample is burnt at 1 atmosphere of air in place of argon atmosphere(inert atmosphere) and the volume of gases liberated is measured by a water displacement technique.

5.6.5
Luminous Intensity

The illuminating formulations are used as a steady source of light and consequently, illuminating flares are of considerable use to illuminate targets. Similarly, tracer flares are used to define the luminous trajectory. The major component of light produced by illuminating and tracer flares belongs to the visible region (0.4–0.75 μm or 400–700 nm) of the electromagnetic spectrum and is known as visible light. The intensity of visible light is defined in terms of luminous intensity (unit is candela) which is the amount of visible light emitted from a source into a solid angle.

The luminous intensity for various types of illuminating and tracer flares is measured by using a photometer which mainly consists of two parts – optical part (mainly photovoltaic detector) and electronic part (consisting of amplifier, digital meter, computer with interface card and printer). The experimental set-up is shown in Figure 5.5.

The set-up consists of a photometer, a tunnel of 1.5 m diameter with an exhaust fan and a stand to mount the flare. First of all, the photometer is calibrated using a standard quartz tungsten halogen lamp of 1000 watts kept at a distance of 1 foot (0.305 m) from the detector. The flare mounted on a stand is positioned in the

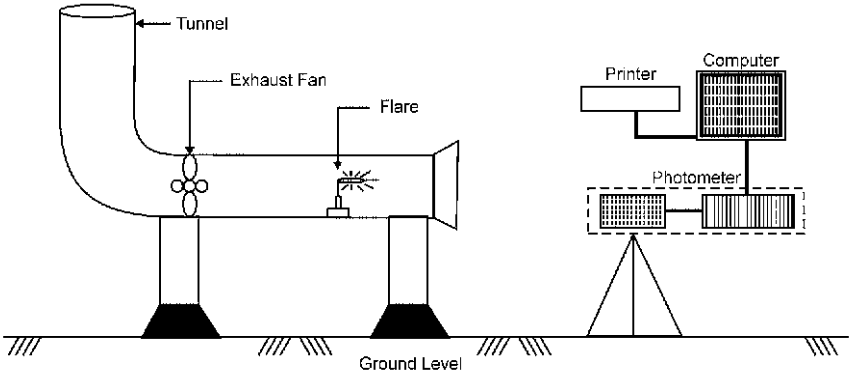

Figure 5.5 Instrumental set-up for measurement of luminosity/IR intensity.

tunnel at a distance of 1 meter from the front surface of the tunnel. The exhaust fan is switched on and when it achieves uniform speed ≈4–5 ms^{-1}, the flare is ignited by a firing control unit. The radiation emitted by the flare is received by the detector system which converts it into an electrical signal, which is amplified by the amplifier. The analog output of photometer is connected to the computer with an interface card where it is further processed and stored. A print-out may be taken whenever required.

5.6.6
IR Intensity

The IR intensity is defined as the amount of optical power emitted from a source in to unit solid angle and is expressed in watts per steradian. The IR efficiency is a product of IR intensity and burning time per gram of formulation.

Infrared radiation plays an important role in defense and is useful for the following military applications:

1) Tracking the path of the missiles, guiding them accordingly and locking the missiles on to the target.
2) Detection of objects in dark.
3) Decoying of the missiles.

The IR intensity of IR flares is measured by using a radiometer which consists of both optical and electronics systems. The radiometer uses the optical system consisting of mirrors and lenses to collect the radiation emitted by the object and focuses this radiation upon an IR detector which converts it into an electrical signal. This signal after amplification is processed by the computer system where it is stored. This stored data can be displayed on the monitor and printed.

The set-up and method of measurement of IR intensity is similar to that of luminous intensity. The distance between the radiometer and tunnel is 82 m in this set-up. While carrying out measurement of IR intensity, the IR flare is mounted on the stand and radiometer is focused onto the flare. The fan is switched on and when it achieves a uniform speed, the flare is ignited and radiation emitted by the flare is received by the radiometer. The radiometer operates in two modes:

(i) Spectral mode The spectral radiant emittance of objects is measured using continuously variable filter (CVF) in the wavelength region of 2.5–14.5 μm.

(ii) Radiometric mode The intensity of the object is measured as a function of time. The measurement is carried out by using any one of the four discreet filters (2.0–2.4, 2.0–3.0, 3.0–5.0 and 8.0–13.0 μm) or any one of the narrowband filter segment using CVF.

The measurement is done in spectral or radiometric mode depending on the mission's requirements.

5.6.7
Burning Rate

Burning rate is of great significance in the case of pyrotechnic formulations as it is indicative of their functional performance. For example, characteristics such as luminosity, IR output etc. are closely related to the burning rate. Similarly, in a pyrotechnic delay formulation, the length of the delay column is decided in the light of the burning rate of the formulation.

The burning rate of black powder varies with its formulation and also with the type of charcoal used for its manufacture. The effect of pressure on the burning rate of black powder has been studied by a number of investigators [69] and they deduced the following relationship (Equation 5.25):

$$R = \beta P^{\alpha} \tag{5.25}$$

Where R = linear burning rate
P = circumambient pressure
and α and β = different constants

It has been reported by Blackwood and Bowden that both the burning rate as well as propagation depend on pressure and are greatly reduced with decrease in pressure [70]. Further, the powder fails to burn at about a quarter of an atmospheric pressure. A general relationship between the burning rate of a pyrotechnic formulation (R) and the ambient pressure is expressed by Equation 5.26:

$$R = R_1 P^{n} \tag{5.26}$$

Where R_1 = burning rate at ground level
P = pressure of the surrounding air in atmosphere
n = fractional index

n can vary from approximately 0.1 for a gasless delay formulation to about 0.7 for a formulation which produces much gas during combustion. The value of n for a gasless formulation based on silicon and lead oxide is 0.08 whereas 0.42 for sulfurless gunpowder.

The linear burning rate which is generally expressed in cm per second is determined using the lead fuse method [71]. However, it is the usual practice in pyrotechnics to report burning rate as inverse burning rate (IBR), expressed in seconds per cm. The method in brief is as follows:

A 25-cm long piece of lead tube is closed at one end by means of a wooden mallet and filled with a pyrotechnic formulation. The tube is tapped on a firm base while filling until it is filled completely. Then the open end is closed with a wooden mallet. The filled tube is then passed successively through 7 grooves and corresponding dies of a lead fuse machine. The lead tube is passed through the dies in descending order of the diameter: 0.653, 0.584, 0.533, 0.490, 0,450, 0.422 and 0.399 cm. The tube is rotated through a right angle as it enters each die in order to prevent formation of fins at the same place. The rolled tube is wiped free from oil and cut into two pieces of length 20 cm each while rejecting the end pieces.

The test piece is ignited at one end with a match-fuse and the burning time is noted by a precision stop-watch from the instant of ignition to the final point. IBR is found by dividing time in seconds by 20. This exercise is repeated with a second piece and the average of the two is reported as the IBR of the pyrotechnic formulation.

5.6.8
Screening Performance of Smokes

The measurement of screening performance of smokes is important because smoke screens are one of the countermeasures for IR surveillance systems. The performance of smoke formulations is decided in terms of total obscuring power (TOP), yield factor (Y), mass extinction coefficient (α) followed by calculation of obscuration effectiveness ($\alpha.\ Y.\ \rho$). These parameters are defined in the following manner.

5.6.8.1 Total Obscuring Power

The quality of a smoke produced by a smoke formulation can be measured in terms of its TOP under standard laboratory conditions. The TOP of a smoke is obtained by dividing the volume of smoke (in cubic meters) produced per kilogram of material by the standard smoke (smoke layer [in meters] necessary to obscure the filament of a 40-watt lamp) and is expressed by Equation 5.27:

$$\text{TOP} = \frac{\text{Volume of smoke produced per kilogram}}{\text{Standard smoke}} \tag{5.27}$$

A set-up consisting of smoke chamber with two windows, IR source and radiometer, as shown in Figure 5.6, is used to study absorption of IR by smoke.

The broad specifications of smoke chamber, IR source, detectors and filters are listed below.

1) Smoke chamber size: $1.8\,\text{m}^3$.
2) IR source: IR lamp 150 W/hot plate.

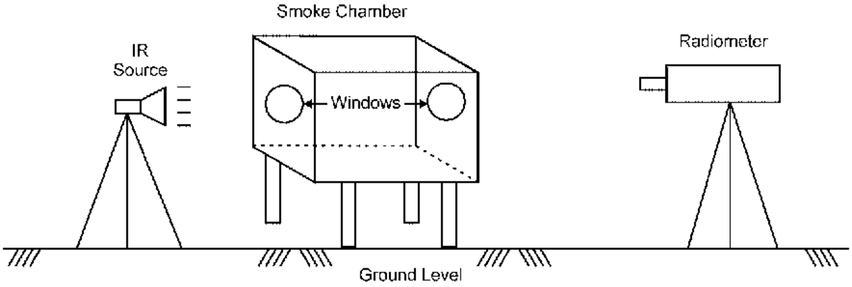

Figure 5.6 Instrumental set-up for measurement of IR absorption by pyrotechnic smokes.

3) Detectors:
   - Pyroelectric detector (Lithium tantalate)
   - Indium antimonide/Mercury cadmium telluride (InSb/MCT) sandwich.
4) IR filters:
   - Discrete filters: 2.0–2.4 μm, 3.0–5.0 μm and 8.0–14.0 μm
   - Continuously variable filter (CVF): 2.5–14.5 μm.
5) Distance between source and radiometer: 12 m.
6) Distance between smoke chamber and radiometer: 10 m.

The smoke chamber is placed between the IR source and the radiometer and the IR output level of the IR source is recorded through the windows of the smoke chamber. Now, smoke is generated in the chamber by burning the smoke pellet followed by recording of the IR output level of the IR source through the smoke generated in the chamber. From these output levels, the percentage attenuation of the IR due to smoke is determined in different wavebands of 2.0–2.4 μm, 3.0–5.0 μm and 8.0–14.0 μm. Similarly, IR radiation and absorption patterns are recorded in the spectral band of 2.5 μm–14.5 μm. The data obtained can be used to assess the efficacy of smokes in attenuating IR target detecting systems.

The TOP values of some well-known smokes given in the literature [28] suggest that the phosphorus class of smokes are most effective for screening and hence are used during military operations.

5.6.8.2 **Yield Factor (Y)**

The yield factor is a measure of efficiency of the conversion of starting material into the airborne obscurant and is defined by Equation 5.28:

$$\mathrm{Y} = \frac{\text{Mass of airborne obscurant}}{\text{Mass of starting material}} \tag{5.28}$$

The smokes produced by WP and RP have large yield factors for various relative humidities. This means that the inference derived on the basis of TOP values of various types of smokes is also supported by the yield factor values, that is, the screening efficiency of the phosphorus class of smokes is maximum.

5.6.8.3 **Mass Extinction Coefficient (α)**

The mass extinction coefficient (α)is a measure of screening effectiveness per unit mass of a material and is defined by the equation based on the Beer–Lambert law. It is related to the transmission of radiation through the smoke and is given by Equation 5.29:

$$\alpha = -\frac{\ln \mathrm{T}_{\lambda}}{\mathrm{c.L}} \tag{5.29}$$

where α = Mass extinction coefficient

T_{λ} = Transmission through a smoke cloud at wavelength λ and is equal to the ratio of final intensity of radiation (I) and initial intensity of radiation (I_0), that is (I/I_0).

c = Mass concentration of smoke
L = Optical path length through smoke cloud

The screening efficiency of a smoke cloud is generally measured in a smoke chamber.

5.6.8.4 Obscuration Effectiveness

As most military smoke systems have limited volume, the effectiveness of the system also depends on the density (ρ) of the obscurant material. The greater the density, the greater the number of scattering particles available. The overall effectiveness of an obscurant material or formulation at a particular wavelength is given by the Equation 5.30:

$$\text{Obscuration effectiveness} = \alpha.Y.\rho \tag{5.30}$$

Based on higher TOP, yield factor and screening efficiency values, it can be safely concluded that WP and RP are better screening agents than HC and other screening agents.

5.7
Life of Ammunition with Pyrotechnic Devices

Armament stores consisting of pyrotechnic devices based on pyrotechnic formulations are subjected to a wide range of natural and induced environmental conditions during handling, transportation and storage. Pyrotechnic devices must be so designed that they function reliably under extreme environmental conditions. Also, the materials for joints and seals used for pyrotechnic devices must be capable of withstanding the expected environmental effects during their lifetime. In order to ensure highest reliability, pyrotechnic devices are tested under simulated environmental conditions. The environmental conditions encountered by armament stores during their lifetime that is, handling, storage, transportation and use are listed in Table 5.12.

At high altitudes, atmospheric pressure is reduced and may induce vaporization and sublimation, which is likely to change the physical and chemical properties of pyrotechnic formulations. Therefore, reliable functioning of pyrotechnic devices depends not only on formulations but also on the quality of seals used to confine the pyrotechnic formulations within the devices. It is the usual practice to carry out all the tests at a higher temperature than the normal storage temperature in order to determine the life and functionality of pyrotechnic devices. Higher temperatures generally affect both the chemical and mechanical degradation of energetic and non-energetic ingredients of pyrotechnic formulations or devices. Therefore, it is not safe to assume that the chemical reactions occurring at such higher temperatures are the same as those occurring at normal storage temperature. It is not possible to predict the exact nature of chemical reactions occurring

Table 5.12 Environmental tests for pyrotechnic stores.

Natural (primary environment)	Induced[a] (secondary environment)
Salt water	Vibration
High temperature	Shock
Low temperature	Collision
Flooding	Acceleration
Freezing	High pressure
High altitude	High temperature
Rain	Chemicals
Thermal shock	Heat radiations
Snow	
Strong wind	
Earthquakes	

a) The conditions are simulated on machines.

at elevated temperatures. However, some rough idea about these reactions may be visualized by the Arrhenius equation (Equation 5.31):

$$k = A.e^{-Ea/RT} \tag{5.31}$$

where k = Rate constant
A = A constant which is independent of temperature
E_a = Activation energy
R = Universal gas constant
T = Temperature in kelvin

The above equation indicates the way in which the rate constant of a pyrotechnic formulation is influenced by the temperature. A rough estimate about the life of the pyrotechnic store may be derived by conducting this study at 5/6 different temperatures and then by using the above equation. Humidity may also have significant effects on the ingredients of the formulation. If moisture ingresses, it may also cause corrosion of mechanical parts in addition to adverse effects on the formulation. Shock and vibration can lead to mechanical failure; vibration being particularly more important in the case of air-launched weapons. Atmospheric pressure may also be important in such cases because rapid changes in atmospheric pressure can cause mechanical failure of the environmental seals. In addition, the apparent performance of a pyrotechnic store is also influenced by:

1) Wind velocity and direction.
2) Background ambient light.

Major qualification tests consisting of a series of functional (static and dynamic) and environmental tests are conducted during the development phase. These tests depend upon the type of device, its performance and application, and functional requirements. The functional tests are also conducted (static and dynamic) before, during and after environmental tests. Such environmental tests are carried out as specified in the Joint Services Guide (JSG) 0102 in two modes – unpacked and packed. The life is assigned to the pyrotechnic store by conducting ISAT (A) and ISAT (B) tests. The general relationships between the duration of the test and corresponding life of the store are as under:

1 year in ISAT (A) = 6 years life at ambient

1 year in ISAT (B) = 9 years life at ambient

5.8
Nanomaterials: Various Aspects and Use in HEM Formulations

Pyrotechnics will take an important step forward by making use of several nanosized fuels and oxidizers for pyrotechnic formulations in the near future. As a result, the performance of such pyrotechnic formulations will become considerably better and thus the problem of availability of space for pyrotechnic devices will not remain as critical as it is now, because several metal powders and oxidizers are commercially available at the nanoscale these days. Before we discuss nanosized fuels, oxidizers and their formulations, it is considered essential to describe in brief nanomaterials (NMs)including carbon nanotubes (CNTs), their methods of preparation, their properties in general, and some important applications.

