
Energetics Science and Technology in China

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Center for Energetic Concepts Development Series



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Preface

When we think of energetics, inevitably we think of explosives, propellants, firecrackers, gunpowder, and then China, since it is there that gunpowder was first invented. It is therefore appropriate that any study of the science of energetics begin with an examination of the developments of energetics in China. Hence this book was written as part of a planned series of six volumes on Energetics Science and Technology. Each volume covers a different region of the world. The motivation for this series is to provide a comprehensive collection of information on this critical technology and identify the energetic materials research being conducted across the globe.

Energetic materials typically provide a great deal of energy in various forms, all of which are in demand all over the world, as their uses are nearly unlimited. Energetics are used in mining and road building, for rocket fuel, aircraft ejection seats, and pyrotechnics among others. The category of "energetic materials" covers a variety of substances, including explosives, propellants, and pyrotechnics. The physical form of energetic materials can be solid, liquid, powder, or gel.

This book is exclusively focused on energetic materials research in China and is prepared for readers interested in an introduction to the field of energetic materials, as well as for researchers interested in past and current work being conducted in energetic materials in China. Of particular note for this book is a section on the history of energetics in China, a country which can arguably claim to be the home of energetics.

In China, much of the information regarding energetic materials can be found in academic journals. The main journal pertinent to this field is the Chinese *Journal of Energetic Materials*, a bimonthly academic collection dating back to 1993, with articles in English first appearing in 2009. Other more specific journals containing information on energetic materials in China include the *Chinese Journal of Explosives & Propellants*, *Explosive Materials*, *Initiators & Pyrotechnics*, and *Journal*

of Projectiles, Rockets, Missiles & Guidance. These journals delve into subcategories of energetic materials and provide articles containing new research and recent advances on these specific materials.

The work presented here addresses the technological progress made in China regarding the energetic materials community and is split into seven chapters. Each chapter includes several references whose abstracts are available on our website www.cecd.umd.edu. To illustrate the style and content of the abstracts to be found on the website, Chapter 4 provides the abstracts used in the development of the chapter.

This book was also written to provide an impetus for the authors and readers to reach out and connect directly with academics working in energetics in China. A special workshop titled “Workshop on Energetics –Past and Present” under the sponsorship of The Center for Energetic Concepts Development at the University of Maryland, College Park, USA and the City University of Hong Kong has been conducted in Hong Kong in December 2010. We hope that other such events will occur as a result of this book.

It is our hope that this book will give the reader a comprehensive view of energetic materials developments in China, the birthplace of energetics. We are most appreciative of those that have helped in the preparation of this volume. We acknowledge Dr. John Fisher for discussions on energetics research and future directions. Thanks to Jason Larson of EHS Inc. for the partial support of the second edition under Contract N00178-05-D-4309 FG 02. Dr. Xin Song, Hester Cheng, and Jefferson Pecht performed some of the background research and helped in the translations. Rashmi Pujar and Gautham Bharadwaj assembled the information for the website. Z. Yong and X. Mian contributed to the history of energetics in Chapter 1 and 2. S. Ouyang contributed material for Chapter 2. Ray Lemar reviewed and edited several chapters for content and style. Finally thanks to Ania Picard and Angie Wong for editing, formatting, and preparation of the final product.

The Authors

Executive Summary

In 1972 the American President Richard Nixon visited China. It was a trip that changed the future history of the world. President Nixon said, at the end of his visit as the official Communiqué was released to the public, that "this was the week that changed the world, as what we have said in that Communiqué is not nearly as important as what we will do in the years ahead to build a bridge across 16,000 miles and 22 years of hostilities, which have divided us in the past. And what we have said today is that we shall build that bridge."

In the spirit of building the bridge, a member of the organizing committee of the 7th Symposium (International) on Detonation, Dr. James Short, wrote a letter to the Chinese Embassy in America in 1980 encouraging Chinese participation in the 1981 Symposium. Professor Ding Jing of the Beijing Institute of Technology led a delegation of four Chinese scientists to the 1981 Symposium. That invitation and participation signaled that change was coming to energetics science and technology in China.

Now, three decades later, the University of Maryland's Center for Energetic Concepts Development celebrates 30 years of Chinese and American interactions in the field of energetics. With this book, we take note of China's historical and current leadership and innovations in energetics science and technology.

A visit to the website of the Chinese Embassy in Washington, DC, offers a hint as to the importance of energetics in the history of China and the history of the world. At the embassy website is a link to a speech (<http://www.china-embassy.org/eng/zmgx/zysj/jzxfm/t36252.htm>) given by President Jiang Zemin at Harvard University, where he mentions China's four great inventions that have had profound impact on the entire world—paper making, concept of the printed word, the navigational compass, and gunpowder. Energetics science and technology began with gunpowder.

During the Han Dynasty, in the year 142 CE (CE is the Common Era of the Gregorian calendar & BCE is Before the Common Era), Wei Boyang wrote about a mixture of three powders that when mixed would “fly and dance” violently. Having no additional facts, it can only be assumed the powders were saltpeter (potassium nitrate), sulfur and charcoal, the ingredients of gunpowder. Wei Boyang and others who came before him and after him were alchemists in search of medicines to make men immortal, or at least to prolong life and cure disease.

During the Chin Dynasty, about 300 CE, Ge Hong wrote more. He wrote of mining sulfur from a yellow rock. He wrote of letting animal manure decay in the open air. A consequence is the formation of potassium nitrate crystals. The crystals are harvested by washing away with water the remainder of the aged manure. Charcoal was made then in the same way as today—by partially burning wood. Ge Hong mixed 15 parts of saltpeter with 3 parts of coal and 2 parts of sulfur. Then, he put a spark to the mixture so he could enjoy a fireworks show of light, heat, and noise.

It was during the Tang Dynasty, about 700 CE, that people began to use gunpowder in purposeful ways. The Tang emperors used gunpowder for entertainment, what we might call fireworks today. In about 900 CE, the concept of fireworks used in a controlled manner as a weapon evolved. Pressing gunpowder into bamboo poles created the first rockets. The bamboo pole was a prototype of the modern gun.

In 1044 CE (Northern Song Dynasty), the earliest known written gunpowder formulas appeared. It was written in the book *Wujing Zongyao* (Collection of the Most Important Military Techniques). Three formulas appeared. One was for a simple bomb. Another was for a bomb launched from a catapult. The third was for a smoke bomb, perhaps the first written example of chemical warfare. In addition to the three classic ingredients, common to all three formulas in the *Wujing Zongyao* are small amounts of hemp roots, bamboo roots, various oils, and wax.

Appreciating both the power and danger of their new technology, the emperors tried to keep gunpowder a secret. But during the 12th century (1100s), the first evidence of gunpowder was appearing to the west in the Roman Empire and Europe. It is assumed the secret was lost through merchants traveling westward on the Silk Road. It was in 1216 CE that Roger Bacon published his famous treatise on gunpowder. As a consequence of that treatise, the Western world credits Roger Bacon as the inventor of gunpowder. In the 1300s, the predecessor to the modern cannon made its first appearance.

With the Bacon’s publication, China lost both its monopoly on gunpowder and leadership in the development of safer use of gunpowder

and more powerful alternatives to gunpowder. While the Chinese advanced beyond gunpowder, those that became famous were people like Nobel and DuPont in Europe and America.

At the time of Roger Bacon, the Mongols invaded China and took charge governing China. Mongol leader Kublai Khan became the first foreigner to rule all of China. This marked the beginning of the Yuan Dynasty in 1279. The Mongols remained in power until 1368 when uprisings drove out the Mongols. The Ming Dynasty was at the beginning of nearly 300 years of rule. The political stability of the times promoted the concept that China's was a perfect civilization. China was an agrarian society requiring no further change. Interaction with foreigners could do no further good, and might do harm.

With this agrarian isolation began more than 500 years of China turning away from science. The establishment of the People's Republic of China in 1949 did not stimulate an immediate return to science. China's First Five Year Plan (1953-1957) signaled a transition to socialism that brought with it a respect for industrialization. It was not until 1975 that China returned to science when Zhou Enlai outlined what came to be known as the Four Modernizations—agriculture, industry, national defense, and science and technology.

This book provides a window on China's rapid ascent back to the energetics science and technology excellence it held for many centuries so long ago. Preparing to write this book, nearly 2,000 Chinese energetics science and technology papers published in the past two decades were assembled. The papers came from five Chinese journals: the *Chinese Journal of Energetic Materials*, *Chinese Journal of Explosives and Propellants*, *Explosive Materials*, *Initiators and Pyrotechnics*, and the *Journal of Projectiles, Rockets, Missiles & Guidance*. Also in the assembly are papers by Chinese authors in Western journals such as the *Journal of Energetic Materials* and *Propellants, Explosives, and Pyrotechnics*.

This book consists of seven chapters. Chapter 1 is an overview of the history of energetic materials in China, beginning with gunpowder. The history begins at least six centuries Before the Common Era (BCE) and continues into the 21st Century.

Chapter 2 is an overview of progress in technology of Chinese energetic materials through the centuries. The Chinese recognized that energetics can bring both joy when in the form of fireworks and agony if used as weapons. Wishing to be a peaceful society, Chinese leaders sought to keep their knowledge of gunpowder a secret. When trade routes opened to Rome and Europe along the Silk Road, the secret could not be kept. Soon thereafter China closed its borders to foreigners in favor of remaining an isolated agrarian society. For the next 500 years

technical progress in energetic materials was a European and American story.

Chapter 3 is a summary of (energetics) science and technology trends. It quantifies the rapid growth of science and technology in China relative to the rest of the world during the past few decades. Based on the number of researchers and number of publications in the public scientific literature, six Chinese institutions have emerged as China's energetic science and technology leaders. The chapter also gives a description of the six institutions based on information on Chinese websites.

The next four chapters summarize the rapid ascent of Chinese science and technology in four topics germane to energetics: Synthesis (Chapter 4 with 126 references including their abstracts); Combustion (Chapter 5 with 174 references); Modeling and Simulation (Chapter 6 with 52 references); and Nanoenergetics (Chapter 7 with 29 references). The first few pages of each chapter are intended for a reader not familiar with energetics science and technology. Those pages will give a brief insight into the role each of the four topics in energetics science and technology plays. The technology that each chapter spans is so broad as to make a thorough summary of the topic impractical. The benefit of the book to an expert is the assembly of a large number of energetics references at the end of each chapter.

Author Biographies

James M. Short is an international leader in energetics, focusing on combustion. He studied detonation physics at the University of California at Berkeley. After that he was a protege of the eminent detonation physicist, Sigmund J. Jacobs, and explosives chemist, Mortimer J Kamlet. In 1983 Dr. Jacobs selected Dr. Short to be the chairman of the International Detonation Symposium. Dr. Short remained chairman of the International Detonation Symposium for more than 20 years. In 1980, Dr. Short invited Professor Ding Jing of the Beijing Institute of Technology and three other Chinese Professors to participate in the Seventh International Detonation Symposium. In 1987, Dr. Short was privileged to represent the United States in Beijing and offer three papers at the International Symposium on Pyrotechnics and Explosives. Now as the Executive Editor of the Journal of Energetic Materials, he is privileged to publish the work of Chinese energetic scholars (<http://www.tandf.co.uk/journals/titles/07370652.asp>) and seeks additional collaboration with Chinese energetics scholars.

Robert A. Kavetsky is currently the Executive Director of the Energetics Technology Center, where he leads a Policy Development Group for a number of Department of Defense clients. He was the founder of the N-STAR(Naval Research – Science and Technology for America’s Readiness) initiative at the Office of Naval Research, a Navy-wide effort aimed at reinvigorating the science and technology community within the Navy’s Warfare Centers. He received a Bachelor of Science Mechanical Engineering in 1975, a Master of Science Mechanical Engineering in 1977, and a Master of Science Engineering Administration in 1978, all from Catholic University. He was head of the Explosion Damage Branch, Program Manager for the Undersea Warheads Program, and Program Manager for Undersea Weapons at the Naval Surface Warfare Center. At the Pentagon, he helped develop

science and technology programs for organic mine countermeasures and expeditionary logistics, and then at Naval Surface Warfare Center Indian Head created “Workforce 2010,” a government, industry, and academic consortium focused on developing Indian Head’s next generation workforce. He has authored a number of technical and workforce policy and program publications for the American Society for Engineering Education, the American Society of Mechanical Engineers, the American Institute of Aeronautics and Astronautics, and other forums.

Michael G. Pecht is a visiting Professor in Electronic Engineering at City University in Hong Kong. He has an MS in Electrical Engineering and an MS and PhD in Engineering Mechanics from the University of Wisconsin at Madison. He is a Professional Engineer, an IEEE Fellow, an ASME Fellow, an SAE Fellow and an IMAPS Fellow. In 2010, he received the IEEE Exceptional Technical Achievement Award. In 2008, he was awarded the highest reliability honor, the IEEE Reliability Society’s Lifetime Achievement Award. He has previously received the European Micro and Nano-Reliability Award for outstanding contributions to reliability research, 3M Research Award for electronics packaging, and the IMAPS William D. Ashman Memorial Achievement Award for his contributions in electronics reliability analysis. He served as chief editor of the IEEE Transactions on Reliability for eight years and on the advisory board of IEEE Spectrum. He is chief editor for Microelectronics Reliability and an associate editor for the IEEE Transactions on Components and Packaging Technology. He is the founder of CALCE (Center for Advanced Life Cycle Engineering) at the University of Maryland, which is funded by over 150 of the world’s leading electronics companies. He is also a Chair Professor in Mechanical Engineering and a Professor in Applied Mathematics at the University of Maryland. He has written more than twenty books on electronic products development, use and supply chain management and over 400 technical articles. He has also written books on India’s, Korea’s and on China’s Electronics Industry. He consults for 22 major international electronics companies, providing expertise in strategic planning, design, test, prognostics, IP and risk assessment of electronic products and systems.

Davinder K. Anand is Professor of Mechanical Engineering and Director of the Center for Energetic Concepts Development, both at the University of Maryland, College Park. He received his doctorate from George Washington University in 1965. Dr. Anand was Senior Staff at The Applied Physics Laboratory of the Johns Hopkins University from 1965-1974. From 1991-2002, he chaired the Department of Mechanical

Engineering at College Park. He has served as a Director of the Mechanical Systems Program at the National Science Foundation, and his research has been supported by NIH, NASA, DOE, DOD, and industry. He has lectured internationally, founded two high technology research companies (most recently Iktara and Associates, LLC), published three books and over one hundred and seventy papers, and has one patent. He is a Distinguished Alumnus of George Washington University, and was awarded the Outstanding and Superior Performance Award by the National Science Foundation. Dr. Anand is a Fellow of ASME and is listed in Who's Who in Engineering.

Acronyms

AE	Acoustic Emission
2HDNPCu	2-Hydroxy-3, 5-Dinitropyridine
2HDNPPb	2-Hydroxy-3, 5-Dinitropyridine
4HDNPPb	4-Hydroxy-3, 5-Dinitropyridine
A-Cu	One of several copper salts
ADR	Accord Européen Relatif Au Transport International Des Marchandises Dangereuses Par Route
AIMD	Ab Initio Molecular Dynamics
AMMO	Poly (3-Azidomethyl)3-Methyl- Oxetane
ANN	Artificial Neural Network
ATF	Bureau of Alcohol, Tobacco, and Firearms
ATO	4-Amino-1,2,4-Triazol-5-One
BAFF	3,4-Bis (Aminofurazano) Furoxan
BAMO	Poly (3,3-Bis (Azidomethyl)-Oxetane
B-Cu	One of several copper salts
BIT	Beijing Institute of Technology
BNNTs	Carbon Nano Tube Technologies
BSSE	Basis Set Superposition Error Correction
CAE	Chinese Academy of Engineering
CAEP	China Academy of Engineering Physics
CARS	Coherent Anti-Stokes Raman Scattering
CAS	Chinese Academy of Sciences
CB	Carbon Black

CBGP	Controlled Burning Gun Propellant
CESTA	Centre d'Etudes Scientifiques et Techniques d'Aquitaine
CF	Composite Fuel
CFD	Computational Fluid Dynamics
C-J	Chapman-Jouguet
CL-20	Hexanitrohexaazaisowurtzitane
CMDB	Composite Modified Double-base Propellants
CNIGC	China North Industries Group Corporation
CNT	Carbon Nanotubes
COMPASS	Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies
COSTIND	Commission of Science, Technology, and Industry for National Defense
CTPB	Carboxy-Terminated Polybutadiene
DAAF	3, 3'-Dinitro-4, 4'- Azoxyfurazan
DAAzF	3,3'-Dinitro-4,4'-Azofurazan
DB	Double Base
DBC	Dibutyl carbito salt
DDT	Deflagration-to-Detonation Transition
DFT	Density Functional Theory
DIANP	1,5-Diazido-3-Nitrazo Pentane
DLCs	Diamond-Like Crystals
DMF	Dimethylformamide
DMSO	Dimethylsulfoxide
DOA	Diethyl Adipate
DoD	Department of Defense
DOS	Diethyl Sebacate
DSC	Differential Scanning Calorimetry
DTA-TGA	Differential Thermal Analysis-Thermo Gravimetric Analysis
DSC-TGA	Differential Scanning Calorimetry-Thermo Gravimetric Analysis
DT	Deuterium-Tritium
DTA	Differential Thermal Analysis