The term ‘nanotechnology’ is derived from two Greek words ‘nanos’ (meaning ‘dwarf’) and technologia (meaning ‘art’/‘craft’) and it is regarded as the science and engineering of making materials, functional structures and devices of the order of a nanometer. ‘Nano’ means 10^{-9} where 1 nanometer is equivalent to one thousandth of a micrometer or one millionth of a millimeter or one billionth of a meter. In other words, nanotechnology is the term used to describe the creation and exploitation of materials with structural features in between those of atoms and bulk materials resulting in properties of NMs significantly different from those of atoms and bulk materials [72, 73].

Nature serves as a model for NMs and several inorganic, organic and biological materials have existed in nature since the evolution of life started on the earth. Some examples are micro-organisms, fine-grained minerals in rocks and nanosized particles in bacteria and smoke. Also in all natural processes, everything plays out in nanodimensions. Scientists are now attempting to imitate Mother Nature and create such materials synthetically.

Manmade nanostructured materials are of recent origin; their domain sizes have been engineered to precision at an atomic level simply by controlling the size of constituent grains or building blocks. About 50 years ago, the concept of atomic precision was first suggested by Physics Nobel Laureate Richard P. Feynman in his 1959 speech at the California Institute of Technology, USA where he stated ‘*The principles of physics, as far as I can see, do not speak against the possibility of maneuvring things atom by atom…*’. Research on nanostructured materials began about two decades ago but did not gain much impetus until the late 1990s. Nanotechnology has now become a very active and vital area of research which is rapidly developing in industrial sectors and spreading to almost every field of science and engineering. It is expected that nanotechnology will grow to a multibillion dollar industry in the near future and will also become the most dominant technology of the twentyfirst century. These fascinating materials whose dimension ranges from 1–100 nanometers include quantum dots, wires, nanotubes, nanorods, nanofilms, nanoprecision self-assemblies and thin films, nanosized metals, semiconductors, biomaterials, oligomers, polymers, functional devices etc.

5.8.1
Synthesis of Nanomaterials

Basically there are two broad synthetic methods [74–76] for NMs – physical methods and chemical methods.

5.8.1.1 Physical Methods

Several physical methods are currently in use for the synthesis and commercial production of NMs which are as follows:

(i) Inert-gas evaporation technique This is the first and most widely used technique for the synthesis of single-phase metals and ceramic oxides. The generation of atom clusters by gas phase condensation proceeds by evaporating a precursor material, either a single metal or a compound, in a gas maintained at a low pressure, usually below 1 atm. The evaporated atoms or molecules undergo homogeneous condensation to form atom clusters via collisions with gas atoms or molecules in the vicinity of a cold-powder collection surface. The clusters once formed are removed from the region of deposition to prevent further aggregation and coalescence of the clusters which are readily removed from the gas condensation chamber either by natural convection of the gas or by forced gas flow.

(ii) Sputtering technique This is another technique used to produce NM clusters as well as a variety of films; it involves ejection of atoms or clusters of designated materials by subjecting them to an accelerated and highly focused beam of inert gas such as argon or helium.

(iii) Mechanical deformation This method involves generation of NMs via severe mechanical deformation. In this method, NMs are produced not by cluster assembly but by structural degradation of coarser-grained structures induced by the application of high mechanical energy. The nanometer-sized grains nucleate within the shear bands of the deformed materials converting a coarse-grained structure to an ultrafine powder. The heavy deformation of the coarser materials is effected by means of a high-energy ball mill or a high-energy shear process. Although this method is very useful in generating commercial or bulk quantities of nanomaterials, it suffers from the disadvantage of contamination problems resulting from the sources of the grinding media. It is not likely to be used for the preparation of nanosized high energy materials (HEMs) in view of safety considerations.

5.8.1.2 Chemical Methods

The advantage of chemical methods is their versatility in designing and synthesizing new materials that can be refined into the final product. The primary advantage that chemical processes offer over other physical methods is good chemical homogeneity. However, there are certain difficulties in chemical processing. In some preparations, the chemistry is complex and hazardous. Contamination can also result from the by-products being generated or side reactions in the chemical process which should be minimized or avoided to obtain desirable properties in the final products. Agglomeration can also be a major cause of concern at any stage in a synthetic process and it can dramatically alter the properties of the materials. There are several chemical methods for the synthesis of NMs.

(i) Precipitation Method Precipitation of a solid from a solution is a common technique for the synthesis of fine particles. The general procedure involves reactions in aqueous or non-aqueous solutions containing the soluble or suspended salts. Once the solution becomes supersaturated with the product, the precipitate is formed by either homogeneous or heterogeneous nucleation. Growth of the nuclei after formation usually proceeds by diffusion, in which case concentration gradients and reaction temperatures are very important in determining the growth rate of the particles, to form monodispersed particles.

(ii) Chemical Vapor Deposition or Chemical Vapor Condensation Method Nanomaterials are also prepared by chemical vapor deposition (CVD) or chemical vapor condensation (CVC). In these processes, a chemical precursor is converted to the gas phase and then it undergoes decomposition to generate the nanoparticles. These products are then subjected to transport in a carrier gas and collected on a cold substrate, from where they are scraped and collected. The CVC method may be used to produce a variety of powders and fibers of metals, compounds, or composites. The CVD method has been employed to synthesize several ceramic metals, intermetallics, and composite materials.

Semiconductor clusters have traditionally been prepared by the use of colloids, micelles, polymers, crystalline hosts, and glasses. The clusters prepared by these methods have poorly-defined surfaces and a broad size distribution, which is detrimental to the properties of the semiconductor materials. The synthesis of monodisperse clusters with very well-defined surfaces is still a challenge to synthetic chemists. However, some recent approaches used to overcome these problems are (i) synthesis of the clusters within a porous host lattice (such as a zeolite) acting as a template and (ii) controlled fusion of clusters.

(iii) Sol–gel Synthesis The sol–gel synthesis involves the reactions of chemicals in solution to produce primary nanoparticles called 'sols' which can be linked in a three-dimensional solid network called a 'gel' with the open pores being

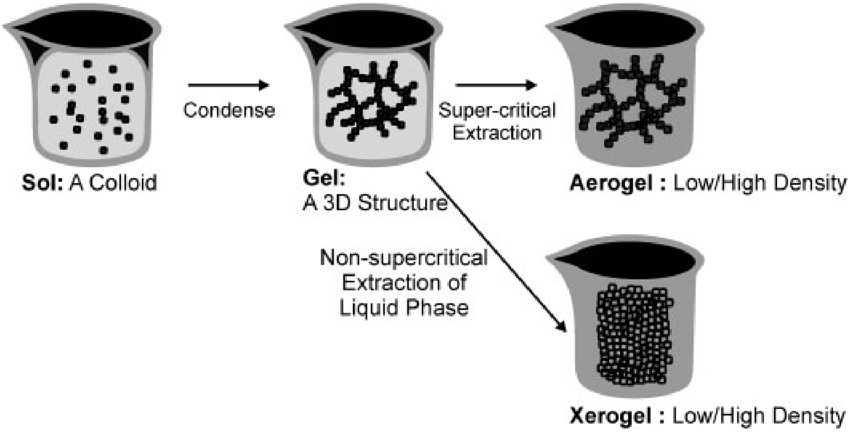

Figure 5.7 General scheme of sol–gel synthesis. Reprinted from A.E. Gash, R.L. Simpson, Y. Babushkin, A.I. Lyamkin, F. Tepper, Y. Biryukov, A. Vorozhtsov and V. Zarko, '*Energetic Materials*', U. Teipel (ed.); © 2005, Wiley-VCH, Weinheim, Germany.

occupied by the remaining solution. There are typically two types of sol–gels: xerogels and aerogels. 'Xerogels' are the result of a controlled evaporation of the remaining solution or liquid phase, yielding a dense, porous solid. On the other hand, 'aerogels' are formed by supercritical extraction (SCE), which eliminates liquid surface tension and thus alters the capillary forces of the regressing liquid that would normally lead to pore collapse. Since the pores are largely kept intact through the use of SCE, the resulting solid is highly porous and light-weight with excellent uniformity. Also the particles and pores are both in the nanometer range. The sol–gel synthesis (Figure 5.7) is fundamentally different from most approaches to energetic material production. It is a relatively simple method performed at low temperatures [77].

In a typical sol–gel synthesis, the metal or the compounds of main group elements undergo hydrolysis and condensation reactions giving gel materials with extended three-dimensional structures. As shown in Equation 5.32 for silicon, addition of an acid or base catalyst to a solution of an alkoxysilane reagent such as tetramethoxysilane (TMOS), water and methanol leads to the hydrolysis of the Si–OMe bonds to form Si–OH functional groups.

$$\begin{tikzcd} \mathrm{Si(OMe)_4 + 4H_2O} \arrow[r, "\mathrm{MeOH}", "\mathrm{Catalyst}"'] & \mathrm{Si(OH)_4 + 5MeOH} \arrow[d, "-2\mathrm{H_2O}"] \\ & \mathrm{SiO_2\ Gel} \end{tikzcd} \tag{5.32}$$

Subsequent elimination of water from two such Si–OH groups eventually gives an extended silica gel matrix (known as a xerogel when dry). Because hydrolysis and condensation reactions occur concurrently, monomeric silanols proceed to result in a xerogel through oligomeric and polymeric intermediates. As these reactions progress, the viscosity of sol–gel solution increases and can reach a ‘spinnable’ stage at which point thin films or fibers can be produced. Otherwise, xerogel products are obtained as porous powders or as monoliths that assume the shape of their container. If desired, the residual Si–OH groups remaining in the xerogel product can be removed at elevated temperature to give fully densified SiO_2.

Nanomaterials are now acquiring major significance and the technology of their production and use is rapidly growing into a powerful industry.

5.8.2
Carbon Nanotubes

Carbon nanotubes were first discovered by Iijima in 1991 during the course of their work on fullerenes. Nanotubes belong to a promising group of nanomaterials. Although other nanotubes based on boron nitride and molybdenum have also been reported, currently CNTs are by far the most important group, and may be characterized in two classes: single-walled (SW) CNTs and multi-walled (MW) CNTs.

5.8.2.1 **Synthesis of CNTs**

Most CNTs are produced by one of the following methods [78, 79]:

(i) Arc Discharge Method This was the first method used to produce CNTs. In this method, two carbon rods are placed end to end with a separating distance of around 1 mm in a closed vessel, which is generally filled with some inert gas (e.g. argon or helium) at low pressure (50–700 mbar). A high temperature discharge is created by a direct current of 50 to 100 amp. driven by approximately 20 V which vaporizes carbon into a hot plasma, some of which recondenses in the form of nanotubes; CNTs are formed on the negative electrode. This method is mainly used for producing MWCNTs. Addition of a small amount of transition metals: iron, cobalt or nickel, favor the formation of SWCNTs. These metals act as catalysts and reduce the temperature required for the growth of CNTs. The disadvantage of this method is that it produces a wide range of CNTs.

(ii) Laser Ablation Method A pulsed or continuous laser is used to vaporize a graphite target in an oven at a temperature ≈1000–1500 °C. Metals such as cobalt, nickel or iron are used as catalysts. This method is well-suited for the production of SWCNTs. The diameter of the CNTs can be controlled by varying the reaction temperature.

(iii) Chemical Vapor Deposition Method All commercial production of MWCNTs is based on catalytic CVD processes. The CVD processes are basically of two types: the catalyst is either deposited on a substrate or the catalyst precursor is continuously fed with the gas stream.

An important innovation in the synthesis of CNTs is the use of organometallic precursors which provide the source of metal as well as of carbon.

5.8.2.2 Some Properties and Applications of CNTs

CNTs exhibit many interesting properties. A SWCNT can be metallic or semiconducting depending on its diameter and chirality. CNTs are characterized by their superior and surprising strength which is 5–200 times greater than that of steel and at the same time, lighter than aluminum. Their electrical conductivity is higher than that of copper and at the same time, heat conductivity is higher than that of diamond. They are resistant to extreme heat and possess superior field emitting properties.

Due to their unique properties, a large number of groups all over the world are working in the area of CNTs for diverse applications and the most important are development and fabrication of sensors and thermal protection for atmospheric re-entry of space vehicles. Gas and glucose sensors based on CNTs have been developed. Some American researchers have recently claimed that they have developed CNT-based sensors for the detection of chemical warfare agents [80].

Nanomaterials and CNTs are of recent origin and their impact is being felt in almost all fields of science, engineering and technology and high energy materials are no exception. It is too early to review their applications in the field of HEMs. However, an effort is being made to outline some nanosized fuels, oxidizers and pyrotechnic formulations along with their applications when used in HEM formulations in order to arouse an interest and motivate researchers to undertake research in this upcoming area.

5.8.3
Nanosized Fuels

Sometimes nanosized powders are also referred as ultrafine (UF) powders with an equivalent size of 10 to a few hundred nanometers. The commonly employed fuels for explosives, propellants and pyrotechnics are aluminum (Al), magnesium (Mg) and boron (B). However, the share in terms of quantity consumed is maximum for aluminum.

5.8.3.1 Nano-Aluminum Powder

Nano-aluminum (n-Al) powder is also called Alex powder in some countries. n-Al powder has been prepared by several researchers through a variety of techniques which are as follows.

(i) Vacuum Vapor Condensation This is regarded as a very suitable method for generating n-Al powder with a narrow particle size distribution [81, 82]. This technique is also known as inert gas condensation (IGC) as condensation takes place in the presence of an inert gas. This is a technique favored by Technology Materials Development (TMD), California, USA for the production of n-Al powder. Now their production rate is around 7–10 kg per day which is likely to go up several times with current continuous operation [83].

(ii) Dynamic Gas Condensation In this technique, radiofrequency induction heating is used to heat Al metal source to ≈1300 °C which results in its volatilization in the reactor containing an inert gas at low pressure. The Al atoms collide, nucleate and then grow in the reactor. UFG particles of Al then condense on cooler parts of the reactor. By changing the reactor conditions, the rate of nucleation, growth and ultimately size of the Al particles can be changed. Finally, oxygen is slowly introduced into the reactor to passivate the resulting UFG Al with a fine layer of Al_2O_3. This process has also been used to prepare UFG of MoO_3.

(iii) Electro-Explosion of Wire (EEW) EEW was first proposed by Narne in 1774 and later by Michael Faraday. It is a well-established method and is suitable for producing nanopowders of any metal available as ductile wire. Sometimes, this method is also known as the plasma explosion method (because plasma is formed as a result of explosion in this process) or simply the wire explosion method. This method has been extensively used for making nanopowders of a number of metals and details are available in the literature [84, 85]. This method is environmentally safe and does not require much energy expenditure and is used for the production of n-powders of tungsten (W), zirconium (Zr), copper (Cu), iron (Fe), silver (Ag), cobalt (Co), titanium (Ti) and platinum (Pt) in the presence of inert gases like nitrogen, argon, helium etc. [86, 87]. Such metal powders are collected and immersed under hydrocarbon or packed under an argon blanket.

(iv) Catalytic Decomposition Process The preparation of n-Al powder (≈30 nm) has also been reported by chemical methods such as catalytic decomposition of H_3AlNMO_3 or $H_3AlN(Me)$ Pyr by $Ti(OPr)_4$ and coated in situ by using a perfluroalkyl carboxylic acid. As Al particles are prepared by using a wet chemical method and coated in solution, in situ, they are free from oxygen passivation, that is, their further oxidation in air is prevented [88].

(v) Cryomelting Process The cryomelting process produces n-Al powder with a diameter of about 40 nm whereas the catalytic decomposition process gives a particle size ≈30 nm. By varying the conditions in the dynamic gas condensation process, an average particle size in the range of 20–200 nm is generally obtained but further larger sizes are also possible. The particles obtained from EEW are generally larger, about 180 nm with a wide particle size distribution [89].

Transmission electron microscope (TEM) images of such n-Al powders indicate the presence of a thin passivation layer of aluminum oxide (Al_2O_3) which provides stability to it in the air. Without this layer, Al nanoparticles would be pyrophoric and also have tendency to agglomerate to form bulk Al metal. In order to protect this n-Al powder further, some researchers have suggested its coating with self-assembled nanolayers using perfluoroalkyl carboxylic acid [90].

Some important characteristics of n-Al are

1) Micron-sized Al powder (m-Al powder) is typically of a light and metallic gray color whereas n-Al powder below 200 nm is dark gray.
2) Bulk density strongly depends on particle size. The small-sized n-Al is very light and fluffy and exhibit bulk densities as low as $0.1\,\mathrm{g\,cm^{-3}}$. On the other hand, large particle sizes exhibit bulk densities above $1.5\,\mathrm{g\,cm^{-3}}$.
3) High surface area of n-Al powder imparts very high reactivity to it.
4) n-Al powder generally absorbs roughly 5% water (by wt) from atmosphere within minutes of exposure. This moisture is likely to have adverse effects on the end use of the powder. Oleic acid and Z6124 (Dow Corning Silane) have both proved to be effective coatings for preventing the reaction of Al with moisture.

In the initial stages, the end use of n-Al was largely dominated by defense-related applications. Small caliber primers for defense munitions, additives for solid and hybrid rocket propellants, enhanced lethality explosives and pyrotechnics and thermite-based weapons are some typical military applications of n-Al powder. The use of n-Al powder has also been reported for some civil applications such as fireworks, automotive inflators and airbag initiators as well as drilling and oil exploration.

5.8.3.2 **Other Nanometal Powders**

1) n-Nickel powder (≈50 nm), nickel–boron alloys amorphous nanopowder (≈20 nm), n-copper (≈90 nm) and nickel–copper alloy (≈45 nm) were synthesized with the use of chemical reduction methods. Further, the effect of these metals and alloy powders on thermal decomposition of AP was also studied and the data suggest favorable performance [91] that is, the catalytic effects on the thermal decomposition of AP are more pronounced compared with the micron-sized metal powders.
2) The preparation of n-Ti powder (≈21 nm) has also been reported by a novel chemical solution synthetic route:

   $$[\mathrm{TiO_2} \rightarrow \text{Titanium catecholate precursor} \rightarrow \text{Titanium hydride} \rightarrow \text{n-Ti}]$$

   by Amarchand and his coworkers [92].
3) Berger *et al.* [93] reported preparation of n-Si (≈10–100 nm) with the use of induction coupled plasma and scaled-up the process to kilogram level. The results of some formulations made with the use of this n-Si powder and potassium perchlorate prove their superior performance over the corresponding formulations based on micron-sized silicon powder.
4) The preparation of n-Li (5–30 nm) and n-W (10–30 nm) powders which possess spherical forms leading to better packing density coupled with higher loadings have also been reported.

5.8.4
Nano-oxidizers

Some nano-oxidizers which play a vital role in HEM formulations, have also been studied and the important among them are:

1) n-Iron oxide or ultrafine iron oxide is a very crucial material for burning rate acceleration of composite propellants and thus for their improved performance. It was prepared by precipitation method by the Chinese whereas the Americans prepared it by a unique vapor-phase decomposition process. It is available commercially in USA under the name: Nanocat Superfine Iron Oxide (Nanocat SFIO) which is a free flowing amorphous powder [94, 95] (reddish brown) with particle size ≈3 nm. Similarly n-Cu_2O (nano cuprous oxide) was prepared by Chinese by the same method that is, precipitation method using $Cu(NO_3)_2$ and NaOH in the presence of a reducing agent (hydrazine hydrate). It was disclosed by the researchers that the concentration of NaOH plays a vital role for the shape of Cu_2O nanocrystals. Needle shaped nanocrystals (≈20 nm) are obtained with high concentration NaOH solution while polygonal nanocrystals of Cu_2O (≈40 nm) are obtained with low concentration NaOH solution [96].

2) A wet chemical method was used for the preparation of WO_3 by Perry and his coworkers [97]. WO_3, on reduction in a stream of hydrogen at 650 °C, is converted to WO_2.

3) The sol–gel method has been extensively used for the preparation of n-metal oxides and organic compounds. The important examples are: n-NiO, n-MnO_2, n-WO_3 and n-Fe_2O_3 etc. which have homogeneous particles, pore sizes and densities. This method affords easy control over the stoichiometry and homogeneity which is not possible with conventional methods. Further, the materials with special shapes: monoliths, fibers, films and powders of uniform and very small particle sizes can also be prepared. The most important attribute of NMs prepared by this method is that they also contain pores of similar dimensions. These pores may be filled with another phase to form a nanocomposite which has proved to be of significant use to the HEMs community [98].

4) Some perchlorates such as n-potassium perchlorate which is expected to be of considerable use in electric matches for primary formulations are also available.

5) In contrast to nano-metal oxides synthesized by chemical methods, some transition metals oxides have also been made by solid state reactions and important among them are NiO (≈10 nm) and Co_3O_4 (≈23–25 nm). Such reactions are very clean and eco-friendly [99, 100].

5.8.5
General Properties of Nanomaterials

Some important general properties of nano-energetic materials (this term refers to nanoparticles of explosives, oxidizers and fuels either in free flowing or encapsulated form) are:

1) The melting temperature of a nanoparticle dramatically decreases and in some cases, it may be nearly 300 k lower than for bulk material [101].
2) Improved homogeneous mixing is obtained using nanosized materials because of their reduced diffusion distances. As a consequence, the time schedule for mixing operations for propellant, explosive and pyrotechnic formulations reduces considerably resulting in the saving of energy.
3) The activation energy of NMs being very small compared with bulk materials, makes them very energetically favored. Thus oxidation becomes relatively easier at the nanolevel compared with the microlevel. Similarly, ignition delay of metallic nanoparticles is expected to be several times smaller than the conventional particles.
4) Thermal conductivity of nano-metal powders (similar to n-Al powder) is, in general, higher compared with micron-sized metal powders. This can increase the energy transfer in the sub-surface region as well as alter the burn-rate characteristics and minimize the incomplete combustion of metal powders.

In a nutshell, the performance of weapons and munitions increases with the use of nanosized particles because of the increased surface area and enhanced heat transfer resulting in reduced ignition delay, burn time, improved mechanical properties and high density-specific impulse. Further, formulations based on micron-sized materials with a wide distribution suffer from defects such as slow energy release, incomplete combustion and inability to support rapid combustion which can be overcome with the use of nanoparticles or nanomaterials [102].

5.8.6
Nanomaterials for Pyrotechnic Formulations

Formulations based on nanoreactants also known as metastable intermolecular composites (abbreviated as MIC and pronounced as ‘Mick’, also referred to as super-thermites or nano-energetic mixtures) were first reported by U.S. Los Alamos National Laboratory (LANL) and appear to be very attractive for a number of applications [103]. Some important MICs are illustrated here along with their properties.

1) Nanoscale thermite, namely Al (≈30–90 nm) and molybdenum trioxide (formulation approx. 40–45% and 60–55% [by wt] respectively) or at O/F mass ratio as 1.4 were studied by Walter and coworkers for burn rates etc. At the end of the investigation, they concluded that the surface area of MoO_3 affects

the burn rate which increases when surface area increases from 40 to 64 $m^2 g^{-1}$. Also, these MICs burn with extremely high burn rates (>100 ms^{-1}) nearly 1000 times higher than the conventional pyrotechnic formulations [104, 105]. This is mainly due to the fact that the diffusion distances between reactants are much smaller in such MICs. This formulation was further evaluated by Kosanke *et al.* and based on their data, the team suggested that it is a potential candidate as an benign substitute for lead-based formulations in electric matches [106].

2) The burning of Al-WOx stoichiometric MICs is relatively easier compared with micron-size-based pyrotechnic formulations [97] and their open-tray burn velocity have been reported to be ≈250 ms^{-1}. Such MICs are likely to find applications in electric matches and gun primers.

3) Bulian and coworkers conducted DSC studies in order to find out the ignition behavior of n-Al with MoO_3, WO_3, Bi_2O_3 and CuO and established that Bi_2O_3 and CuO possess higher reactivity than other oxides. Similarly, the reaction rate of a new MIC-based on Al–$KMnO_4$ is faster than some more widely known MICs such as Al–CuO and Al–MoO_3 as shown by two most commonly employed techniques for measuring reactivity of MICs: open-burn test for measuring propagation velocity and pressure-cell test for measuring the pressurization rate during confined combustion [107, 108]. However, the Al–$KMnO_4$ MIC, though very reactive, has a poor shelf-life compared with other traditional MICs, the reason being the strong oxidizing nature of $KMnO_4$, which slowly converts all the n-Al into its oxide after its manufacture and consequently, the shelf-life is reduced.

4) The sol–gel process is a very important and interesting process for the synthesis of MICs. A team of scientists consisting of Prentice, Pantoya and Clapsaddle validated this by synthesizing a MIC of a ternary thermite: Al–Fe_2O_3–SiO_2 that is, n-Al particles mixed with a sol–gel prepared oxidizer (where Fe_2O_3 and SiO_2 were chemically combined during the aerogel oxidizer synthesis by sol–gel process). The combustion velocity of this ternary thermite was found to be 40 ms^{-1} compared with 9 ms^{-1} for mixed ternary thermite (n-Al powder and commercially available n-Fe_2O_3 and n-SiO_2 that were mechanically mixed in the same ratio using an ultrasonification process). This is believed to be the outcome of the unique mixing between Fe_2O_3 and SiO_2 phases resulting from the two synthetic techniques [109]. By means of sol–gel process, fuel and oxidizer can be put together to mixtures with homogeneities that were not achievable earlier [110].

5) A study of burning rate for a series of conventional thermite mixtures (Fe_2O_3[s]–Al[s] [micron-sized]) and nanocomposites (Fe_2O_3[s]–UFG[s] [nano-sized]) indicates that nanocomposites appear to burn much more rapidly and are more sensitive to thermal ignition than conventional thermite mixtures. At the same time, it is interesting to observe that most of the nanocomposites are found insensitive during standard impact, spark and friction tests [103].

Furthermore, the synthesis of nanocomposites through a sol–gel process (wet process) provides additional safety because wet nanocomposites cannot be ignited until drying is complete. Thus, in other words, large quantities of nanocomposites can be stored safely and dried shortly before use.

6) The replacement of Mg by Alex in MTV formulation, that is, magnesium/Teflon/Viton, accelerates its burning rate considerably. Based on this study, it was suggested that Alex could be used as burn-rate accelerator in high energy materials' formulations. In a study, Tulis *et al*. established an increase in VOD of a pyrotechnic formulation based on lactose–aluminum–AP when Alex was compared with Al flakes [105, 111].

Sarawadekar and Agrawal have recently published an excellent review entitled, '*Nanomaterials in Pyrotechnics*' and readers may refer to this review for additional information on nanopyrotechnic formulations [112] or MICs.

Further, some investigators have conducted research with the use of nanomaterials in propellant and explosive formulations and a gist of their general findings is summarized in the subsequent paragraphs.

5.8.7
Nanomaterials for Propellant Formulations

The effect of addition of n-Al in propellant formulations has been studied extensively in different countries. Their findings are described here without giving much detail; interested readers may refer to the related bibliography.

1) Burn rates of propellants are inversely proportional to the particle diameter of Al powder particles. This is corroborated by the increase in burn rate of propellants on incorporation of Alex in their formulations. The burn rate of solid propellant increases by about 100% on replacement of 9% Al by Alex powder (in a total of 18% Al) coupled with decrease in pressure index.
2) The replacement of Al powder by n-Al powder (Alex) tends to increase the temperature sensitivity of the propellant.
3) The burning surface is much smoother and n-Al enhances the heat feedback to the unburnt solid propellant [113–116].
4) n-Al is also useful as an additional accelerator and also for applications in high-pressure rocket propulsion as an igniter or as a booster. The investigation of Ramaswamy and Kaste suggests the use of n-Al powder and CNTs as energetic burn-rate modifiers not only for propellant formulations but also for all energetic materials [117].

The combustion behavior of Alex was also studied in gun propellants (up to high pressure ≈280 MPa) and it was observed that the burn rate is nearly doubled compared with high-calorie conventional DB propellants [118]. Simultaneously, '*n*' decreases from >0.8 to 0.66.

5.8.8
Nanomaterials for Explosive Formulations

Similar to the effects of Alex addition in pyrotechnics and solid propellants, replacement of conventional micron-sized Al powder by nanosized Al powder (Alex) increases the detonation velocities and heats of detonation of TNT/Al formulations. The increase of VOD is more pronounced in small diameter charges, close to the critical diameter. On the contrary, n-Al powder does not increase the VOD of aluminized PBXs based on inert binders. It is very interesting to observe that the VOD of PBXs based on an energetic binder decreases on substitution of micron-sized Al by Alex [119, 120]. Reshetov and his coworkers [121] reported in the early 1980s that the addition of Alex enhanced VOD of RDX. More recently, an increase in both VOD as well as brisance was demonstrated for a number of TNT-based tritonal and H-6 formulations containing Alex. The improvements in VOD ≈200–300 ms^{-1} and brisance ≈ up to 27% were observed in a number of tritonal charges on replacement of conventional or micron-sized Al by Alex [122].

The Chinese scientists [123] have reported the preparation of nanoscale RDX (≈50 nm) and nanoscale HMX (≈70 nm) by an impinging method [124]. Researchers from China have also reported preparation and characterization of n-NTO and their data indicate that it decomposes at a lower temperature and at the same time, it is less sensitive to impact compared with m-NTO. This property of n-NTO is likely to be of tremendous significance for insensitive munitions [125]. The preparation of n-RDX particles with a mean size (≈110–120 nm) but narrow distribution has also been reported by a novel method known as rapid expansion of supercritical solution (RESS) [126].

5.9
Recent and Future Trends in Pyrotechnics

Some recent and future trends in terms of new materials for pyrotechnic applications are as follows:

5.9.1
Energetic Binders, Plasticizers and Oxidizers

As discussed under explosives and propellants, a number of energetic binders: GAP, NHTPB, poly(NiMMO), poly(GlyN), poly(BAMO), poly(AMMO) and BAMO-AMMO copolymers etc. have been reported in the recent past and are at various stages of development and introduction for bulk production of explosives and propellants for various applications. These polymeric binders are reasonably stable and are of established compatibility with a wide range of ingredients used for explosive and propellant formulations. The data on their explosive properties: impact, friction and electric spark sensitivities, indicate that it is safe to handle these materials. However, there appears to be no report in the open literature on their use in pyrotechnic formulations and coordinated efforts are required in this direction. Similarly, a number of energetic plasticizers: BDNP A/F, butyl-NENA, K-10 etc. need their evaluation in pyrotechnic formulations based on non-energetic or energetic binders [127, 128]. A new explosive called DNNC [1,3,5,5-tetranitro hexahydropyrimidine] which possesses m.p. ≈151–154 °C, density ≈$1.82\,\mathrm{g\,cm^{-3}}$, O.B. ≈ 6% coupled with very low impact sensitivity, holds tremendous potential as an oxidizer for pyrotechnic formulations [129] and needs evaluation for this purpose.

5.9.2
Exotic Salts of Lithium, Rubidium and Caesium and their Formulations

All alkali metal atoms have only one electron in their outermost orbits and as a natural consequence, its removal is easy. The removal of electron from the outermost orbit becomes progressively easier from Li → Na → K → Rb → Cs.

The alkali metals in general yield intense visible light emission due to the radiative transitions of the S^1 electrons. Further, the low ionization energy of these metals (Rb and Cs) results in ease of thermal electron emission which gives rise to a number of interesting applications. In fact, the use of Rb and Cs salts stems from these facts.