EDC	Eddy-Dissipation-Concept
EDDN	Ethylenediaminedinitrate
EI	The Engineering Index
EMCDB	Elastomer Modified Cast Double Base
EOS	Equation of State
EPDM	Ethylene Propylene Diene Monomer
ETPE	Energetic Thermoplastic Elastomer
FAE	Fuel Air Explosive
FM	Fractal Model
FTIR	Fourier Transform Infrared
G8	Group of Eight
GAP	Glycidyl Azide Polymer
GCMS	Gas Chromatography Mass Spectroscopy
GDN	Guanidine Dinitramide
GDF	Granular Diffusion Flame
GDP	Gross Domestic Product
GEKKO XII	High-Power 12-Beam Neodymium-Doped Glass Laser at the Osaka University Osaka Institute for Laser Engineering
GERD	UNESCO Gross Expenditure in R&D
GPa	Giga-Pascal, Measure of Pressure
HB	Brinell Surface Hardness Number
HEDCs	High Energy Density Compounds
HEMDB	High Energy Modified Double-base
HMMO	3-Hydroxymethyl-3-Methyl Oxetane
HMX	Cyclotetramethylene Tetranitramine
HMX	The Structure of β -Octahydro-1, 3, 5, 7-Tetranitro-1, 3, 5, 7-Tetrazocine
HNIW	Hexanitrohexazaisowurtzitane
HNIW	Hexa-Nitro-Hexaaza-Iso-Wutzitane
HOMO-LUMO	Highest occupied molecular orbital & lowest unoccupied molecular orbital
HRc 54-59	Rockwell Hardness Scale
HTPB	Hydroxy-Terminated Polybutadiene
HX-752	3M Dynamar Curative/Bonding Agent

ICF	Inertia Confinement Fusion
IMPUE	Isocyanurate-Modified Polyurethane Elastomer
IR	Infrared
ISTP	Index to Scientific & Technical Proceedings
ITO	Indium Tin Oxide
JWL	Jones-Wilkins-Lee
LEH	Laser Emission Holes
LLNL	Lawrence Livermore National Laboratory
LM-1	Long Mach-1
LM-2E	Satellite
LMENDT	The Laboratory of Materials Evaluation and Nondestructive Testing
LOVA	Low Vulnerability Ammunition
LPMM	The Laboratory of Physics and Mechanics of Materials
LS-DYNA	Livermore Software Finite Element Code
MAPO	Tris-1- (2-Methyl Aziridiny) Phosphine Oxide
MBMS	Molecular Beam Mass Spectrometry
MD	Molecular Dynamics
ML-STD-1901A	USA Military Standards document
mNPF	Fullereno-Pyrrolidine
MOCVD	Metal-Organic Chemical Vapour Deposition
MOE	The Ministry of Education
MPa	Mega Pascal
MS	Mass Spectroscopy
MSD	Molecular Structure Describers
NBO	Natural Bond Orbital
NC	Nitrocellulose
Nd: YAG	Neodymium-Doped Yttrium Aluminium Garnet; Nd:Y ₃ Al ₅ O ₁₂
NEPE	Nitrate Ester Plasticized Polyether
NG	Nitroglycerin
NGEC	Nitric Acid Ester of Cellulose Glycidyl Ether
NG-TEGN	The Volatilization and Decomposition of Nitrate Plasticisers
NHA	Nickel Hydrazine Azide
NHN	Nickel Hydrazine Nitrate

NM	Nitromethane
NMP	N-methylpyrrolidone
n-ONPP	Nanoscale Organic Lead Salt
n-PAC	Nanoscale Organic Cupric Salt
NSAF	National Natural Science Associated Foundation of <i>China</i>
NSFC	National Natural Science Foundation of China
NSSPERC	The National Special Superfine Powder Engineering Research Center
NT-Cu	N-(5-nitro-2-thiazolyl)-N'-carboxymethylurea
NTO	3-Nitro-1,2,4-Triazol-5-One
NUC	The North University of China
NUDT	The National University of Defense Technology
NUST	Nanjing, Nanjing University of Science and Technology
PBX	Plastic Bonded Explosive
PDSC	High-pressure Differential Scanning Calorimetric
PEG	Polyethylene Glycol
PET	Polyethylene terephthalate
PETN	Pentaerythritol Tetranitrate
PHCs	Pinhole Cameras
PIR	Pre-Ignition Reaction
PNACs	Polynitroaromatic Compounds
PSAN	Phase Stabilized Ammonium Nitrate
PVA	Polyvinyl Alcohol
PVC	Polyvinyl Chloride
QSPRs	Quantitative Structure-Property Relationships
R&D	Research And Development
RDX	Cyclotrimethylene Trinitramine
SAXS	Small Angle X-ray Scattering
S&T	Science and Technology
SCB	Semiconductor Bridge
SCF	Signature Characterization Facility
SCI	Science Citation Index
SDE	Substituted Diphenyl Ethers
SDT	Shock to Detonation Transition

SEM	Scanning Electron Microscope
SHS	Self-Propagation and High Temperature Synthesis
SKLEST	State Key Laboratory of Explosion Science and Technology
sol	Solution
SOP	Scanning Optical Pyrometer
SPETC	Solid Propellant Electro Thermal Chemical
SPH	Smoothed-Particle Hydrodynamics
SPRS	Structure-Property RelationshipS
SXS	Soft X-ray Spectrometer
T313	Boron Trifluoride Triethanolamine Complex
TADNSIW	Tetra-Acetyldi-Nitro-Sohexaaza-Iso-Wurtzitane
TATB	Triaminotrinitrobenzene
TCDNB	2, 4, 6- Trichloro- 1, 3- Dinitrobenzene
TCTNB	2,4,6- Trichloro- 1, 3, 5- Trinitrobenzene
TEGDN	Triethyleneglycol Dinitrate
TEM	Transmission electron microscopy
TG	Thermogravimetric
TGA	Thermogravimetric Analysis
TG-DTG	Thermogravimetric-Derivative Thermogravimetric
TG-FTIR	Thermogravimetric Fourier Transform Mass Spectroscopy
TG-MS	Thermogravimetric Mass Spectroscopy
TNT	2,4,6-Trinitrotoluene
Tz	Tetrazene
UFC	Ultra-Fine Carbon
UFD	Unique factorization domain
UHBRP	Ultra High Burning Rate Propellant
UNESCO	United Nations Educational, Scientific and Cultural Organization
UP	Unsaturated Polyester
UPR	Unsaturated Polyester resin
VISAR	Velocity Interferometer System for Any Reflector
VLWR	Very Long Wavelength Infrared
WWII	World War II

XRD

X-ray diffraction

ZPE

Zero Point Energy Correction

Contents

Preface	v
Executive Summary	vii
Author Biographies	xi
Acronyms	xv
Chapter 1 The History of Energetic Materials in China	1
1.1 The Discovery of the Components of Gunpowder	1
1.1.1 The Discovery of Saltpeter	1
1.1.2 The Discovery of Sulfur.....	3
1.1.3 The Discovery of Carbon.....	4
1.1.4 The History of Alchemy	4
1.1.5 The Invention of Gunpowder	7
1.1.6 Song Dynasty	10
1.1.7 Yuan Dynasty.....	10
1.1.8 Ming Dynasty.....	11
1.1.9 Modern China	11
1.2 Fireworks.....	12
1.2.1 Han Dynasty.....	12
1.2.2 Tang and Song Dynasties.....	12
1.2.3 Ming Dynasty.....	13
1.2.4 Modern China	13
1.3 Firearms.....	17
1.3.1 Song Dynasty	17
1.3.2 Yuan Dynasty.....	17
1.3.3 Ming Dynasty.....	19
1.3.4 Qing Dynasty	26
1.3.5 Modern China	27

1.4	Solid Propellants	27
1.4.1	Modified Low-signature Double-base Propellants.....	28
1.4.2	Deterred Low-signature Double-base Propellants	28
1.4.3	The Gap between China and the World	28
1.5	Space Solid Rocket Motor.....	30
1.5.1	Sounding Rocket Motor	30
1.5.2	The Third Stage Motor of Launch Vehicle	30
1.5.3	Retro-motor of Returnable Satellite	31
1.5.4	Apogee Motor	31
1.5.5	Perigee Orbit Transfer Motor.....	31
1.6	Latest Research Progress.....	32
1.7	Summary	34
1.8	References	34
Chapter 2	Progress in Technology of Chinese Energetic Materials – An Overview	37
2.1	Introduction	37
2.2	The Chinese Black Powders—A Historical Note.....	38
2.3	Industrial Energetic Materials	44
2.3.1	General Application Class (Detonation Velocity between 5000 and 9000 m/s).....	45
2.3.2	High Energy Application Class (Explosion Wave Speed above 9000 m/s)	51
2.4	Results and Discussion	54
2.5	Concluding Remarks	55
2.6	Acknowledgement.....	55
2.7	References	55
Chapter 3	Science and Technology Trends.....	61
3.1	Energetics Research	65
3.2	Xi'an Modern Chemistry Research Institute	67
3.2.1	Areas of Research in the Xi'an Modern Chemistry Research Institute and Achievements	68
3.2.2	Research Projects	68
3.2.3	Facilities of the Institute.....	69
3.3	Beijing Institute of Technology.....	69
3.3.1	Energetics Research in the SKLEST.....	70
3.3.2	Research Capability	71
3.4	Nanjing University of Science and Technology	74
3.4.1	Energetics Research in the School of Chemical Engineering ...	75
3.4.2	Research Capability in the School of Chemical Engineering ...	76
3.4.3	Energetics Research in the NSSPERC.....	77
3.4.4	Research Capability in the NSSPERC	77
3.5	China Academy of Engineering Physics	79
3.5.1	Energetics Research at the Institute of Chemical Materials	80
3.5.2	Research Capability	80
3.6	North University of China.....	81

3.6.1	Energetics Research in the School of Chemical Engineering and Environment.....	82
3.6.2	Research Capability	82
3.7	National University of Defense Technology	85
3.7.1	Energetics Research in the College of Aerospace and Materials Engineering	86
3.7.2	Research Capability	87
3.8	References	88
Chapter 4 Synthesis.....		93
4.1	Energetics Synthesis Research	94
4.2	References	98
Chapter 5 Combustion.....		153
5.1	Research in Combustion.....	156
5.1.1	Detonation and Deflagration	157
5.1.2	Combustion Ignition	160
5.1.3	Combustion Catalyst	165
5.1.4	Explosive Combustion	168
5.1.5	Propellant Combustion.....	172
5.1.6	Others.....	184
5.2	References	186
Chapter 6 Modeling and Simulation		209
6.1	Modeling and Simulation Methods in Energetic Field.....	210
6.2	Modeling and Simulation Research in the Energetics Field.....	213
6.2.1	Modeling and Simulation in Phase Transformations of Energetic Materials	213
6.2.2	Modeling and Simulation in Molecular Geometry Optimization	214
6.2.3	Modeling and Simulation in Theoretical Thermodynamics Investigations	215
6.2.4	Modeling and Simulation of Detonation Waves in Energetic Materials	216
6.2.5	Modeling and Simulation in Chemical Reactions of Energetic Materials	216
6.2.6	Modeling and Simulation in Propellants	217
6.2.7	Modeling and Simulation in Other Areas of Energetic Materials	218
6.3	References	219
Chapter 7 Nanoenergetics		229
7.1	Research in Energetic Nanomaterials.....	230
7.2	References	232

Chapter 1

The History of Energetic Materials in China

Gunpowder is one of the four great inventions of ancient China. It has a long history. It was discovered as people searched for substances which could be used as medications. In the study of alchemy these substances were experimented with and put in fire. Gunpowder was the accidental result of experiments conducted by alchemists. The original recipe was kept secret, and the date of invention is impossible to discover.

This chapter discusses the developmental history and trends of energetic materials - gunpowder, fireworks, firearms, and solid propellants - in China.

1.1 The Discovery of the Components of Gunpowder

The three major components of ancient gunpowder are saltpeter, sulfur, and carbon. The manner in which these components were discovered is discussed below.

1.1.1 The Discovery of Saltpeter

Saltpeter, or potassium nitrate, has the chemical formula KNO_3 . It is commonly found in its natural state in soil that contains potassium, sodium, magnesium, and calcium. More commonly it coexists with sodium, magnesium, and other minerals. It can be refined by water leaching, evaporation, and crystallization.

China was able to identify saltpeter long ago. In the 6th century BCE, Fan Li, the celebrated politician, militarist, and economist during the Spring and Autumn Period, wrote that saltpeter was quite abundant in Long Dao City (now in Gan Su Province).

During the Han Dynasty, people not only knew of saltpeter, but also made it into a medicine to cure the blind. Historical records, “史记”, document the use of saltpeter. At the time, saltpeter was not only used in medical treatment, but was also considered an important material used by alchemists. In the “36 Water Laws”, (“三十六水法”), there are 33 formulas that use saltpeter. It is generally believed that “36 Water Laws” was written by eight people who were commissioned by Huainan Wang Liu An of the Han Dynasty. It has been demonstrated that the main content of “36 Water Laws” was written during the Han Dynasty. Therefore, saltpeter was first used as a reagent at least as early as the Han Dynasty [1].

After the Western Han Dynasty, saltpeter was widely used in medicine and alchemy, and the nature of saltpeter was understood further. In November 1972, in Wuwei, on the beaches of Gansu, medical bamboo slips from the early Eastern Han Dynasty were found, the contents of which were very rich. About 100 drug names were listed, of which 16 recipes used saltpeter. “神农本草经” (Shen Nong Ben Cao Jing), a book written during the late Han Dynasty and early Eastern Han Dynasty, records the use of saltpeter and Pu Xiao: “消石, 味苦寒, 主五脏积热, 胃胀闭, 涤去蓄结饮食, 推陈致新, 除邪气。炼之如膏, 久服轻身。” (“Xiao Shi tastes bitter and cold. The main effect is that when there is heat in the five internal organs and bloating in the stomach, it can be used to remove the residual food and put forward new things to dispel the evil influence. When it is smelting, it looks like cream. Eating it for a long time can result in weight loss.”) “朴硝, 味苦寒, 主百病, 除寒热邪气, 逐六腑积聚, 结固留癖。能化七十二种石。炼饵服之, 轻身神仙。” (“Pu Xiao tastes bitter and cold. The main effect is to cure hundreds of diseases, dispel chills, fever, and evil influence, and remove the residual food in the six hollow organs. It can be used to smelt 72 kinds of stone. A man would become immortal if he took the medicines which are made by smelting it”) [1].

Modern research has shown that Pu Xiao in “Shen Nong Ben Cao Jing” refers to potassium nitrate and Xiao Shi to sodium; Pu Xiao not only can cure “all diseases” but can also be altered to smelt “72 kinds of stone”. It can be seen that although there is confusion in the names, people had an in-depth understanding of the chemical properties of potassium nitrate. And clearly by that time it was already widely used in medicine and alchemy. It should also be noted that tests were conducted involving the firing of saltpeter in alchemy.

In the Northern and Southern Dynasties, people not only understood the nature of saltpeter, but also mastered the scientific methods of the identification of saltpeter and Pu Xiao. “Zheng Lei Ben Cao” (“证类本草”)

reads [1]: “陶隐居云：(消石) 疗病亦与朴消相似。仙经多用此消化诸石，今无正识别此者。顷来寻访，犹云与朴消同山，所以朴消名消石朴也。如此，则非一种物。先时有人得一种物，其色理与朴消大同小异，舐舐如握盐雪不冰。强烧之，紫青烟起，仍成灰，不停沸，如朴硝，云是真消石也。” (“Tao Yin Ju said: ‘Xiao Shi can cure similar diseases to Pu Xiao. It is always used to digest stones according to most books. Till now, there has been no positive identification. It is said that it can be found in the same mountain as Pu Xiao, and it is believed that Pu Xiao and Xiao Shi are not the same thing. Long ago, people had an object, whose color, shape, and character were similar to Pu Xiao. It was like salt and snow but it was not as cold as ice. When it was burnt by strong fire, there would be purple smoke, and the ash, still boiling, was quite like Pu Xiao. This is the real Xiao Shi.’”) Here, the key is “purple smoke”. When potassium salt burns, there is an immediate purple flame. When sodium salt burns, it produces a yellow flame. This is the same as the flame test method used in chemistry. This record of identifying saltpeter and Pu Xiao flames is not only the earliest record of potash chemical identification in China’s history but also in the world. It is similar to modern analytical methods which are used to identify potassium and sodium. The discovery of and ability to identify saltpeter and Pu Xiao laid the groundwork for mass production of gunpowder [1].

1.1.2 The Discovery of Sulfur

Monomer sulfur is yellow. Most sulfur exists in nature in the form of sulfate, sulfide, and similar forms. The recognition and understanding of sulfur occurred very early. People often used sulfur for medical treatment. In “Shen Nong’s “Herbal Classic”, sulfur was included as a drug ingredient along with realgar and orpiment. According to many medical books, sulfur could cure many diseases and was an important drug in ancient Chinese medicine. People also had knowledge of sulfur from chemistry, knowing that it could react with copper, iron, and other metal compounds. Shen Nong Ben Cao Jing said: “石硫磺能化金、银、铜、铁，奇物” (“The sulfur stone can melt gold, silver, copper, iron, and it is a strange thing.”) Alchemists also frequently used sulfur. For example, 硫磺水 (sulfur solution) recorded in the “36 Water Laws” consisted of sulfur, chalk, vinegar, and urine. 《朴子·内篇·金丹》(Bao Pu Zi • Nei Pian • Jin Dan) wrote: “第一支丹名曰丹华。当先作玄黄，用雄黄水、矾石水、戎盐、卤盐、磐石、牡蛎、赤石胆、滑石、胡粉各数十斤，以为六一泥，火之三十六日成，服之七日仙。” The name of the first recipe was “Dan Hua”. Xuan Huang was to be made first, using ten Jin of red orpiment water, alum water, Rong

salt, salt brine, rock, oysters, Akaishi lamps, talc, and pepper powder to mix with the mud. The mixture was then put into a fire for 36 days. People could be immortal for seven days after taking it. 矾石水 (Fan Shi Shui), mentioned by Ge Hong, also known as “矾石液” (Fan Shi Ye), was sulfur. Tao Hongjing’s 《“名医别录”》 (Ming Yi Bie Lu) explained [1]: “石硫磺生东海牧牛山谷中及太行河西山, 矾石液也。” (“The sulfur stone could be found in Mu Niu Mountain by the East Sea and Xi mountain by the Da Xing River, and it is Fan Shi Ye”) [1].