The nitrates, chlorates and perchlorates of alkali metals are well-known salts for their application in pyrotechnics. The nitrates of sodium and potassium find application in pyrotechnic formulations on a large scale. In the recent past, several researchers all over the world have explored the use of corresponding salts of other metals belonging to the same group in the periodic table that is, lithium (Li), rubidium (Rb) and caesium (Cs). The nitrate salts of Rb and Cs are high density oxidizers and the HEMs community is mainly interested in them due to the ease of their emissions in the far IR (Rb salts) and the near IR (Cs salts) regions. The exotic salts of Li, Rb and Cs are also likely to find extensive use in illuminating devices and advanced screening smoke ammunition. The excellent reviews by Koch reveal that the elements Li, Rb and Cs, their alloys and compounds serve a surprisingly wide spectrum of applications in pyrotechnics, explosives and energetic devices [130].

Both lithium chlorate and perchlorate have been proposed as oxidizers in explosive formulations [131]. Li nitrate/K nitrate/Na nitrate eutectics (23.5/60.2/16.3) have been proposed by Kruse as oxidizers in illuminating flare formulations [132]. Similarly, $LiClO_4$ has been proposed as an oxidizer in obscurant formulations with B or boron carbide(B_4C) or Si. The obscuring power is mainly due to the presence of hygroscopic LiCl in the aerosol. The formulation B/$LiClO_4$ (60/40) possesses the best performance [133–135] compared with Si/Li ClO_4 (35/65) and B_4C/Li ClO_4 (30/70) formulations.

Caesium compounds find application in pyrotechnic formulations to provide a source of near IR radiation for night vision devices which are widely used as electro-optical equipment for surveillance, searching and tracking in the near IR(NIR) region of the electromagnetic spectrum. Lohkamp suggested the use of flares based on $CsNO_3$/Rb NO_3, hexamine, silicon and epoxy resin binder for this purpose [136]. Similarly, small arms tracers can be tracked in the NIR region with a suitable enhanced night vision device for special operations [130]. The requirement for covert IR illumination flares possessing high IR output, a fast burning rate and a very favorable IR/visible light ratio without chunking of the burning flare formulation is also met by a formulation based on $CsNO_3$. This formulation, consisting of an oxidizer with strong emission in the NIR region ($CsNO_3$ or mixtures in which $CsNO_3$ is the major ingredient ≈70% [by wt] and KNO_3, a metallic fuel with low visible light emission [Si ≈ 9%], a NIR emission enhancer [hexamine ≈16%], a binder [nitrogen containing epoxy resin ≈4%] and a small amount of an additive[single/double/triple-base propellant ≈1%]) was patented by Farnell. These flares are capable of producing a large amount of radiation in the NIR region in addition to conforming to all the stipulated requirements. The effect of the additive is to impart a faster burning rate which increases the intensity of the NIR illumination [137].

Some RP-containing pyrotechnic formulations: RP 50–70, $NaNO_3$ 15–25, epoxy resin 5–25, $RbNO_3$/$CsNO_3$ (IR screening additive) 0.1–10.0 and Mg(combustion accelerator) 0.1–10.0% (by wt) possessing high screening efficiency in the visible and IR regions of electromagnetic spectrum have been reported in the Czech Republic and are claimed to be very efficient for masking military objects and terrain [138].

Berger synthesized $CsNO_3$ and $CsClO_4$; found $CsClO_4$ to be less hygroscopic than $CsNO_3$ and therefore investigated $CsClO_4$/Ti formulations as a possible source for IR radiation in military pyrotechnics. It seems that these formulations may be more suitable for tracking flares in either surface-to-air or anti-tank missiles [139]. In addition to improving concealment in military operations, there are some minor uses of $RbNO_3$ and $CsNO_3$ which are:

1) As additives for muzzle flash suppression [140].
2) Rb and Cs salts of bitetrazole amines (BTAs) as burning rate modifiers for pyrotechnic formulations based on $CsNO_3$ and BaO_2 together with fuels such as B and Si and VAAR as non-sooting binder [141].
3) $CsNO_3$ and $RbNO_3$ as substitutes for KNO_3 in glitter formulations [142].

5.9.3
Dinitramide Salts of Alkali Metals and Their Formulations

Ammonium dinitramide (ADN) and hydrazinium nitroformate (HNF) are potential high performance and eco-friendly replacements for AP in composite propellants and efforts are being made all over the globe in this direction. Similarly, there is a need to study these high performance oxidizers and their salts for pyrotechnic applications. Some groups of researchers have already initiated research in this direction and several alkali dinitramide salts have been synthesized and characterized for their elemental content, solubility, thermal behavior and crystal structures.

Alkali metal dinitramide salts are synthesized from aqueous solution of commercially available ADN by adding corresponding alkali metal hydroxide:

$$NH_4N(NO_2)_2 + MOH \rightarrow MN(NO_2)_2 + H_2O + NH_3 \qquad (5.33)$$

where M is Na, K, Rb and Cs.

The yields are reported [143, 144] to be more than 70%.

Some pyrotechnic formulations: Ti/KDN/NC and Ti/CsDN/NC were formulated and tested for combustion velocity, sensitivity to impact, friction and electrostatic discharge etc. The data show that both formulations are extremely sensitive to impact (the sensitivity being in the range of pure HMX and PETN). Further, it is also seen that the Ti/KDN/NC formulation is less sensitive [145] than Ti/CsDN/NC. On the contrary, the formulations show a moderate sensitivity to friction and electrostatic discharge. The evaluation of such systems as components in ignition formulations appear to be very promising as this may allow replacement of the heavy metal primary explosives which are toxic in nature.

5.9.4
Moisture Resistant Coatings for Metal Powders

Aluminum and magnesium are the metal powders most commonly used on a large scale in pyrotechnics. Whenever, pyrotechnic formulations are exposed to atmosphere specially having high humidity, normal deterioration is intensified by the action of moisture on metal powders and as a result, their performance is affected (the reaction of metal powders with moisture degrades the metal surface resulting in possible reduction in reactivity and hence the performance). This problem is resolved by coating metal powders with organic compounds or polymeric materials etc. The coating greatly reduces or possibly eliminates the reaction of these finely divided reactive metals with moisture during handling, processing and storage etc. to produce hydrogen gas. In addition to deterioration of performance of stores, production of hydrogen gas in systems having minimal free volume can rupture the seals and produce highly non-conducive atmosphere in magazines. Further, coating also reduces the sensitivity of pyrotechnic formulations (to heat, impact, friction and spark etc.) by introducing a somewhat unreactive (inert) coating between the metals and inorganic oxidizers. A wide range of materials: waxes, oils, titanates and a number of polymeric materials (unsaturated polyesters, epoxy resins, fluoropolymers, VAAR, polysulfides etc.) are used to coat metal powders. They have their own advantages or disadvantages in view of the ingredients of pyrotechnic formulations and their intended use. Ethylene–vinyl acetate copolymer has been a subject matter of various reports and research papers and Elvax-360 (trade name of Du Pont, UK) is reported to be very promising because of features such as: (i) coats metal powders very efficiently, (ii) produces individual free flowing particles and hence, free flowing powder, (iii) significantly reduces hydrogen gassing, (iv) imparts comparable performance to the present flare systems using acrylate (Hycar) and Viton-A binders, (v) imparts greater pellet strength compared with the present binders and (vi) renders formulations less impact sensitive than conventional binders [146, 147]. This has been validated through the experimental research of Taylor *et al.* who concluded that Mg/Teflon flares containing 5% Elvax-360 have faster burning rates but equal or greater efficiencies compared with the flares containing Hycar and Viton-A. Further, Elvax-360 containing Mg/Teflon flares have crush strength (an important property for general handling and ability of the formulation to withstand various setback forces) more than double the strength of the Hycar and Viton-A systems.

5.9.5
New Fuels as Substitute for Charcoal

Charcoal is an important ingredient of black- or gunpowder. It is derived from natural sources and therefore its properties depend on the source of its origin resulting in variation in the properties of black- or gunpowder. Several groups of researchers have made an attempt to replace charcoal in black- or gunpowder by synthetic materials and gist of their conclusions is:

1) ERDL, Pune investigated a series of compounds such as 1,3,6,8-tetranitro carbazole (TNC); 2,2′4,4′-tetranitro oxanilide (TNO); 3,3′,5,5′ tetranitro azoxy benzoic acid (white compound), tetranitro diphenyldisulfide (TNDPDS), hexanitro diphenylamine (HNDPA) and nitroindene polymer etc. in order to develop a substitute of charcoal for gunpowder type delay formulations in conjunction with KNO_3 and $Ba(NO_3)_2$. The compounds TNC, TNO, white compound, TNDPDS, HNDPA and nitroindene polymer were synthesized and characterized for physical, chemical, thermal and explosive properties followed by preparation of formulations with KNO_3 and $Ba(NO_3)_2$. These formulations were evaluated for their burning rates, moisture absorption and impact, friction and spark sensitivities. The data of this study concluded that TNC and TNO satisfy all the requirements and are useful fuels for gas producing pyrotechnic delay formulations with oxidizers such as KNO_3 and $Ba(NO_3)_2$. Some general findings of this study are: (i) TNO/$Ba(NO_3)_2$ formulations absorb more moisture than KNO_3-based formulations, (ii) KNO_3-based formulations have faster burning rates compared with those of $Ba(NO_3)_2$ which is attributed to the difference in the m.p.s of KNO_3 and $Ba(NO_3)_2$ and (iii) TNO/KNO_3 (45/55%) is the fastest burning formulation. These formulations were developed by ERDL for some special applications and are finding increasing use as pyrotechnic delay formulations because they burn smoothly and very uniformly. Further, they have excellent storage properties under widely varying climatic conditions [148, 149].

2) Wise *et al.* investigated a number of crystalline organic compounds: polynuclear aromatics, polyphenols, diacids, phthalein salts and phenolphthalein etc. as a substitute for charcoal in pyrotechnic formulations. Charcoal in black powder was substituted by these compounds in order to probe the chemical functionality of charcoal required for combustion. The data indicate that polynuclear aromatics which do not contain any oxygen do not sustain

> combustion. On the other hand, polyphenols, diacids, phthalein salts and phenolphthalein all produced sustained combustion and some even burned faster than charcoal-based black- or gunpowder. One of the formulations containing phenolphthalein which holds tremendous potential to substitute charcoal was investigated further for burning rates at various nitrogen pressures. The combustion rates and photographic features are parallel to those of black powder [150].

A modified black powder consisting of KNO_3, Na_2CO_3 and/or $NaHCO_3$ and S was recently formulated by a German scientist. It possesses decreased sensitivity to impact, friction and does not ignite spontaneously by spark. The author of the patent further claims that the modified black powder is non-hygroscopic, contrary to the original black powder. Thus the modified black powder appears to be suitable for pyrotechnic applications and rock blasting. However, exhaustive trials including storage properties under widely varying climatic conditions with modified black powder are necessary before it really replaces black powder for military applications and rock blasting [151].

5.9.6
High Nitrogen Content-High Energy Materials for Pyrotechnic Formulations

Los Alamos National Laboratory (LANL) USA explored a new area of research recently and reported a new class of HEMs with high nitrogen content (HNC) designated as HNC-HEMs. The HNC-HEMs belonging to the tetrazine family, that is, 3,3′-azobis(6-amino-1,2,4,5-tetrazine) (DAATz) and 1,4-dihydrazino tetrazine (DHTz), received their attention due to their positive heats of formation (+1032 and +530 $kJ\,mol^{-1}$ respectively). Based on the properties of DHTz, it has been reported as an energetic eco-friendly smoke ingredient of pyrotechnic formulations for special applications [152, 153]. Similarly, because of their unique properties and distinct advantages, ammonium, guanidinium and triaminoguanidinium azotetrazolate are likely to find applications as ingredients in pyrotechnics and gas generants [154]. However, these studies being preliminary, need further exploration in detail before they are used in future for project applications.

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6
Explosive and Chemical Safety

The entire spectrum of high energy materials (HEMs) has been discussed in Chapters 1 to 4. As these materials are sensitive, highly hazardous and dangerous in nature, the UNO has formulated some guidelines which are mandatory in order to ensure their safe handling, transportation and storage. In this chapter, all aspects of explosive and chemical safety, including fire safety are discussed. Toward the end of this chapter, a section on prevention or elimination of explosions, accidents and fires is given, which is based on the theoretical aspects, UN guidelines and the author's experience of over 42 years in this field.

6.1
Safety

There seems to be no general acceptance of what is implied by the term 'Safety' and different authors have identified different ways to denote it. Licht has identified five distinct ways in which the term 'Safety' is used.

- Safety or its derivatives used in a 'health' context.
- Safety or its derivatives used in a 'security' context.
- Safety or its derivatives used in a 'special or technical' context.
- Safety or its derivatives used in a 'accident prevention' context.
- Safety or its derivatives used in a 'accident mitigation' context.

Around the same time, Lowrance also explored the meaning of safety. According to Lowrance, a thing is safe if the risks associated with it are judged to be acceptable; judging the acceptability of that risk (judging safety) is a matter of personal and social value judgment. Safety can also change from time to time and be judged differently in different contexts. Lowrance further points out that the term 'Safety' as used in the past was vague and has long been misused. He contends that risks, not safety, should be measured and a thing is safe if the risks associated with it are judged to be acceptable [1, 2].

Everyone faces varying degrees of risks at home, in the workplace or on the road. An example of an 'acceptable risk' would be an act almost everyone of us performs many times a week: opening our mail. Have you ever got a cut while tearing open

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the flap of an envelope? That is an injury associated with a paper envelope. Yet, we do not consider a paper envelope to be hazardous. The risk of injury involved in tearing open an envelope is acceptable. Objects with sharp edges present an interesting example of 'unacceptable risks' which can also be considered 'acceptable' depending on the circumstances. Anything with a sharp edge is hazardous. But we simply accept the risk whenever we use a knife, and use it carefully to minimize the hazard. However, children do not understand this concept of risk and hazard as they certainly cannot exercise the same kind of care as adults. So while a sharp edge on a kitchen knife constitutes an acceptable risk to an adult, the risk becomes unacceptable for children. Similarly, a sharp edge on a child's toy presents an unacceptable risk.

Lowrance defines risk as something we can measure, and safety as something we must judge. Take the matter of a paper envelope. We can measure the severity of the cuts and the probability or the frequency with which they occur. This gives us a measure of the risk involved in opening a paper envelope. We also judge whether this risk is worth taking. Yes, we say, it is acceptable, and we infer that paper envelopes are safe. In the example of knives, we can measure the risk of a cut. We judge that knives are safe for adults who can handle them carefully, but are unsafe for children who cannot. On a child's toy, a sharp edge involves a high probability of harm, poses a high risk and therefore, we judge it unsafe for children. *In other words, safety can be defined as an act of being free from any risk or danger which should be the prime object of any safety program.*

6.2
Explosive Safety

Explosives are sensitive materials which are inherently hazardous unless proper care is taken. Explosives may misbehave if they are not properly handled, stored or transported and hence, the utmost care must be exercised while dealing with them. Therefore ensuring explosive safety is one of the most difficult and demanding tasks. Absolute safety is never possible with explosives and ammunition, although the chance of an explosion may be only infinitesimal, however, it is always present [3]. Explosives are meant to explode but that should not occur at the wrong time or wrong place. If it happens, it becomes an accident causing damage to human beings and property. Accidents also bring down the morale of the workers, disrupt production and entail unnecessary expense. Accidents have been among the major problems faced by all chemical and explosive industries. Experts in safety agree that accidents are 'caused' and do not 'just happen'. A person who feels that an accident was an 'event' which could not have been avoided, reveals his ignorance. Heinrich, the famous 'accidentologist' claims that around 98% of accidents are caused by unsafe acts or unsafe mechanical or physical conditions or both. Further, most accidents can be prevented by correcting the unsafe conditions and by disciplining and educating employees against unsafe acts [4]. The basic Heinrich theory of accident occurrence is summarized below.

- An accident happens only due to unsafe conditions or unsafe acts or both.
- Human faults are inherited or acquired from the environment.
- Unsafe acts or unsafe conditions exist only because of human faults.
- An injury occurs only as a result of an accident.
- Management can remove unsafe conditions and can control the actions of employees thereby preventing unsafe acts which ultimately leads to the prevention of accidents.

Accidents occur only after several repeated unsafe acts and repeated exposure to unsafe conditions. In other words, accidents occur when employees tend to ignore safety rules and regulations, and the management tends to ignore the presence of unsafe conditions. Based on this, it may be summarized that accidents are caused by negligence and can be prevented by forethought. Also, we must learn a lesson from every accident and take appropriate measures to avoid and prevent their occurrence in future. The most important key to avoid accidents while working with explosives is *'Think Before Handling'* as depicted in Figure 6.1.

Explosives and propellants are sensitive, highly hazardous and dangerous materials. Sometimes, they behave in an unpredictable manner leading to serious accidents or explosions resulting in loss of life and property and undesirable

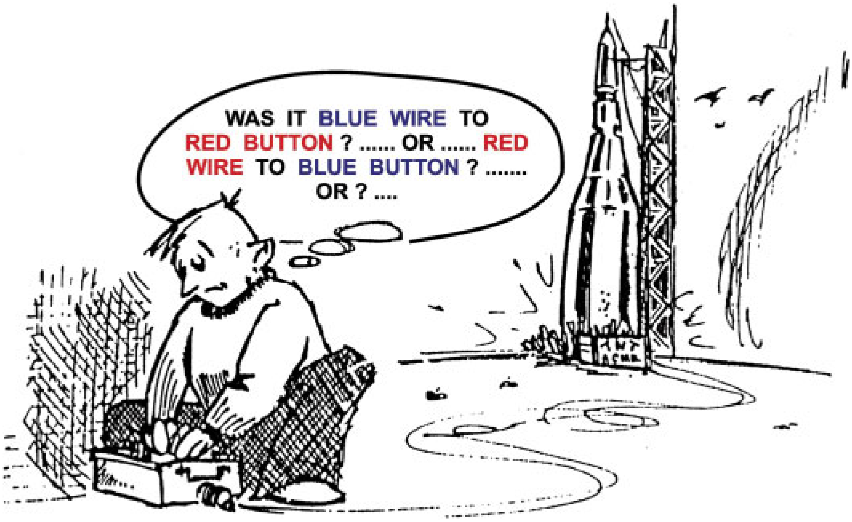

Figure 6.1 Think before handling.*
*Handling of explosives includes – their synthesis, drying, grinding, sieving, testing, destruction, scaling-up and manufacture, coating/treatment, processing, packing, use, collection, offering for sale, transportation and storage etc. Reprinted from M. Defourneaux and P. Kerner, Minutes of the 25th Explosives Safety Seminar, Vol. IV, 1992, p 1; © 1992, Department of Defense Explosives Safety Board, USA.

effects on the environment. Explosions caused by improper handling and improper use of explosives have had devastating effects on humans. For example, Bright Sparklers accident in Sg. Buloh in 1990 resulted in heavy losses in terms of life and property and emphasized the need for proper handling of explosives during their manufacture. Similarly, in a recent explosion in Shaoyang, China, a massive blast ripped through an unauthorized underground explosives warehouse in a residential area killing 90 people and injuring 400 people with flattening of buildings within 100 meters radius. This accident demonstrates the need for a proper storage area for explosives, away from human dwellings and with adequate safety storage conditions. Such accidents have aroused a greater consciousness toward safety, prevention of loss and protection of the environment.

Safety pays and we need to practise safety during every moment of our life, be it at the workplace or at home or on the road. When we are able to convince each and every person about the universal truth of this maxim, accidents along with their impact would be minimized to a great extent, if not totally prevented.

Explosive safety is one of the most difficult tasks due to the fact of striking a balance between operational considerations, that is, delivery of goods or completion of tasks within the stipulated time and safety considerations, that is, protection of life and property. It is well known that safety is one of the factors that ensures progress and prosperity in all walks of life, particularly in the industrial sector and R&D laboratories dealing with HEMs. Further, safety acquires a special importance for agencies dealing with explosives: R&D laboratories, production agencies and users including the Services (Army, Navy and Air Force) as they handle them day in and day out. The entire edifice of safety is not built overnight in any organization and can only be done over a period of time with the concerted efforts and total involvement of all concerned: bench workers, supervisors, managers and top level management. The true hallmark of safety is the progressive reduction of the accident rate and to ultimately achieve the desirable goal of zero accident rate.

6.2.1
UN Classification of Dangerous Goods and Hazardous Chemicals

Based on the recommendations of the United Nations (UN) Committee of Experts on the ‘Transport of Dangerous Goods’, the UN International System of Classification was devised in order to promote the safe transport of dangerous goods and hazardous chemicals. This UN System is detailed in the UN Publication entitled, ‘Recommendations on the Transport of Dangerous Goods’ which is a two-volume set commonly referred to as the ‘Orange Book’ [5]. Further, its use has also been extended universally to promote safety during storage and handling. The basis of this system is classification of dangerous goods and hazardous chemicals by the type of hazards involved. The system consists of nine classes of which Class 1 comprises explosive substances and articles containing explosives (ammunition). Each hazardous substance included in the list of dangerous goods by the UN

Committee of Experts has been allocated a unique four-digit number, called the Substance UN Number (or simply the UN Number). Thus a hazardous substance can be distinctly identified by the Substance UN Number (also called the Substance Identification Number or SIN). UN Serial number 0001 to 1000 are reserved for Class 1 items, that is, explosives and ammunition. The nine classes of dangerous goods and hazardous chemicals with a distinctive diamond shaped label bearing a pictorial diagram for quick hazard recognition are:

Class 1: Explosives and ammunition.
Class 2: Gases – compressed, liquefied, dissolved under pressure or deeply refrigerated.
Class 3: Inflammable liquids.
Class 4: Inflammable solids, substances liable to spontaneous combustion, substances which on contact with water, emit inflammable gases.
Class 5: Oxidizing substances, organic peroxides.
Class 6: Poisonous (toxic) and infectious substances.
Class 7: Radioactive substances.
Class 8: Corrosive substances.
Class 9: Miscellaneous dangerous substances.

Various labels according to the class have been prescribed for each class of dangerous substances and are given in Figure 6.2. The labels prescribed for a particular class of dangerous substances have characteristic background color which are as follows:

Explosive substances	Orange
Inflammable substances	Red
Water reactive substances	Blue
Oxidizers	Yellow
Toxic or infectious substances	White
Radioactive substances	White or yellow and white
Corrosive substances	Black and white

The purpose of these labels is to provide a warning to the general public to keep away and in case of an accident, the emergency services are provided with an indication of a primary hazard likely to be encountered. It is important to recognize that such warning diamonds are intended for use during transport situations. The currently required symbols in terms of the UN recommendations are available from the UN and may be used for national or international transport of dangerous goods.

Military explosives safety is a complex technical matter and, of course, we need to understand it. However, technical understanding is not enough and the world will no longer simply accept the experts' view without logic. We need to assess the risks and quantify the benefits more clearly than perhaps we did in the past.

6.2.1.1 **Hazard Divisions**

Class 1 is sub-divided into six Hazard Divisions (HD) as shown below:

Figure 6.2 Symbols for transport of dangerous goods by road. Based on the 'Transport of Dangerous Goods (Recommendations Prepared by the United Nations Committee of Experts on the Transport of Dangerous Goods)', United Nations, New York, USA, 1956.

Class 1 Hazard Division (HD)

HD 1.1	Mass explosion and blast hazard.
HD 1.2	Major projection hazard.
HD 1.3	Mass fire and heat radiation hazard.
HD 1.4	Only moderate fire hazard.
**HD 1.5	Extremely insensitive detonating substances.
**HD 1.6	Articles containing extremely insensitive detonating substances.

Hazard Division 1.1 Comprises items which have a mass explosion hazard. The major hazards of this division are blast, high velocity projections and flame; the explosion results in severe structural damage, the severity and range being determined by the quantity of explosives involved. There may be a risk from heavy debris propelled from the structure in which the explosion occurs or from the crater.

Examples Initiators, high explosives, mines, 120 mm ammunition, HE shells.

**At present, no military explosives or substances or military explosives articles (ammunition) have been introduced under these two Hazard Divisions for the Services in India. The likely candidates are HNS, TATB, NTO and some plastic bonded explosives (PBXs) which may be introduced to the Services in the near future.

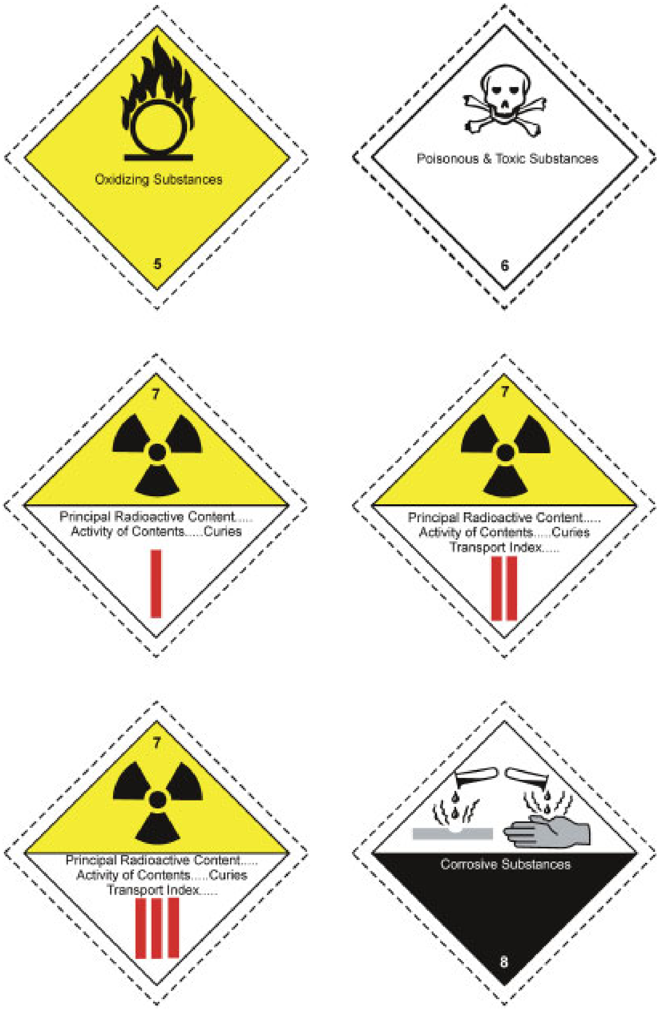

Figure 6.2 *Continued*

Hazard Division 1.2 Comprises items which have a projection hazard with minor explosion effects but not a mass explosion hazard. Items burn and explode progressively, a few at a time. A considerable number of fragments, firebrands and unexploded items may be projected. Some of these may explode on impact and cause fire or explosion. Blast effects are limited to the immediate vicinity.

Examples 81 mm ammunition, 106 mm RCL, grenades

Hazard Division 1.3 Consists of items which have a mass fire hazard and either a minor blast hazard or a minor projection hazard or both, but not a mass explosion hazard. Some items burn with great violence and intense heat, emitting considerable thermal radiation whereas others burn sporadically. They may form dangerous fragments. The firebrands and burning containers may be projected.

Examples Propellants and propellant charges.

Hazard Division 1.4 Consists of items which present no significant hazard and includes items which are primarily a moderate fire hazard. They do not contribute excessively to a fire. The effects are largely confined to the package. No fragments of appreciable size or range are expected. An external fire does not cause the simultaneous explosion of the total contents of a package of such items.

Examples Small arms ammunition, caps, fireworks.

Classes 4, 5 and 6 have been sub-divided:

Class 4 Inflammable solids, substances liable to spontaneous combustion, substances which on contact with water emit inflammable gases.

HD 4.1	Inflammable solids.
HD 4.2	Substances liable to spontaneous combustion.
HD 4.3	Substances which on contact with water emit inflammable gases.

Class 5 Oxidizing substances, organic peroxides

HD 5.1	Oxidizing substances.
HD 5.2	Organic peroxides.

Class 6 Poisonous (toxic) and infectious substances

HD 6.1	Poisonous (toxic) substances.
HD 6.2	Infectious substances.

6.2.1.2 **Compatibility Groups for Explosives and Ammunition**

In order to identify the kinds of explosives deemed to be compatible and also those which have to be segregated to promote safety during storage and transport, they are assigned one of 13 compatibility groups (A, B, C, D, E, F, G, H, J, K, L, N and S) on the basis of similarity of characteristics, properties, stability and accident effects potential. Ammunition and explosives are considered compatible when they can be stored together without significantly increasing either the probability of an accident or, for a given quantity, the magnitude of the effects of such an accident.

Group 'A' Primary explosives, for example, mercury fulminate, lead azide, basic lead azide, styphnic acid, lead styphnate etc.

Group 'B' Ammunition containing primary explosives and not containing two or more effective protective features. For example, detonators, detonating fuses, medium warheads (in boxes).

Group 'C' Propellants or other deflagrating explosives or ammunition containing an explosive such as cordites, propelling charges for rocket motors, power cartridges.

Group 'D' Secondary detonating explosives or gunpowder (black powder) or ammunition containing secondary detonating explosives, in each case without its own means of initiation and without propulsive charge. Also includes ammunition containing primary explosives and two or more effective protective features. For example, demolition charges, aircraft bombs (HE), exploders (RDX/Wax), igniters (gunpowder) and warheads.

Group 'E' Ammunition containing secondary detonating explosives, without its own means of initiation with a propulsive charge (other than the one containing a flammable or hypergolic liquid), for example, missiles A/T HE, mortar ammunition, HE (medium) (plugged).

Group 'F' Ammunition containing secondary detonating explosives, with its own means of initiation, with a propulsive charge (other than the one containing a flammable or hypergolic liquid) or without a propulsive charge. For example, aircraft bombs, HE (medium charges) (fused), mortar ammunition, HE (medium) (fused).

Group 'G' Pyrotechnic substances or ammunition containing pyrotechnic substances or ammunition containing both an explosive and an illuminating, incendiary or lachrymatory or smoke producing substance (other than a water-activated device or one containing white phosphorus, phosphide or a flammable liquid or gel), for example, incendiary bombs, smoke bombs, signal cartridges, pyrotechnic rockets.

Group 'H' Ammunition containing both an explosive and white phosphorus. For example, smoke shell (WP), mortar ammunition smoke (WP).

Group 'J' Ammunition containing both an explosive and a flammable liquid or gel.

Group 'K' Ammunition containing both an explosive and a toxic chemical agent.

Group 'L' Explosives or ammunition presenting a special risk needing isolation of each type.

Group 'N' Extremely insensitive detonating substances (EIDS)s and ammunition based on them.

Group 'S' Explosive or ammunition so packed that any hazardous effects arising from accidental functioning are contained within the package, unless the package has been degraded by fire in which case all blast or projection effects are limited to the extent that they do not significantly hinder or prohibit fire fighting or other emergency response efforts in the immediate vicinity of the package, for example, safety fuses, igniting fuses, small arms tracers cartridges.

These definitions are based on the recommendations of the UN Panel in their publication popularly known as the 'Orange Book'.

Table 6.1 UN Scheme of Classification of Explosives (Combination of Hazard Division and Compatibility Group).