1.1.3 The Discovery of Carbon

Carbon comes in the form of charcoal. The understanding and use of carbon by Chinese people has a long history. There are remnants of the Bauhinia tree carbon blocks in the caves of 北京猿人 Beijing ape-men who lived 45 million years ago. This may be the earliest charcoal ever found. About 50,000 years ago, human ancestors lived in caves, where carbon black was also found. During the Shang and Zhou Dynasties, people not only understood that charcoal was a better fuel than wood, but they also knew that charcoal was a reducing agent in smelting and could be used to smelt copper, iron, and other metals.

The ancient Chinese had an understanding of saltpeter, sulfur, and charcoal, and laid the technical foundation for the invention of gunpowder. China’s rich saltpeter, sulfur, and charcoal resources laid the material foundation for the invention of gunpowder.

1.1.4 The History of Alchemy

Gunpowder was not the result of one single invention. It developed gradually in the context of ancient alchemy.

1.1.4.1 Qin and Han Dynasties

During the Qin and Han dynasties, alchemy was quite popular. At that time, people knew that they could get copper, tin, iron, and other metals by smelting certain minerals and carbon. People hoped to produce valuable metals, such as gold and silver, by smelting the metals with certain substances. On the other hand, people also appreciated the rust-proof nature of gold, and they hoped to develop a similar substance that could help humans become immortal, just like gold. Thus, the alchemists conducted a lot of experiments to try to produce gold, silver, and other elixirs to maintain life indefinitely. As a result, many potential medications were mixed, heated, and burned on stoves. The alchemists used various substances, including five kinds of metal (gold, silver, copper, iron, tin), eight kinds of stone (vermilion, arsenic sulfide,

orpiment, azurite, mother geosyncline, halite, saltpeter, brimstone), and three yellows (sulfur, arsenic sulfide, and orpiment). Among them, mercury and saltpeter were the special ones. If the three yellows were burned with saltpeter, the result was an explosion and a fire, which led to the invention of fireworks [1].

“Shen Nong Ben Cao Jing”, work created during the Qin and Han Dynasties, listed saltpeter as a top-grade medicine, while sulfur, arsenic sulfide, and orpiment were listed as middle-grade medicines. This is when the conditions for the invention of fireworks were set. Unfortunately, most of the alchemy books written in the Han Dynasty have been lost. Yet during that time essential knowledge was delivered by word of mouth as a pithy formula. Most practitioners were under their master’s guidance, so they had no access to the formulas except after years of practice. All these are reasons why textual research on this issue is difficult.

1.1.4.2 Eastern Han Dynasty

The Wei Boyang document from the Eastern Han Dynasty points out that (“东汉时魏伯阳就已指出”) “if the medicine is not correct in terms of species or amounts, it will be like a flying turtle and dancing snake, and become more severe”. This records the alchemy of explosions. Later, in a defense of the Three Kingdoms Period, Hao Zhao used the “火射连石” (stones of fire shooting) in Cheng Cang City to repulse the attack of Zhuge Liang (as described in Li Dao Yuan’s “水经注” (“Shui Jing Zhu”). This may be the earliest record of the use of gunpowder in firearms for defense. In “九国志” (“Jiu Guo Zhi”), it says “以所部发机飞火,烧龙沙门” (“His troops made the flying fire and burned Long Sha Men”). This occurred when Zheng Fan attacked Yuzhang in the early years of Tian You Chu Nian in the Tang Ai Zong (904 CE), which is the earliest record of offensive firearms [1]. (“炼丹时”若药物非种、分剂参差、失其纪纲,“就会”飞龟舞蛇,愈见乖张”。这正是记载了炼丹中的爆炸现象。后来在三国时期又有郝昭保卫陈仓城用“火射连石”打退了诸葛亮的进攻(见酈道元《水经注》)。这可能是利用火药作的防御性火器的最早记载。而在《九国志》中又记载有唐哀宗天佑初年(904年)郑燧攻豫章“以所部发机飞火,烧龙沙门”是为进攻性火器的最早记载”)

1.1.4.3 Western and Eastern Jin Dynasties and Northern and Southern Dynasties

In the Western and Eastern Jin Dynasties and the Northern and Southern Dynasties, alchemy was developed further. There were many famous alchemists, among whom were Ge Hong and Tao Hongjing. Ge Hong was a famous ancient Chinese Taoist theorist, alchemist, and

physician, who wrote many books, such as “抱朴子” (“Bao Po Zi”), “金匱藥方” (“Jin Gui Yao Fang”), (后节略为“肘后备急方”) and “神仙传” (“Shen Xian Zhuan”), and so on. Tao Hongjing was a famous ancient Chinese Taoist and chemist. From a young age he had a desire to find ways to keep people healthy. He lived through the Southern Song, Qi, and Liang Dynasties, and he was a Zou Wei Dian Zhong General in the Qi Dynasty. In the Liang Dynasty, he hid in Maoshan and concentrated on his study of Taoist theory and medical arts. He wrote many works, such as “真灵位书图” (“Zhen Ling Wei Shu Tu”), “陶氏效验方” (“Tao Shi Xiao Yan Fang”), “药总诀” (“Yao Zong Jue”), “本草经集注” (“Ben Cao Jing Ji Zhu”), and so on [1].

1.1.4.4 Sui and Tang Dynasties

In the Sui and Tang Dynasties, alchemy reached a peak with the integration of the emperor and religion. A lot of famous alchemists appeared, including Sun Simiao, Chen Shaowei, and Zhang Guo. Sun Simiao was a famous chemist and alchemist. He wrote medical books, including “备急千金要方” (“Bei Ji Qian Jin Yao Fang”), “千金翼方” (“Qian Jin Ji Fang”), and so on. His alchemy works have been lost, but some of his medical books are still available. Chen Shaowei edited the alchemy works “大洞炼真宝经修伏灵砂妙诀” (“Da Dong Lian Zhen Bao Jing Xiu Fu Ling Sha Miao Jue”) and “大洞炼真宝经九还金丹妙诀” (“Da Dong Lian Zhen Bao Jing Jiu Huai Jin Dan Miao Jue”), which describe the alchemy stone drugs and alchemy methods in great detail. They represent rare alchemy monographs [1].

1.1.4.5 Song Dynasty

In the Sui and Tang Dynasties, alchemy reached its peak. But after the Song Dynasty, it declined gradually. During the Yuan and Ming Dynasties, it reached its end and disappeared into history. In short, alchemy had a long history of over a thousand years in China. Alchemists researched and explored herbs and minerals, made medicines, and worked tirelessly on various chemical experiments in mountain caves and other inaccessible locations. These alchemists were actually physicians and scientists. Long-term practice of alchemy helped them make discoveries in chemistry and medicine and make an indelible contribution to the scientific and cultural development of mankind. Even the invention of the compass and printing were related to the alchemists, but their greatest contribution was the invention of gunpowder.

1.1.5 *The Invention of Gunpowder*

Stage 1: Water Mixing

Back in the late Western Han Dynasty and the early Eastern Han, the alchemy book “36 Water Laws” recorded a few alchemy recipes:

- “雄黄水：去雄黄一斤，纳生竹筒中，硝石四两，漆固口加上，纳华池中，三十日成水。” (“Red orpiment solution: put 500 g red orpiment and 200 g saltpeter in the bamboo, and then seal it with paint. After burying in the pond for 30 days, it will be a solution.”)
- “硫黄水：先以淳醋溼硫黄，漉令浥浥，纳竹筒中，加硝石 2 两，如上法埋地中，十五日成水。” (“Sulfur solution: first, immerse the sulfur in vinegar, and dilute with water to make it wet. Add 100 g of saltpeter, seal it in bamboo, bury it in the earth as in the last method, and in 15 days it will transform into the solution.”)
- “雌黄水：取雌黄一斤，纳生竹筒中，加硝石四两，纳华池中，三十日成水。” (“Orpiment solution: put 500 g of orpiment and 200 g of saltpeter in the bamboo and then seal it. After burying it in the pond for 30 days, it will be the solution”) [1].

According to research, “36 Water Laws” included 58 recipes in all, 33 of which involved saltpeter and other drug materials. In these 33 recipes, there were six involving the three refined yellows and saltpeter, and these uniformly avoided fire and used water instead. The book “黄帝九鼎神丹经” (“Huang Di Jiu Ding Shen Dan Jing”) from the Han Dynasty, which is about fire alchemy, also has no records about heating nitrate and the three yellows together by fire. From the information currently available, it is hard to find any record of heating saltpeter and three yellows by fire in the entire Han Dynasty. Some have inferred that this was deliberate avoidance. The belief is that early alchemists had learned the lesson that saltpeter could be mixed and heated with certain drugs. This is logical, but it lacks sufficient historical basis. What is certain is that during the Han Dynasty alchemists used saltpeter and other materials for water mixing. This was the first stage in the production of gunpowder.