Compatibility Group	A	B	C	D	E	F	G	H	J	K	L	N	S	A-S Σ
H.D.														
1.1	1.1A	1.1B	1.1C	1.1D	1.1E	1.1F	1.1G		1.1J		1.1L			9
1.2		1.2B	1.2C	1.2D	1.2E	1.2F	1.2G	1.2H	1.2J	1.2K	1.2L			10
1.3			1.3C			1.3F	1.3G	1.3H	1.3J	1.3K	1.3L			7
1.4		1.4B	1.4C	1.4D	1.4E	1.4F	1.4G						1.4S	7
1.5				1.5D										1
1.6												1.6N		1
1.1–1.6Σ	1	3	4	4	3	4	4	2	3	2	3	1	1	35

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6.2.1.3 **Hazard Classification**

The combination of the Hazard Division and the Compatibility Group is known as Hazard Classification. Though 78 combinations seem possible from 6 Hazard Divisions and 13 Compatibility Groups, only 35 Classification Codes exist as shown in Table 6.1.

6.3
Fire Safety

Fire safety is a key issue for all organizations dealing with explosives as fires cause fatalities, serious injuries and serious disruption to normal work activities. Once explosives are involved in a fire, they create sudden and intense pressure on its surroundings, usually characterized by the evolution of a large amount of heat, sound and flash. Consequently, any fire involving explosives or ammunition might very well lead to disastrous consequences as a result of mass explosion or fire unless dealt with speedily and effectively. Therefore, manufacture, processing and storage of explosives in any building is always associated with a serious fire and explosion hazard. Unlike other combustible or flammable substances or liquids, explosives, once involved in a fire, do not allow any time to assess the situation and any action needed to avoid catastrophe must be preplanned and embodied in well -established procedures. It may however, be noted that not all explosives in use are of similar characteristics and behavior. Therefore, a knowledge of the behavior and characteristics of different explosives and ammunition is considered essential in order to deal effectively with fires involving explosives or ammunition. Besides the knowledge of the behavior of explosives, a knowledge of the application of proper fire-fighting measures in accordance with the behavior of the explosives when involved in a fire is also essential. An outbreak of fire in the vicinity of explosives or among the explosives themselves, is a potential source of great and immediate danger to life and property.

6.3.1
Fire Divisions

To facilitate fire fighting, explosives and ammunition are divided into four Fire Divisions according to their behavior when involved in a fire and the action to be taken in dealing with such fires. The Fire Divisions are synonymous with the UN Hazard Divisions 1.1 to 1.4 and the hazard decreases with the ascending Fire Division, as described below:

1) **Fire Division 1:** These explosives are susceptible to explosion 'en masse'. The explosion may result in severe structural damage, the severity and range being determined by the quantity of high explosive involved. There may be a risk from heavy debris being propelled from the structure in which the explosion occurs. Possibility of a major hazard to the nearby surrounding area is also there due to the blast, flame and high speed fragments.

2) **Fire Division 2:** These explosives do not explode 'en masse' but have projection hazard and minor explosion effects. These may be exposed to fire for some time before exploding. Although the risk of mass explosion is not involved, small sporadic explosions may occur with increasing frequency as the fire takes hold. These burn and explode progressively a few at a time, coupled with a fragment hazard. A considerable number of small and large hot fragments, firebrands, unexploded and self-propelled items may be projected, some of these may explode on impact and propagate fire or explosion. Blast effects are limited. These explosions may give rise to toxic and corrosive hazard.

3) **Fire Division 3:** This Fire Division consists of low explosives, that is, solid and liquid propellants. When under fire, these explosives pose serious mass fire hazard with minor explosion or no explosion. These would not explode 'en masse'. These are readily ignited and burn fiercely emitting intense heat and thermal radiation over a wide area but may or may not explode. These may give rise to dense smoke with toxic effects during burning, in some instances. These are entirely free from explosion. These items do not form dangerous fragments. Firebrands and burning containers may be thrown around.

4) **Fire Division 4:** These explosives present no significant explosion hazard but have a moderate fire hazard. The effects of fire are usually confined within the package. An external fire would not cause mass explosion of a package of such items. There could be toxic substances in them which may evolve toxic fumes on burning. These explosives belong to UN Compatibility Group K.

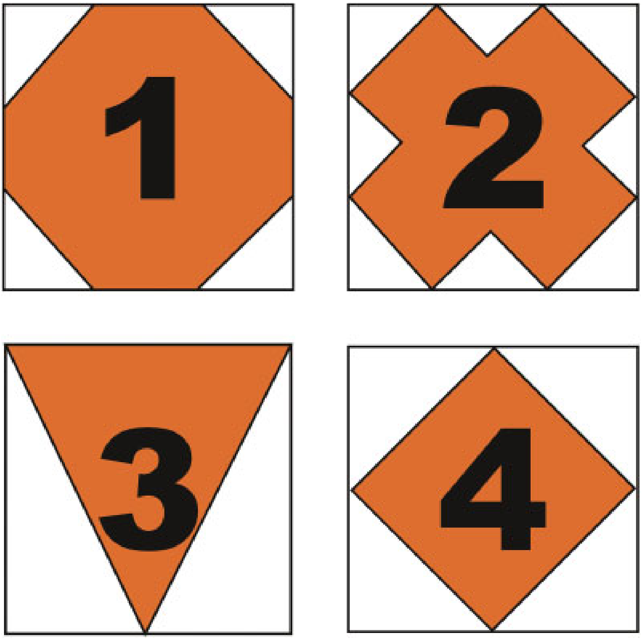

Figure 6.3 Fire division symbols for use on explosive buildings and stacks. Reprinted from DRDO's 'Storage and Transport of Explosives Committee (STEC)' Pamphlet No.6, 1995 (As Amended).

Each of the four fire divisions is indicated by a distinctive symbol (Figure 6.3) in order to be recognized by fire-fighting personnel approaching a scene of fire. The color of all four symbols is 'orange' in accordance with the color code of UN for Class 1 (Explosives and Ammunition) and the numbers are painted in black so that these symbols can be identified from a long range, the symbols differ in shape as follows.

Fire Division	Shape
1	Octagon
2	Cross
3	Inverted Triangle
4	Diamond

6.3.2
Classes of Fires, Fire Extinguishers and Fire Fighting

The combustibles (fuels) differ and therefore, all fires also differ. The use of wrong type of fire-fighting equipment can compound the problems by increasing the intensity of the fire. Fires are classified according to the type of material being consumed.

6.3.2.1 Classes of Fires

1) **Class A Fires:** Fires arising mainly because of paper, wood, textiles etc. are known as Class A fires. The use of foam extinguishers, water pumps, water sprays, and gas cartridges etc. is recommended to fight Class A fires. Further, experts are of the opinion that almost any type of extinguisher is satisfactory for such fires.

2) **Class B Fires:** Such fires are due to fuels such as oil, fat, grease, organic solvent, paint etc. and the use of dry-chemical, liquid, CO_2, or foam extinguishers is recommended.

3) **Class C Fires:** These are electrical fires in equipment and electrical gadgets where live electricity is present. The material that burns is the insulation and component parts. The use of only CO_2 or dry-chemical fire extinguishers is recommended.

   Caution: Do not use water or foam extinguishers! The persons involved may become part of the electrical circuit and get electrocuted.

4) **Class D Fires:** Fires as a result of sodium, potassium, magnesium, lithium, zirconium and all metal hydrides come under this category. The use of dry soda ash fire extinguishers, sodium chloride, dry sand or graphite is recommended to fight such fires.

6.3.2.2 Designations and Ratings of Fire Extinguishers

Portable fire extinguishers are identified as 'UL approved' which means that they have been approved by the Underwriters Laboratories. On the label is a letter which refers to the class of fire for which the extinguisher is intended. The numeral on the label indicates the approximate square-foot area of an average fire which the extinguisher can extinguish. For example, A 5-B extinguisher should be able to extinguish an area of 5-square-feet of a deep-layer flammable-liquid fire. Similarly, A 20-B extinguisher would extinguish a 20-square-feet area of the same deep-layer flammable-liquid fire.

6.3.2.3 Fire-fighting Procedures

1) **Fire in clothing:** Smother the fire by blanket or heavy toweling. The use of emergency shower is also recommended.

2) **General fires:** Determine the type of combustible substance and select a proper fire extinguisher. Cool the area which immediately surrounds the fire and fight the fire with a suitable extinguisher to prevent it from spreading. Then, aim the extinguisher at the base of the fire and finally, extinguish any scattered remnants of the fire.

3) **Electrical fires:** First disconnect the apparatus or equipment by pulling the safety switch or switch off the mains to avoid possibility of being electrocuted. Then use Class 'C' fire extinguisher.

4) **Poisonous-gas fires:** First use the proper self-contained oxygen respirator and then select a proper fire extinguisher. If the fire goes beyond control of the available fire extinguishers, get out of the room immediately. Close the door to prevent drafts and gas spread.

   Caution: Always ensure that no one is left behind.

5) **Fire in explosives:** Explosions invariably accompany a fire especially where combustibles are available. An explosion differs from a fire because an element of pressure is also involved here and it generally occurs in closed volumes. It requires fuel, oxidizer and source of ignition which results in light, pressure and heat (source of fire). The mode of fighting fires involving explosives generally depends upon their fire divisions and the success largely depends on the action taken before the fire develops. It may be noted that a fully developed fire cannot be fought in the absence of the following information:

   - The type of explosives or ammunition stored at the scene of fire.
   - The duration for which the explosives or ammunition may be exposed to fire before they explode.

Most of the time, a fire is fought during the incipient stage with all available means and without waiting for specific instructions. Availability of copious water supply is a must at the site and water should be used in a form that provides effective fire-fighting consistent with the need of fire fighters. However, the general approach may be as follows:

1) The electricity supply to the building should be disconnected.
2) The fire alarm must be operated immediately and the fire brigade called. At the same time, all non-concerned personnel must be evacuated from the scene of fire to a safe place.
3) If drenchers are provided in the building, they must be operated immediately.
4) If fire is detected before the explosives are involved, prompt action with suitable fire-fighting equipment should be taken to prevent development of a serious accident.
5) Upon arrival of the fire-fighting service, action should be directed toward preventing the explosives from getting involved.
6) Fire-fighting operations must be carried out from a safe distance only.
7) Simultaneously, action should be taken to prevent the involvement of adjacent buildings or stacks by the application of large quantity of water sprays onto them.

In other words, the best strategy under the circumstances is to ensure that the fire does not spread to the adjacent buildings or surrounding areas or buildings by following the standard established fire-fighting procedures, that is, by cooling the area which immediately surrounds the fire followed by fighting the fire with suitable fire extinguishers to prevent the fire from spreading. For fighting fires involving incendiary ammunition with magnesium and other metallic powders, extinguishants such as dry sand or dry chemical powder must be used.

It is therefore considered necessary to provide first-aid fire appliances to deal with the incipient fires which if allowed to grow unchecked, might pose hazard to personnel, plant and property. Adequate water supply is essential for fire fighting and the protection of explosives from attack by fire.

Caution: Think! Never underestimate the potential of any fire and never overestimate the capacity of the available fire extinguishers to extinguish the fire. The sooner you attack the fire, the easier it is to put out. Any delay means possible disaster to life and property. Also ensure that the higher authorities, other local laboratories and fire departments are immediately notified.

6.4
Safety Aspects for Transportation of Explosives and Ammunition

Military explosives may be transported by road or by rail, however, rail transport is normally preferred as road transport has serious limitations. Sometimes use of duly approved freight containers for transport of explosives and ammunition both by rail and road is resorted to. Under special circumstances, explosives and ammunition are also transported by air in Service aircraft.

1) Special vehicles known as *'Explosive Vans'* are used to transport explosives. Private vehicles conforming to the requirements of *'Explosive Vans'* may also be used under exceptional circumstances with the approval of a competent authority.

2) A petrol- or diesel-driven vehicle or a trailer towed by a petrol- or diesel-driven vehicle is used. It is better to use either battery-operated trucks or diesel engine vehicles in an enclosed explosive area. If a petrol engine vehicle is used, it must be parked outside the traverse of an explosive building or at least 5 m away from an untraversed building.

3) Explosives are transported by rail in the following types of wagons after the approval of a competent authority.

   - Explosives van (X)
   - Covered wagon, ordinary (C)
   - Covered wagon, with floor covered with wooden planks (CX)
   - Covered wagon, with end ventilators (CV)
   - Covered wagon, eight wheeled (BCXT)
   - Open wagon (KC)
   - Refrigerated wagon (RFG)
   - Freight container (CTR)

Wagons fitted with (i) grease lubricated axle boxes (ii) end falling doors and (iii) doors on the floor (hopper type) should not be used for the conveyance of military explosives.

4) Explosives belonging to different Compatibility Groups are normally transported in separate road vehicles. However, under special circumstances where a full load cannot be made from one group, explosives of Compatibility Groups C, D and E may be mixed and transported together. Further, Compatibility Group 'S' can be mixed with any other Group except 'A' and 'L' Groups.
5) Fused ammunition (Compatibility Group 'F') should invariably be transported separately.
6) The net explosives content in the vehicle should not exceed 4000 kg.
7) After loading the explosives, the appropriate Fire Division symbol should be displayed on the vehicle by the side of the red flag, for guidance to the fire-fighting personnel. If the vehicle is loaded with explosives of more than one Fire Division, the Fire Symbol to be displayed on the vehicle should be of the more hazardous Fire Division.
8) No smoking should be permitted within 30 m of the vehicle or stack containing explosives and no fire or naked flame or light must be allowed within 90 m of the vehicle or stack.
9) The vehicle should not be refueled within an explosives area.
10) No fuel except in the fuel tank must be carried in a vehicle loaded with explosives.
11) All journeys should be completed during daylight as far as possible.
12) The authorized speed of the vehicle is $35\,\mathrm{km\,h^{-1}}$.
13) The vehicle loaded with explosives should never be left unattended.
14) The vehicle loaded with explosives or ammunition should be parked near the police station at the end of the day.

6.5
Safety Aspects for Storage of Explosives and Ammunition

Explosives and their accessories are perishable goods which are liable to deteriorate after prolonged storage especially if subjected to high temperature and high humidity. The methods of packing used by the manufacturers are designed to give maximum protection against moisture. The explosives should remain in good condition for long periods provided they are properly packed and the cases remain unopened.

Explosives and ammunition present a risk of explosion and/or fire. In order to minimize loss of life and damage to property which may be caused due to an accidental explosion or fire involving explosives or ammunition, it is necessary that these are manufactured, stored, or repaired sufficiently away from:

- other buildings or stacks containing explosives or ammunition;
- structures where explosives or ammunition are handled, manufactured, processed or repaired;
- administrative offices controlling such areas;
- neighboring utilities, public or service.

Further, proper storage for explosives and accessories is important, not only to make sure that these materials are kept out of the hands of unauthorized persons but also to maintain them in good condition for use. Explosives and ammunition are generally stored in buildings known as magazines, specially constructed at isolated locations and designed to suit local conditions in the light of established specifications by maintaining the safety distances stipulated in the regulations. Also, flameproof electrical fittings should be provided in these magazines and process buildings.

The safe distances (now referred to as quantity-distances) at which such buildings and structures are to be located from each other depend on a number of factors such as the nature of explosives or ammunition, quantities involved, mode of storage and the degree of protection required. To achieve this objective, regulations have been drawn up laying down the essential features of quantity-distances including a set of 'Tables of Distance' required to be observed for different conditions relating to the nature of risks involved. These regulations have been drawn as a result of the statistical analysis of available information on the effects of experimental and accidental explosions and German bombing in UK together with the results of extensive series of large-scale explosion trials carried out in Germany and Canada by the Explosives Storage and Transport Committee (ESTC), London. Any increase in the explosive limit stipulated in these tables for a building or stack-containing explosives is not permitted without the approval of a competent authority.

The quantity-distance (Q-D) is the minimum permissible distance between a building or stack containing explosives and ammunition or any other exposed structure, assembly place or traffic route. It is based on an acceptable risk to life or property from the effects of mass fire or an explosion. There are two kinds of Q-Ds: inside quantity-distance (IQ-D) which is applicable within the enclosed explosive area whereas outside quantity-distance (OQ-D) which is applicable outside the enclosed explosive area. The term IQ-D refers to the clearance to be observed between a building or stack containing explosives and other buildings or stacks containing explosives or any other building inside an enclosed explosive area. On the other hand, the term OQ-D refers to the clearance to be observed between a building or stack containing explosives and buildings, works and other installations outside an enclosed explosive area. The Q-D necessary for a building or a stack containing explosives to achieve the required degree of safety depends upon the following factors:

1) The Q-D category of the explosive, that is, UN Hazard Division.
2) Whether the building or stack is traversed or not.

3) The net explosive quantity (NEQ) (total net weight of explosive, incendiary and smoke substances) in the building or stack.
4) The charge/weight ratio of the explosive.

The following are some universally accepted rules and regulations, which must be followed ‘in toto’ in order to promote safety during storage.

1) Explosives and ammunition should be stored only in locations designed for that purpose. The types and quantities of ammunition which may be stored in these locations, must be in accordance with the prescribed Q-D regulations.

2) Explosives and ammunition should be properly packed and stored in approved containers, closed and suitably sealed. These should be separated in stacks according to their nature, type and lot number. *Explosives and ammunition in damaged containers should not be stored in a magazine with other explosives and ammunition.*

3) Explosives and ammunition packages should be in good condition, marked properly and free from grit or any other contamination before storage in magazines.

4) Sufficient space should be left between ammunition stacks and the floor, ceiling and walls of the magazine to permit air circulation. The specified distances are

   – 0.6 m between walls and the stack. This clearance may be reduced to 0.3 m if the floor area of storehouse is less than 40 sq. m.

   – 0.6 m between ceiling and top of the stack

   – Width of the gangways between the main stacks shall be 1.2 m.

   – The stacking height of explosive and ammunition packages should not normally exceed 3.5 m. At the same time, toppling of stores or deformation of the containers in the lower tiers should be avoided.

   – Ammunition stacks should be placed at least 1 m away from doorways to provide protection from direct sunlight, rain etc. when the doors are opened.

5) Dunnage should be used to secure the stacks and its minimum height should be 10 cm. which protects the ammunition boxes from dampness, termite infestation and allows proper aeration of the packages in order to ensure long storage life.

6) All doors in the magazine should open outwards.

7) All magazines should be provided with adequate ventilation. The temperature control inside the magazines is also important.

8) The ‘Explosive’ and ‘Man’ limits should be prominently displayed at the entrance of the magazine. Each magazine should have a Bin Card indicating the nature of explosives and their quantities that are stored. *The authorized ‘Explosive’ and ‘Man’ limits should never be exceeded.*

9) The stocks should always be used in the sequence of the date of manufacture which is marked on the cases. This eliminates any accumulation of old stocks and helps to make sure that the materials are in best condition. The contents should be used as early as possible once a case is opened. If all explosive is not used on the same day, the original packing should be folded over and the case closed so as to give maximum possible protection to the contents.

10) Explosive magazines and storehouses should not be used for the storage of non-explosive stores. Inert ammunition should normally be stored in non-explosive storehouses.

In addition, there are some general recommendations which should be kept in mind for explosive magazines.

1) Buildings for storing explosives should be situated at a safe distance from other occupied places. Most countries specify minimum distance between explosive stores and other buildings which must be strictly observed.

2) Explosive stores should be at a safe distance from stores containing highly inflammable materials such as oils, petrol etc.

3) All buildings containing explosives should be securely locked when not attended. All fastenings, locks, hinges, etc. should be designed such that they cannot be removed by unauthorized persons.

4) All storage buildings should be equipped with an efficient lightning conductor and fire-fighting equipment.

5) *Primers, primer materials and detonators should never be stored with other high explosives.* A separate building or annex to an explosive store is usually desirable for keeping detonators. Similarly, black powder must also be kept in separate locations away from high explosives.

6) Boxes of explosives should be opened with a hardwood wedge and hardwood mallet or specially designed non-sparking tools, outside the magazine and at a safe distance from it. *The use of tools such as steel hammers, hatchets or chisels is prohibited. Breaking bulk (removal of explosive from its original packing or cartridge wrapping) is not recommended in storage buildings.*

7) All possible precautions must be taken to exclude the chance of accidental fire or explosion by prohibiting smoking and carrying of matches or any other means of producing light in the magazines.

8) All undergrowth and vegetation should be kept cropped close to the ground for a sufficient area around the magazine and overhanging trees should be felled or have their branches removed.

9) Care should be taken to make sure that explosive magazines are kept in good condition. They should be inspected regularly for the condition of magazine and for the condition of stocks.

10) The inside of all buildings containing explosives should be kept clean and free from grit and packing materials.

11) It is advisable to erect a strong fence at a suitable distance from the magazine to prevent the access of unauthorized persons or animals.

12) The location of sites for magazines is also very important and therefore, this should be kept in mind before taking a decision for construction of a magazine,

    - Explosive magazines should be located as far as possible away from inhabited buildings or places where people congregate. It is recommended that the local inspector of explosives or other licensing authorities should be consulted before constructing a new explosive magazine and care should be taken to ensure that the statutory distances from other buildings and property are maintained. This also depends on the quantity of explosives involved.

    - The best sites for magazines are on well-drained and sloping grounds. *It is not advisable to build underground explosive magazines since these are almost invariably damp. This is liable to induce deterioration of the explosives more rapidly. In some countries, it is illegal to store explosives underground.*

    - The vegetation around magazines and explosives operating facilities should be controlled to minimize potential damage to the magazine or facility from grass, bush or forest fires or from erosion. A firebreak of about 15 meters wide (free from combustible materials) should also be maintained around the magazine or facility.

    - Flame or heat-producing devices should not be allowed in or around any explosive facility or magazine.

6.6
Safety Aspects for Handling of Explosives and Ammunition

Handling includes practically every activity with explosives. Some commonly performed operations are: synthesis; washing; heating and drying; sieving; wet and dry milling; blending, formulating and mixing; punch and die pressing; isostatic pressing; extruding; machining; melting and casting; assembly and disassembly; packaging; in-plant movement; transportation; storage and sale. *In other words, before planning any activity with explosives, think before you proceed* [6] (Figure 6.1). In addition, the following measures will promote safety while handling explosives:

1) All personnel who handle explosives or ammunition should always remember that a high degree of care is to be exercised since even the slightest degree of negligence may lead to accidents.

2) All personnel should have a detailed knowledge of UN Classification of hazardous or dangerous chemicals and other regulations pertaining to storage and transportation of explosives in order to reduce the inherent hazards associated with the explosives-related work.
3) All personnel handling explosives are recommended not to wear garments made of synthetic fibers.
4) Any tools used for the explosive related work should be of soft non-ferrous metals such as brass, copper or bronze, that is, tools made of non-sparking metals. *Iron and steel tools should be prohibited as they might cause sparking. Tools made of beryllium–copper alloys which are non-sparking are also recommended for this purpose.*
5) Personnel working in the magazines must be familiar with the general rules governing their conduct, that is, use of overshoes, prohibiting smoking or carrying of matches etc.
6) Excessive handling of explosives should be avoided as far as possible.

6.7
Static Electricity Hazards

This chapter on safety would be incomplete without a discussion on hazards associated with static electricity and connected issues.

When two dissimilar bodies rub against each other, it causes disturbance of the electric charge at the interface. As a result, excess positive charge is localized on one body and at the same time, excess negative charge on the other. When the accumulated ‘static charge’ exceeds the breakdown potential of the medium (air), it results in a high voltage–low current discharge in the form of a ‘spark’. This electric spark which is a result of the accumulated charge may have sufficient energy to initiate explosives because of their low ignition energy. Therefore, static charge poses a potential hazard especially while handling sensitive materials like explosives during the course of processing and manufacture of the explosives, their transportation, assembly and breakdown of ammunition, conduct of tests, firing trials etc. Stringent precautions should therefore be taken in order to avoid formation of static charges while handling explosives and hence accidents.

The electrostatic charge can accumulate on various moving parts, human bodies and explosives during processing, that is, flowing, pouring, filling, sieving, blending, coating etc.

A person wearing garments made of synthetic fibers and insulated from earth by non-conducting footwear can acquire static charge easily because of the friction between clothes and body. Thus that person becomes a source of hazard in a building where explosives are being handled or processed. Therefore, persons working in explosive buildings should not wear synthetic clothes. Also, they should discharge themselves before entering the building with the help of electrostatic discharger installed at the entrance of the building.

There are two types of hazards caused by static electricity while handling explosives.

- The spark discharge might initiate the explosives.
- An electric shock (high voltage–low current) might cause involuntary movement of the person handling explosives, and thus cause an explosion.

Some methods for prevention of accidents due to static electricity are given below.

1) **Bonding:** The voltage difference between two conductive materials is reduced to zero by bonding them, for example, bonding one end of a conducting wire to one of the materials and other end to the second material.

2) **Grounding and earthing:** Even after bonding the materials, some voltage difference may still exist between them. This difference is reduced to zero when they are earthed or grounded after bonding. This eliminates the charge build-up between various parts of a system, thus eliminating the possibility of any spark formation.

3) **Conducting flooring:** Conducting flooring should be provided in a building where initiatories or other compositions with spark sensitivity of less than 45 mJ are handled. The conducting floorings are usually made of polymeric materials which have been mixed with conducting materials such as carbon or a metallic powder. These materials remain good conductors despite changes in environmental parameters like humidity, temperature etc. and are considered to be bulk/volume conductors. These should be used in areas where maximum precaution against static charge is needed, that is, in buildings where initiatory compositions, electro-explosive devices (EEDs), pyrotechnic compositions (with ignition energy of 1 mJ or less) etc. are handled.

4) **Antistatic flooring:** These are made of polymeric materials mixed with detergent type of materials which, when exposed to humid environment absorb water and behave like conducting flooring at the surface. The conducting properties of these materials change rapidly with environmental conditions. These are used in areas where less stringent precautions are acceptable (i.e., ignition energy greater than 1 mJ but less than 45 mJ) but where there is a risk of electric shock to the personnel.

5) **Humidification:** As water (moisture) is a better conductor than air, humidification of the room where explosives are handled reduces the chances of accumulation of static charge. In many explosives process buildings, RH of about 60 to 65% is invariably maintained.

6) **Ionized atmosphere around the materials:** Accumulation of static charge can also be controlled by the ionization of air close to the surface which is vulnerable to such accumulation of static charge. A beta-ray emitting device (using Tl-204) is placed close to PETN sieving equipment. The beta rays ionize the air around the PETN surface thereby increasing its conductivity, so that the accumulated static charge on the surface is conducted away safely [7–13].

6.8
Extremely Insensitive Detonating Substances and Ammunition

Common explosives like TNT, RDX and HMX which are in use, were considered adequate in the past for all weapon applications. But because of a number of accidents involving the initiation of munitions by impact or shock aboard ships, aircraft carriers and ammunition trains, these explosives have become less attractive. Hence, there has been worldwide research to synthesize explosives which possess respectable performance coupled with low sensitivity. The problem of warhead vulnerability has also become acute in the recent past. The first solution offered to this problem was the invention and use of plastic bonded explosives (PBXs) which consist of a polymer matrix encasing a conventional granular explosive, thereby offering some immunity to fire and bullet impact. It was observed subsequently that the use of PBXs alone is no longer sufficient. This problem gave rise to the idea of using an intrinsically less-sensitive explosive and as a result, spawned another class of explosives (thermostable explosive molecules coupled with low-impact sensitivity) termed insensitive high explosives (IHEs). TATB is the first member of this class and is considered as a reference explosive for non-vulnerable explosives. TACOT and DINGU are other explosives of this class. TATB is well-known for its insensitivity and is currently employed as an IHE for specialized applications such as modern ordnance, space and nuclear applications. The research conducted in the last two decades indicates that the recent trend in the field of HEMs is the development of extremely insensitive detonating substances (EIDS) coupled with performance matching with at least Composition B (RDX/TNT 60/40) and ammunition based on them. Such substances and formulations are particularly attractive for applications where resistance to accidents, that is, safety is of prime importance. The 'United Nations Committee of Experts (UNCOE) on Transport of Dangerous Goods' approved a new test protocol known as UN Test Series-7 in 1998, and a new Hazard Division (HD 1.5) for EIDS and Hazard Division 1.6 (HD 1.6) for articles based on these substances (Table 6.2).

Several national laboratories in the USA in association with the military services provided the driving force in this direction. Similarly in Europe, the North Atlantic Treaty Organization (NATO) was the focal point for a similar effort, culminating in guidelines to be used for the testing, storage and transportation of EIDS and articles based on these substances (now called EIDS ammunition). The benefits include greater material and personnel safety in all logistics phases in the life-cycle of munitions and the potential for increased density of munitions in land-limited storage areas that are adversely affected by encroachment of civilian populations [14]. The UN Committee has defined HD 1.6 as the Hazard Division which comprises articles that contain only extremely insensitive detonating substances and which demonstrate a negligible probability of accidental initiation or propagation. The risk from the articles or ammunition of HD 1.6 is limited to the explosion of a single article or item of ammunition. A new 'Compatibility Group' was also created at the same time, namely the Group 'N' which is only used for HD 1.6 articles or ammunition which then necessarily carry the Classification Code '1.6N'.

Table 6.2 UN test series – 7 for hazard class/division 1.6 articles.

Test number	Test name	Number of trials	Test vehicle	Failure criteria
A. Extremely insensitive detonating substance tests				
7(a)	EIDS cap test	3	No.8 blasting cap in explosive contained in 80 mm × 160 mm cardboard tube and resting on a 1 mm thick steel plate.	Detonation as evidenced by hole punched in witness plate
7(b)	EIDS gap test	3	73 mm × 280 mm Steel Pipe with 70 mm long Plexiglass gap between Pentolite donors and explosive fill and resting on a 20 mm thick witness plate	Detonation as evidenced by hole punched in witness plate
7(c)(i)	SUSAN test	5	51 mm × 102 mm explosive billet in aluminum cup as nose of massive steel projectile. Launched from 81.3 mm gun @ 333 m/s into steel wall	≥27 kPa overpressure at 3.05 m
7(c)(ii)	Friability test (alternate for SUSAN test)	3	Explosive billet 18 mm diameter launched at 150 m/s into standard wall. Impacted material burned in closed bomb.	>15 MPa/ms pressure rise rate in closed bomb
7(d)(i)	EIDS bullet impact test	6	Single 50 caliber AP bullet impact into explosive-filled 45 mm id × 200 mm steel pipes with torqued end caps	Explosion or detonation
7(d)(ii)	Friability test (alternate for EIDS bullet impact test)	3	Explosive billet 18 mm diameter launched at 150 m/s into standard wall. Impacted material burned in closed bomb.	>15 MPa/ms pressure rise rate in closed bomb
7(e)	EIDS external fire test	3	Explosive-filled 45 mm id × 200 mm steel pipes with torqued and caps tested in kerosene-soaked wood fire. Five items per trial or fifteen in one trial	Detonation or >15 m fragment throw

Table 6.2 *Continued*

Test number	Test name	Number of trials	Test vehicle	Failure criteria
7(f)	EIDS slow cook-off test	3	Explosive-filled 45 mm id × 200 mm steel pipes with torqued and caps tested to destruction at 3.3 °C/hr rise in temperature.	Detonation or >3 fragments
B. Article tests				
7(g)	1.6 article external fire test	1	Ammunition in shipping configuration containing EIDS in kerosene-soaked wood fire. Three items, minimum	C/D 1.1, 1.2, or 1.3 response
7(h)	1.6 article slow cook-off test	2	Ammunition containing EIDS heated to destruction at 3.3 °C/hr rise in temperature	>Burning
7(j)	1.6 article bullet impact test	3	Ammunition containing EIDS subjected to triple 50-caliber AP bullet impact.	Detonation
7(k)	1.6 article stack test	3	Ammunition containing EIDS in both unconfined and confined shipping configuration stacks	Propagation

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The tests and criteria which allow to assign an article (munition) to the Hazard Division 1.6 during storage are same as those decided by UN for transport. This decision fits the general policy of the Group which stipulates the use of the same tests and criteria in storage, as in transport, since the aggressions encountered in storage and transport are generally considered not significantly different. The UN Test Series-7 may be considered as the most complete and severe list of requirements for insensitive munitions, and UNCOE on the Transport of Dangerous Goods approved a new test protocol (UN Test Series – 7) which describes how to assign a classification in HD 1.6 to a new ammunition containing only EIDS as high explosive, by applying:

1) Tests 7a–7f for substances to qualify a new explosive as an EIDS;
2) Tests 7g–7k for articles containing only EIDS as high explosive.