Stage 2: Refining by Fire

In the Eastern Jin, Ge Hong’s alchemy work, 抱朴子, 内篇 (Bao Po Zi, Nei Pian), records the following: “又雌黄当得武都山所出者, 纯而无杂, 其赤如鸡冠, 光明晔晔者, 乃可用耳。其但纯黄似熊黄色, 无赤光者, 不任以作仙药,

用以合理病药耳。饵服之法，或以蒸煮之，或以酒饵，或先以硝石化为水，乃凝之，或以玄胴肠裹蒸之于赤土下，或以松脂和之，或以三物炼之，引之如布，白如冰...” (“The orpiment in Wudu Mountain is pure, without impurities. One is as red as a chicken’s crest and as bright and is great to eat. Others are pure yellow with no red light and are not suitable for immortal medicine but for reasonable medication. The methods of making it include cooking it with wine or first smelting it with saltpeter into solution. The red condensate is produced by steaming the Xuan Dong Chang with turpentine and refining these three things to produce something that looks like cloth, as white as ice”) [1].

It can be seen that in the Jin Dynasty alchemists manipulated saltpeter, sulfur, and carbon and refined them by fire. When these things were heated in the fire, in some cases (such as when the saltpeter content was small, etc.) the oxidation of arsenic was obtained. When the three materials were refined together, in some cases (if the saltpeter content was higher and it was heated at a high temperature) there was an explosion. But this explosion was not the result the alchemists wanted to achieve. Therefore, records of explosives are not found in the alchemy works of this time.

This is the second stage of the long history of alchemy regarding the invention of gunpowder. However, the alchemy books only recorded the result of “lead similar to cloth, white as ice” resulting from the refining the nitrate, sulfur and carbon together. But the explosions that occurred when the nitrate content was higher have not been recorded.

Stage 3: Fu Huo

In order to prevent explosions, alchemists took certain measures called 伏火 (Fu Huo)—(“control the fire”). Fu Huo involved taking measures to remove or change certain characteristics of stone materials. For example, drug toxicity, flammability, explosiveness, liquidity, and volatility of stone materials can be changed by heating and drying and other methods. Fu Huo first appeared in the “黄帝九鼎神丹经” (Huang Di Jiu Ding Shen Dan Jing) in the early Western Han Dynasty. In the Tang Dynasty, alchemists had detailed records of the Fu Huo of stone materials. In “Fu Huo Liu Huang Fa”, the amount of saltpeter and sulfur was specified to be 100 g each. However, although this form of combustive system with equal amounts of materials could burn very fast after ignition, there was not enough carbon, and the temperature was too low to melt the sulfur. Consequently, the unburned sulfur quickly plugged the channel in which the flame spread in the drug materials and thus interrupted the burning. In order to avoid the disruption and complete Fu Huo, the alchemists took two precautionary measures. First,

they added an appropriate amount of carbon, that is, “就口上着生熟炭三斤, 簇煨之” (“cooked with 3 Jin of charcoal and refined”). Secondly, there was multiple ignition combustion, “将皂角子不蛀者三个, 烧令存性, 以钐逐个人之” (“burn the gleditsia without the moth and keep firing to maintain the character so as to be sealed by individuals”). Because of this, the combustion continued under Fu Huo.

It can be seen that correct amounts of saltpeter, sulfur, and carbon produced the first gunpowder. In the Fu Huo process, alchemists took measures to prevent explosion, indicating that the explosive power of gunpowder was known. This was the third stage of the invention of gunpowder. The formula in “Fu Huo Liu Huang Fa” and “Fu Huo Fan Fa” represents the earliest formula for gunpowder.

Unfortunately, there is no precise date for “Fu Huo Liu Huang Fa”. And according to the records in the “铅汞甲庚至宝集成” (“Qian Gong Jia Geng Zhi Bao Ji Cheng”), in the “Fu Huo Fan Fa” there was a specific amount of saltpeter and sulfur, and the precise ratio had been determined. Second, the material configuration and operation process was different from the “Fu Huo Liu Huang Fa”. Third, there were three precautionary measures, which indicated that the explosive power of “Fu Huo Fan Fa” was known to be larger than the “Fu Huo Liu Huang Fa”. To sum up, “Fu Huo Fan Fa” was developed from the “Fu Huo Liu Huang Fa” and “Fu Huo Liu Huang Fa” appeared earlier. “Fu Huo Fan Fa” could be found in the alchemy book “太上圣祖神丹诀” (“Tai Shang Sheng Zu Shen Dan Jue”) in Tang Xian Zong Yuan He (808 CE). The discovery of the three gunpowder components in China could be traced back at least to the year of “Fu Huo Liu Huang Fa”. It is generally believed that this happened during the Late Sui and Early Tang Dynasties.

“真元妙道要略” (“Zhen Yuan Miao Dao Yao Lve”), which was written in the Tang Dynasty, recorded the phenomenon of the Fu Huo of saltpeter: “有以硫黄、雄黄合硝石并蜜烧之, 焰起, 烧手、面及烬屋舍者”。 (“When burning sulfur, realgar, and saltpeter together, there will be flame, then burning of the hand, face, and whole cottages.”)

“硝石, 宜佐诸药, 多则败药。生者, 不可合三黄等烧, 立见祸事。凡硝石伏火, 赤炭火上试, 成油入火不动者即伏矣。...不伏者才入炭上, 即便成焰。” (“Saltpeter can be medicine in a small amount, but too much will distort the drug. The amateur cannot burn the 3 yellows together, or there will be accidents. When using saltpeter in Fu Huo, the result should be tested on the charcoal. If combined with oil, it will be successful. If it is not, there will be flames from the carbon”) [1].

This was the alchemy recipe for gunpowder after the Middle Tang Dynasty. They not only knew that burning saltpeter, sulfur, and carbon together would lead to combustion and explosion, but they also had a better understanding about its power and destructive force. This is the earliest historical record describing gunpowder's power and destructive nature. This shows that, in the Tang Dynasty, gunpowder had been developed and used.

In summary, the invention of gunpowder in China dates back to the Han Dynasty. Han alchemists laid the foundation for the invention of gunpowder through alchemy experiments. In the Jin Dynasty there was a prototype of gunpowder. In the Late Sui and Early Tang there were written records showing that the three components of gunpowder had been discovered.

1.1.6 Song Dynasty

Although in the Jin Dynasty there was a prototype of gunpowder, and in the Late Sui and Early Tang Dynasties the three components of gunpowder had been discovered, the written records of the military's gunpowder formula did not emerge until the early years of the Northern Song Dynasty. After four years of effort, Zeng Gongliang, Ding Du Feng, and others under the order of Song Ren Zong completed the book “*武经总要*” (“*Wu Jing Zong Yao*”) in Qing Li Si Nian (1044 CE). In this book, three types of powder formulations were documented: *火炮火药法* (the formula for cannon gunpowder), *蒺藜火球火药法* (the formula for Ji Li gunpowder), and *毒药烟球火药法* (the formulation for poison gunpowder).

It can be seen that these three powder formulas were created and applied in the early Northern Song Dynasty. This three-part system has been in use to the present day. And the ratios of the three components in the powder formulations are generally similar to each other. In the Song Dynasty, in addition to the three main components—saltpeter, sulfur, and carbon—more than ten kinds of secondary materials were added, which were mostly flammable substances. But the gunpowder manufacturing process was also so simple that the products were of rough and poor quality and were therefore not very lethal [1].

1.1.7 Yuan Dynasty

In 1974, a cache of Yuan gunpowder was unearthed in Xi'an and compared with the formula in the Song Dynasty document “*Wu Jing Zong Yao*”. There were some significant improvements: the composition of powder components was better, as useless components had been removed, and the combination of saltpeter, sulfur, and carbon powder

had been formally established. The powder ratio was more scientific. In Yuan, the method of purifying the saltpeter and sulfur had improved and the purity had increased. Processing and manufacturing techniques had also become more advanced.

1.1.8 Ming Dynasty

In the Ming Dynasty, military gunpowder had been significantly improved. In particular, people had begun the study of gunpowder theory. In the Ming Dynasty, gunpowder uses were divided into a total of eight categories with nearly a hundred subcategories. The ingredients for the different types of gunpowder varied widely. Different types of gunpowder included Du Huo Yao, Lie Huo Yao, and Shen Huo Yao, etc., to meet the different needs of the war.

The “Huo” of Tang Shun Zhi’s “Wu Bian”, the “Huo Gong Yao Xing” of He Ru bin’s “Bing Lu”, the “Huo Yao Fu” in Mao Yuan Yi’s “Wu Bei Zhi”, the “Huo Yao Liao” and “Lun Qi” in Song Ying Xing’s “Tian Gong Kai Wu”, and the “Huo Yao Zhu Yao Xing Qing Xu Zhi” in Jiao Xu’s “Huo Gong Qi Yao” were the basis for theoretical research into gunpowder. These were the China’s first academic research papers on gunpowder. These works can be summarized as follows:

First, they discuss the roles and relationships of the three components of gunpowder, emphasizing the leading role that saltpeter plays.

Second, they discuss the “硝性竖而硫性横” (“vertical nature of nitrate and horizontal nature of sulfur”) feature of gunpowder, they raise the idea of “直击” (“attack”), and they discuss “爆击” (“knock”) and other new terms [1].

Third, they discuss the powder and importance of processing technology:

1. Pay attention to the purity of saltpeter and sulfur;
2. Pay attention to manufacturing methods and processes;
3. Adjust the ratio of saltpeter, sulfur, and carbon according to local conditions.

Fourth, they discuss air shock waves and the lethality of gunpowder explosions.

1.1.9 Modern China

Although China is the country that invented gunpowder and was the first to use firearms in war, firearm technologies developed very slowly in China. In the 17th century, there was a large gap between China and the rest of the world in the field of firearm technology. At the end of the Ming Dynasty, because of frequent wars, there was a climax in the

development of advanced weapons. Therefore, the quantity and quality of weapons used by the Ming army were enhanced. After the beginning of the Qing Dynasty, firearms in China stagnated until the 1960s.

1.2 Fireworks

Fireworks have become essential for festivals around the world. In China, fireworks are distinguished from firecrackers. Fireworks are for beautiful scenes while firecrackers are for sound. Fireworks spout fire and flares shaped like flowers. Fireworks are made by putting gunpowder and other chemicals in a paper or mud shell. Colorful patterns will then be produced when the fireworks are ignited. Firecrackers are made by rolling gunpowder with paper. When it is burned it will make a loud sound because of the gas and heat produced by the heating of the powder. Firecrackers can be classified as squib, cracker, petard, banger, loud banger, and so on.

1.2.1 Han Dynasty

In the Han Dynasty, people began to perform tricks to make it appear that they had supernatural powers, such as swallowing swords and spitting fire. In the Northern and Southern Dynasties, when Xiao Qi edited the book “拾遗记” (“Shi Yi Ji”), he stated that “含雷吐火之术，出于万毕之家” (“the art of spitting fire is from Wan Bi”), which was a quotation from “淮南子” (“Huai Nan Zi”). Thus, in the Han Dynasty there was the illusion of spitting fire, and this was an embryonic form of fireworks [1].

1.2.2 Tang and Song Dynasties

After the Tang Dynasty, when gunpowder was invented, fireworks production techniques and color categories reached a remarkable complexity. In the Song Dynasty, the custom of having fireworks at the Lantern Festival also began. There were two kinds of early fireworks. One was a light-emitting material, in which the gunpowder was placed in a shell made of paper or mud (commonly known as a “battlement”). The other type of fireworks was made by rolling gunpowder and light-emitting materials into a combustible and soft paper, known as the “medicine line”. This was then wrapped around the wire and arranged into pavilions, flowers, birds, and other kinds of shapes. When it was hung and the medicine line was lighted, the entire frame would burn in sequence, showing a colorful drawing. In the Southern Song Dynasty, in the “武林旧事” (“Wu Lin Jiu Shi”), Zhou Mi described the recreational activities of the Southern Song capital of Lin’an in the fifteenth day of

Lunar January. He wrote: “宫漏既深，始宣放烟火百余架，于是乐声四起，烛影纵横，而驾始还矣。” (“When it is dark in the palace, hundreds of fireworks are placed, then music plays everywhere, and candles and shadows cross”) [1].

Fireworks using jet propulsion promotion began in the Song Dynasty in the form of 起轮 (Qi Lun), 走线 (Zou Xian), and 流星 (Liu Xing). Qi Lun was used to produce jets in two opposite directions to make the fireworks rotate and rise steadily. There are still many varieties of such fireworks in modern times. Zou Xian involved hanging human-shaped spray fireworks on a taut wire. The line was the directional guide. When it was ignited, fire spread along the line. This developed into the modern fireworks show. “流星” (“Liu Xing”) is “起火” (“Qi Huo”)—a small rocket.

1.2.3 Ming Dynasty

In the Ming Dynasty, Shen Bang recorded descriptions of various types of fireworks in 宛署杂记 (Wan Shu Za Ji): “有声者曰响炮；高起者曰起火；起火中带炮连声音曰三级浪；不响不起旋绕地上者曰地老鼠；筑打有虚实，分两有多寡，因而有花草人物等形者曰花儿，名几百种。” (“The fireworks with sound are called Xiang Pao. The ones with tall flames are called Qi Huo. Qi Huo with fire and sound are called I San Ji Lang. The ones that have no sound and are not fired into the air but instead rotate on the ground are called Di Lao Shu. The fireworks called Hua could be sorted into hundreds of species according to different shapes and burning times”) [1].

There are few differences between the fireworks recorded 400 years ago and modern fireworks. Fireworks are still made by using the explosion and jet produced by the burning of gunpowder. It should be noted that fireworks that are made using the jet reaction are the predecessors of the modern rocket, and so China is the birthplace of the rocket.

1.2.4 Modern China

Today, fireworks are usually classified into six categories: ground fireworks, hand-held fireworks, hanging-wire fireworks, aerial fireworks, water fireworks, and modeling fireworks. Within each category there are several hundred varieties.

Ground fireworks are ignited on the ground and then spray sparks up in the air. Figure 1.1 shows the setting off of ground fireworks. In the past, clay or ceramic shells were usually used as battlements filled with

gunpowder and other materials. Today, multi-purpose paper shells are used. Varieties include “Tong Zi Hua” and “Quan Jia Le”.



Figure 1.1: Ground fireworks

Hand-held fireworks are small fireworks that can be held by hand, as shown in Figure 1.2. They include “Di Di Hua” and “hand flowers”.

Hanging-wire fireworks can be hung on bamboo branches or wires. After lighting, the fireworks will rotate quickly and change color, as shown in Figure 1.3. A representative variety is “San Jiao Yan Huo”.

Aerial fireworks are fired into the air and the flames dissipate into the atmosphere, as shown in Figure 1.4. According to their range, aerial fireworks are classified into two kinds: low-altitude fireworks and high-altitude fireworks. The representative varieties are “Qi Huo”, “Cai Ming Zhu”, “Lu Mu Dan”, and “Tian Nu San Hua”.

Water fireworks are a special group. They are installed on a fixed underwater launchers and are fired from the surface of the water and discharged into the air, as shown in Figure 1.5.



Figure 1.2: Hand-held fireworks



Figure 1.3: Hanging-wire fireworks



Figure 1.4: Aerial fireworks



Figure 1.5: Water fireworks

Modeling fireworks originated in “He Zi Hua”. Usually, metal wires are packed with powder and made into various shapes or frames. After ignition, the layers are ignited in a prepared order and a variety of images will show and be accompanied by sound. “Shu Hua” and “Dian Gan” are examples.

Currently, there are at least 500 kinds of fireworks. Pyrotechnics are also used in aerospace (more than 200 pyrotechnic devices were used when Apollo was sent to space), navigation (marine flares, etc.), industry (cutting, smelting, etc.), agriculture (pesticides, crops, anti-frost), arts (stage effects), weather reports (such as research devices), and other fields.

1.3 Firearms

Because China was ruled by the Qing Dynasty for 270 years, many Chinese mistakenly think that gunpowder was wasted on entertainment when it ought to have been used for advanced weapons. But this is not so. Firearms development was emphasized in the Yuan Dynasty and Ming Dynasty. China has a long history in the field of firearms.

1.3.1 Song Dynasty

There is no doubt that the firelock first appeared in China. The earliest firelocks were used in the 10th century in the Song Dynasty. Based on developments in the Yuan Dynasty and Ming Dynasty, firelocks ought to have been very advanced by the end of the Ming Dynasty. But, after the wide usage of blunderbusses in China, in the early 14th century Arabs made a “Madafa”, which is a tube-shaped firearm made of wood. In the middle of the 14th century, the Italians made the musket, which is a tube-shaped firearm made of metal. The flintlock technology in Europe developed separately and had a significant influence on China’s firelock technology in the 17th century [2], Figure 1.6 shows the most commonly used blunderbuss in the Song Dynasty in China.

1.3.2 Yuan Dynasty

The killing power of the “erupter” that appeared in the Song Dynasty was not strong and its range was only 5~10 m. In the Yuan Dynasty, the development of new firearms was emphasized. In 16th year of the Yuan Dynasty (1279 CE), craftsmen were concentrated in the Great Capital of Yuan (Beijing) to conduct research on new weapons and gunpowder formulas. The efficiency of improved firearms was enhanced by a factor of three. In 1332 CE, the earliest copper blunderbuss marked with an inscription was cast. Its length was 1.3 m and its weight was 14

kg. The hand-blunderbuss shown in Figure 1.7 was made around the same time. But this kind of hand-blunderbuss had no value because of its weak power and low range. It was only used for entertainment by military officers.



Figure 1.6: Blunderbuss



Figure 1.7: Hand blunderbuss



Figure 1.8: Artillery

During the war period at the end of the Yuan Dynasty, artillery, which is shown in Figure 1.8, was widely used. The number of blunderbusses and artillery pieces was very large. The appearance of metallic firearms opened up a new era for the development of ancient weapons. Because of its advantages—durability, strong power, and long range—metallic firearms became the most important weapons in succeeding dynasties and were used all over the world [2].