In the USA, six types of EIDS tests are performed at the substance level. These include a No. 8 Blasting Cap test, an Extended Card Gap test (at one fixed gap), External Fire, Slow Cook-off, Bullet and SUSAN Impact tests. In Europe, the Friability test has been substituted for the Bullet Impact and SUSAN Impact tests. The testing apparatus and methods are described [15, 16] in UN Test Series-7. The Atlantic Research Corporation (ARC), USA, through sustained research and careful formulation to maintain performance while decreasing sensitivity, assigned Formulation E as EIDS and MK-82 bombs loaded with Formulation E as EIDS ammunition [17]. SNPE, France, based on their exhaustive study, proposed two true EIDS: B2211 for underwater and air blast applications and B2214 for naturally fragmented warhead [18]. In a further study, Pitts *et al.* concluded that AFX-770 and AFX-931 also meet EIDS criteria and AFX-770 article test results appear to be encouraging [19]. EIDS and insensitive munitions is a subject of research all over the world and is being pursued vigorously in view of overall safety [20, 21].

6.9
Hazard and Risk Analysis

Hazard and risk analysis is a vast subject by itself and is extensively covered in the literature [22]. In order to plan to avoid accidental hazards, the hazard potential must be evaluated. Many new methods and techniques have been developed to assess and evaluate potential hazards, employing chemical technology and reliability engineering. These can be deduced from 'Fault Tree Analysis' or 'Failure Mode Analysis'[23]. In these techniques, the plant and process hazard potentials are foreseen and rectified as far as possible. Some techniques such as Hazards and operability (HAZOP) studies and Hazard Analysis (HAZAN) have recently been developed to deal with the assessment of hazard potentials [24]. It must be borne in mind that HAZOP and HAZAN studies should be properly viewed not as ends in themselves but as valuable contributors to the overall task of risk management.

6.9.1
Hazards and Operability (HAZOP)

It is meant for systematic examination of the design to identify hazards. For a HAZOP study, the operability part is important, and more operating problems which are likely to contribute to the hazards are identified. HAZOP analysis aims at two particular outcomes: (i) identification of serious incidents known as 'Top Events' which may endanger the lives of people and environment; (ii) causes which can lead to 'Top Events'. HAZOP is now widely used for designs of new plants or plant extensions and less widely used on existing plants. HAZOP is therefore recommended for application to all new designs in order to identify the hazards and problems that stifle efficient operation. HAZOP is carried out only after the line diagrams or process and instrumentation (P&I) diagrams are worked out completely. This technique provides opportunities for people to let their imagination run free and think of all possible ways in which hazards or operating problems may arise [25, 26].

6.9.2
Hazard Analysis (HAZAN)

HAZAN, on the other hand, is a process to assess the probability of occurrence of such accidents and to evaluate quantitatively the consequences of such happenings, together with value judgments, in order to decide the level of acceptable risk. HAZAN is also sometimes referred to as Probabilistic Risk Assessment (PRA) and its study uses the well-established techniques of 'Fault Tree Analysis' and/or 'Event Tree Analysis'

HAZAN has become an essential feature for each operation in a chemical processing plant and includes all techniques to assess hazard quantitatively in terms of workers, material, machine, time, and profit. Hazard (indicator of an unexpected happening) is avoidable and a proper foresight can make a system foolproof to overcome Murphy's Law [27], that is, *'Things will go wrong in any given situation, if you give them a chance'* or *'Whatever can go wrong, will go wrong'* or *'Anything that can go wrong, will'*. The hazards associated with the loss of workers, machine or material are frequently analyzed but the loss of time and quality cannot be removed from the scope of HAZAN.

A HAZOP study is cumbersome and time-consuming. However, it is believed that the outcome of a perfectly carried out HAZOP study is that no HAZAN (or PRA) study is needed.

6.10
Chemical Safety

The HEMs are basically chemicals containing groups such as $-NO_2$, $-ONO_2$, $-N_3$, $-OClO_2$/$-OClO_3$, $-O-O-$, $-C{\equiv}C-$etc. usually termed 'explosophores' as they impart special features and are the major ingredients of explosive, propellant and pyrotechnic formulations. Therefore, the regulations of explosive safety are equally applicable to chemical industries. In other words, by following the regulations of explosive safety, the number of accidents in the chemical industry may be minimized or totally eliminated.

6.11
Prevention and Elimination of Explosions, Accidents and Fires

The author of this book came in contact with explosives when he commenced his research on explosives leading to a Ph.D. in Chemistry [28] way back in 1967. The study consisted of the synthesis, characterization and performance evaluation of some transition metal picrates and picramates in order to explore the feasibility of their use in place of existing primary explosives. During the last 42 years, he has worked in various universities: Gorakhpur University, St. Etienne University France, Cavendish Laboratory (Cambridge University) UK and Explosives R&D Laboratory/High Energy Materials Research Laboratory (Defence Research and Development Organization) India, in various positions. While working in these universities and R&D Laboratories, he has acquired vast experience as a bench worker, researcher, scientist, supervisor, manager and Associate Director. The author:

- worked with his own hands as a research scholar and scientist;
- supervised the work (as a Sectional Head);
- managed the work (as a Group Head);
- directed the work (as an Associate Director);
- investigated the causes of accidents as a result of explosion for many accidents.

In other words, the author has sufficient insight into the causes of explosion from different angles and concludes that the areas mentioned in the subsequent paragraphs require special attention at all levels, that is, right from the most junior (bench level) worker to the top management (head of the organization, laboratory or factory) to eliminate or reduce the frequency of explosions, accidents or fires.

6.11.1
Operations and Organization

The most important point which should be kept in mind while working in a laboratory or factory dealing with explosives or hazardous chemicals is

'Think before you commence your work' or
'Know what you are going to do before you really do it'

This implies that while working with explosives, think for a while even before thinking of going to the toilet: 'Is my absence going to affect my work?' or 'Can this lead to an explosion?'

Remember

1) Advance planning to counteract the possibility of an accident will greatly minimize the consequences.
2) Any experimental work related with explosives or hazardous chemicals should always be performed by a team of two persons using minimum possible quantity.

The planning of a process involving explosives, ammunition and toxic chemicals that can lead to explosion at the workplace should always be based on the following basic rule known as the cardinal principle of safety [29–31].

- a minimum number of persons for handling;
- the smallest possible quantity of explosive;
- the shortest possible time.

In other words, the cardinal principle of explosive safety is exposure of a minimum number of people to the minimum amount of explosive for the minimum amount of time [32].

For all operations, activities or tasks, written procedures usually termed Safe Operating Procedures (SOPs) should be made, vetted by a Committee of Experts (COE) and approved by the Central Authority. Subsequently, no deviation/s should be made without the approval of the Central Authority. All operations or activities should be supervised by the next level of leadership, that is, supervisor or senior scientist. Thus, careful planning and strict supervision must be followed to eliminate accidents or fires.

Remember

1) Constant vigilance is the best safeguard.
2) The concept of careful planning, strict supervision and Central Authority appears to be the solution to this problem.

It is observed that the task of safety is frequently assigned to less-qualified or incompetent persons. In reality, there are only one or two individuals who are competent or active in the Safety Group. The safety is adversely affected if these competent individuals change their position within the organization or leave the organization for any reason. The management should therefore foresee this problem and provide a workable solution [33].

Remember

Only experienced and dedicated persons should be assigned the task of safety.

6.11.2
Honor the Explosives

Explosives are sensitive materials which are inherently hazardous unless proper care is taken and work is done with a relaxed mind. Any work done in a hurry while handling explosives may prove to be disastrous. A casual attitude adopted because of the small amount of explosive involved or an insignificant task, such as disposal of explosive waste etc. or overconfidence that nothing will go wrong, may be treated as an open invitation to accidents or fires. *To work with explosives with a relaxed mind coupled with not hurrying will ensure proper response from the mind and is an individual's best safeguard*. Working with an attitude that each day may bring us to the inevitable (accident or fire), would postpone the inevitable to another day. This attitude coupled with an intelligent approach will make working in the explosive industry as free of hazards as in most other chemical industries.

Remember

Work slowly and deliberately with a relaxed mind.

6.11.3
Use of Personal Protective Equipment

Safety advisors and directors state that one of their greatest difficulties is to convince the workers to make use of personal protective equipment (PPE) while working. However, the management must strictly pursue with them till they imbibe the habit of using personal protective equipment as a routine. This will not only provide personal protection to them but will also be in the interest of the organization. *There must not be any relaxation of this rule*. A list of PPE for any explosive or chemical laboratory or factory is as follows:

1) **Protective Garments:** While working with explosives and toxic materials, workers must wear approved coveralls or laboratory coats (preferably full length) to prevent contamination of their personal apparel. The use of flame-retardant coveralls is desirable for some explosive operations where there is a possibility of a flash. Cotton or other anti-static material should be worn wherever there is a possibility of generation of static electricity.
2) **Gloves:** Contact of skin with some explosives or toxic chemicals may result in dermatitis and therefore there is a need to use proper type of gloves.
3) **Respirator:** The use of approved respirators is recommended during explosive operations where airborne particulates, gases and vapors etc are liberated.
4) **Safety Goggles or Glasses:** The use of shatterproof safety goggles or spectacles is recommended in order to protect the eyes while working with explosives. Contact lenses are not considered suitable for eye protection.
5) **Footwear:** The workers should wear conductive and non-sparking footwear while working with electrostatic-sensitive explosives.

The use of personal protective equipment is considered an important element of safety management. The top management and supervisors at the workplace should make it a habit to preach on this aspect periodically without fail, till it becomes a habit of the workers.

Remember

Practise safety until safety becomes a practice.

6.11.4
Cleanliness and Good Housekeeping

Many major accidents result apparently from certain insignificant causes. For example, a major fire can erupt from a harmless looking cigarette stub carelessly thrown away on the previous night or a worker slipping on an oil-soaked floor may end up in a hospital. These acts sound so common that they are not paid any attention. Good housekeeping takes care of your workplace and doing it daily and regularly ensures a safe, clean and congenial place to work.

In many laboratories and factories, a common feature is the accumulation of cartons, rubbish, packing material, gunny bags and other waste materials. These must be consigned immediately to metal bins and disposed off quickly, as fire loves to feed on such materials. Further, any spills must be cleaned immediately, as the chemicals may react with other substances, leading to accidents. It is axiomatic in the explosive industry that the material in process is not normally so hazardous but the spillages and wastes are extremely dangerous. Therefore, keep the floors free of spills and leaks. Explosive work areas, laboratories, storage magazines and any building that contains explosives should be kept clean and orderly. A regular cleaning schedule must be followed in order to maintain a safe and clean working environment.

The cleaning of machines, their lubrication and proper maintenance is also part of good housekeeping. The availability of stocks, parts and tools in their assigned places is also important and reduces the time lost in locating things every now and then. Good housekeeping also results in efficiency and makes the job easier, safer and better. It also pays rich dividends by making the work more pleasant, light and fast.

Remember

1) A dirty house causes dirty work environment and therefore, it must be kept clean.
2) Clean-up before you start, keep things clean while you are working and clean everything after all operations are over.

6.11.5
Waste Collection and Disposal

The explosive waste generated during any operation should be collected and maintained separately from conventional waste. Properly labeled scrap containers should be readily available for each class of explosives. Mixing of incompatible explosive wastes should be avoided. Waste collection is normally accomplished by collecting the dust or fibers in a wet/dry vacuum system or by collecting the solid waste in clearly labeled receptacles.

The waste should be destroyed at frequent intervals by spreading out in small quantities in thin layer on several thickness of paper or other combustible material. A train of inflammable material should be used to ignite the material. Destruction of the scrap is accomplished by burning or detonation at the disposal ground. The increased awareness about the effects of open burning or detonation on the ecosystem and the ever increasing cost of raw materials have forced the authorities to explore ever newer technologies for disposal. The emerging trends of waste disposal are

- incineration using modified burner;
- incineration after treatment to desensitize the major ingredients;
- chemical and biological degradation;
- methods for material recovery.

The disposal of explosives in huge quantities should be avoided as far as possible. No explosive waste should be discharged into the sewer or buried. The details of waste disposal are described meticulously in USA, DoE Manual [34]. All agencies dealing with explosives should have an approved procedure for disposal of explosive wastes or damaged or rejected explosive articles at regular intervals.

The author investigated several accidents that took place during waste disposal and arrived at the following most likely reasons for accidents:

1) Waste disposal is considered an insignificant task and the team in question intends to complete it as hurriedly as possible. As a result, the team deviates from the established procedure or drill, leading to accidents.
2) The workers are overconfident or complacent and maintain a casual attitude that nothing will go wrong.
3) Explosive waste gets accumulated as its disposal is not done on day-to-day basis.

Remember

- Dispose of explosive waste with a calm and relaxed mind without any hurry.
- Do not allow waste to accumulate
- Dispose of waste on a day-to-day basis without fail, especially during the summer months.

6.11.6
Training

All persons should be properly trained before they are assigned any explosive-related operation. Training for explosive-related work results in awareness and also helps in conducting the work safely. The essential elements of training are:

- To cultivate and maintain a safe attitude toward explosives-related work.
- To define and understand the potential hazards involved.
- To develop the skills for the safe performance of various tasks.
- To impart skills for the proper storage, handling, transportation and disposal of explosives.
- To prepare all persons for unexpected hazardous conditions.
- To ensure that the workers read and understand the correct operating procedures as a matter of routine before commencing their work.
- To update the course content of these training programs periodically in order to keep pace with new developments and the operations involved.

The author still remembers a fatal accident in one of the DRDO laboratories at Pune, India in which 6 persons lost their lives in addition to large scale damage to the government property. The root cause, which came to light after the enquiry, was that the persons involved were not properly trained and were unaware of the consequences of not following the stipulated procedures.

In a nutshell, continued vigilance by the workers coupled with the use of personal protective equipment and unrelenting surveillance by the management remain the best remedy for prevention of accidents, be it explosions or fires. Further, we must learn a lesson from each accident but unfortunately this does not really happen [35]. The findings of the enquiries and investigations conducted do not yield meaningful results. The main reasons being:

1) **Lack of concrete evidence:** Most of the time, explosives or propellants related accidents are fatal and the evidence is lost. As a result, the actual reasons leading to such accidents do not come to light. Therefore, it is difficult to comprehend the true reasons for such accidents and hence, preventative measures cannot be implemented in order to avoid subsequent accidents.

2) **Humanitarian approach of the investigating team:** The 'investigating team' responsible for investigating the causes and circumstances of the accidents is generally able to conclude the possible causes and circumstances leading to accidents. Most of the time, accidents are due to deviations from the established procedures or lapses on the part of workers . The maxim *'Disregard of an accepted practice ruins a life' proves to be correct in most of the cases*. However, these facts cannot be put in reports in black and white, otherwise the victims of accidents or their family members would lose all benefits, leading to discontentment in the organization.

In conclusion, it is not possible to prevent all accidents. It is therefore prudent to follow the precautionary measures outlined in the preceding section and also the cardinal principle of safety while handling explosives or ammunition and allied chemicals [36].

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Index

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