1.3.3 Ming Dynasty

In the Ming Dynasty, because of the rapid development of the economy, weapons were vastly improved. Non-firearm weapons mainly included the long-handled falchion, the short-handled falchion, the scimitar, and so on. Besides traditional weapons, the development of firearms also flourished. Many books on the art of war written at the end of the Ming Dynasty provide detailed records about manufacturing methods, atlases, and tactics. There were also many famous firearm experts such as Zhao Shi-Zhen, Bi Mao-Kang, Hu Zong-Xian, Mao Yuan-Yi, Sun Yuan-Hua, and Dai Zi, and many famous generals such as Qi Ji-Guang, Sun Cheng-Zong, Yuan Cong-Huan, and so on.

The development of firearms in the modern sense began during the war between China and Japan. In 1512 CE, after the battle of the South China Sea, China seized three pirate ships and obtained a kind of firearm called a “French cannon”. Firearm experts in China then improved the

French cannon and produced a new firearm called the “Shenji cannon”, which is shown in Figure 1.9. This innovation was a leap forward in the Chinese weapons industry. One Shenji cannon required three soldiers to operate it. Nine years later, in 1521 CE, China seized two Portuguese warships and obtained the European match-lock gun. This batch of match-lock guns did not arouse the military officers’ attention. The Ming army did not produce this kind of match-lock gun in mass until the Japanese used them to invade the coastal regions of China.



Figure 1.9: Shenji cannon

In 1548 CE, in the battle to recover Shuang-Yu Island, which had been seized by the Japanese and Portuguese, the Chinese army seized some cone drums and some Japanese who were good at manufacturing cone drums. Experts such as Ma Xian and Li Kui learned the manufacturing method of the match-lock gun and improved it. In 1558 CE, the first batch of match-lock guns (about 10,000) was produced. Thus, the government of the Ming Dynasty attached special importance to equipping its army with firearms.

The match-lock guns made in China were called “bird blunderbusses”, as shown in Figure 1.10, and they became the Chinese army’s main weapons in later battles. The range of the bird blunderbuss was about 120 m. Its barrel was made of wrought iron. The fire orifice at the bottom had a gunpowder pool. The copper cover on the powder pool kept out the wind and rain. The extractor rod inserted in the butt was used to fill up the ammunition. The bottom of the barrel was sealed with a bolt so that the barrel could be cleaned easily.



Figure 1.10: Bird blunderbuss

At the same time, Lumi (from Turkey) sent an envoy to China, and a harquebus was given as a tribute. The famous firearm expert Zhao Shi-Zhen, who was born in a seaside region that had been invaded by the Japanese, was fully aware of the importance of reinforcing national defense and improving weaponry. In 1597 CE, Zhao Shi-Zhen suggested to the Ming Emperor that they try to reproduce the harquebus that came from the Lumi.

To achieve better quality, Zhao Shi-Zhen found natives to teach the production and usage of the harquebus. In 1598 CE, a new harquebus was produced whose range was further than the traditional harquebus. It was called the “Lumi blunderbuss”, which is presented in Figure 1.11. The barrel of this kind of blunderbuss was longer (1.5 m), 3-4 kg heavier than the traditional bird blunderbuss, and its range was larger (150 m) than the traditional harquebus. Simultaneously, the Chedian blunderbuss and the Xunlei blunderbuss, which are shown in Figure 1.12 and Figure 1.13 respectively, were also developed. The Chedian blunderbuss resembled the French cannon. The Western blunderbuss and the Xunlei blunderbuss had the same advanced features as the bird blunderbuss and the Sanyan blunderbuss. In 1608 CE, these new firearms developed by Zhao Shi-Zhen were verified by the emperor and the government of Ming Dynasty, and mass production was authorized.



Figure 1.11: Lumi blunderbuss

In the 17th century, many European firearms, like gunmetal, casting cannons, wheeled cannons, and rifles, were better than China's firearms. The government of the Ming Dynasty spent much money to introduce the advanced technologies learned from Portuguese experts. In the cannon factory located in Macao, China mass produced advanced firearms based on European technology and equipped the Chinese army with them. These firearms were of great utility in battles. At the end of the Ming Dynasty, the cannons used by the Ming army were cast with refined iron and their production technologies were close to the most advanced level in the world. The quantity of cannons in China at that

time was also the largest in the world. The maximum range for cannons on land was 5 kilometers and for cannons on ship was 2 kilometers. It is said that the Duth cannon used by the Ming army could kill a thousand people at one time. Its weight was 1.5 tons and its range was 5 kilometers. Figure 1.14 is a photo of ancient Duth cannon.

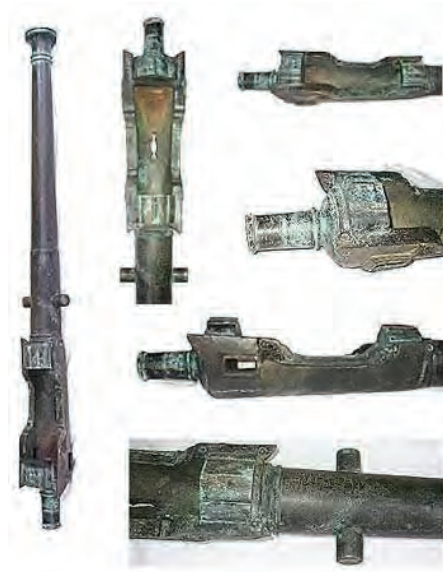


Figure 1.12: Chedian blunderbuss



Figure 1.13: Xunlei blunderbuss



Figure 1.14: Duth cannon

Firelocks were the main firearms used by the Ming infantry. Every hackbuter was equipped with two gunpowder tanks and 300 lead pellets. It is noteworthy that the lead pellets used granular gunpowder and not powdery gunpowder. It contained 75.8% nitrate, 10.6% sulfur, and 13.7% carbon, which was close to the optimum proportions for black powder. Because of the long preparation time, there were always three rows of infantry during the battle. The first row charged the gunpowder, the second row inserted the gunpowder, and the third row shot. This cycle was then repeated continuously.

Up to the end of the Ming Dynasty, the tubular firearms (including guns and cannons) developed by the Ming military institutions were numerous. Jet firearms (ancient rockets) and exploding firearms were also developed. Exploding firearms included land mines, as shown in Figure 1.15, and water mines, as shown in Figure 1.16, produced in large quantities and in many varieties. History has proven that China is the country that invented mines [2].

Until the middle of the 17th century, at the juncture of the Ming and Qing Dynasties, the development of firearms in China did not lag behind the rest of the world. Because of the Ming army's fighting, the government of the Qing Dynasty also made great strides in the development of firearms. After the establishment of the Qing Dynasty, military experts still made improvements to firearms. For example, the

Qing government developed three kinds of flintlocks in succession, including the turning wheel type, the spring type, and the impinging type. But these kinds of flintlocks were mainly used for hunting and not for equipping the army. In the Qianlong period, besetting bone flintlocks were produced that were the equivalent of the mode rifles made in Europe. The besetting bone flintlock was only used for hunting.



Figure 1.15: Ancient land mine



Figure 1.16: Ancient water mine

1.3.4 Qing Dynasty

In the Kangxi period, military expert Dai Zi invented the continuously shooting blunderbuss, as shown in Figure 1.17, which could continuously shoot 28 lead pellets and was very powerful. The invention of the continuously shooting blunderbuss preceded the invention of the machine gun in Europe by about 200 years. The Panchang blunderbuss and the Weiyuan general cannon were also important inventions of Dai Zi. Figure 1.18 shows the photo of Weiyuan general cannon. The Weiyuan general cannons were similar to the modern howitzer, which had a long range and strong firepower. But the Qing government paid more attention to the cavalry. Dai Zi was finally transported to the border area for penal servitude, and the development of firearms in China stopped. In order to commemorate the contributions of Dai Zi, the Emperor Kangxi engraved his name on the gun barrel of the Weiyuan general cannon.



Figure 1.17: Continuously shooting blunderbuss

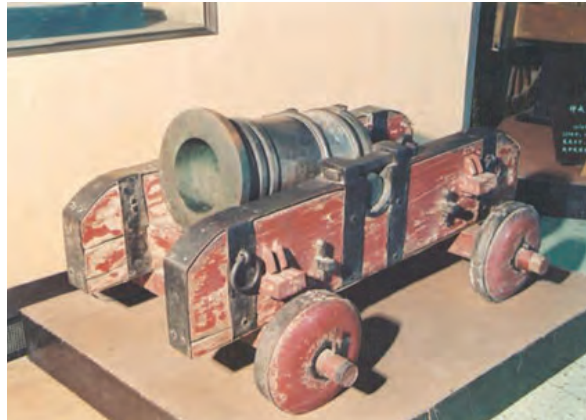


Figure 1.18: Weiyuan general cannon

In 1757, the Qing government issued a proclamation that foreigners were forbidden to carry firearms in China. In 1842, twenty thousand Chinese soldiers were defeated by four thousand British expeditionary forces equipped with new cannons. In 1860, when British and French troops encroached on the Summer Palace in Beijing, they were surprised to learn that the serviceable cannons donated by the British diplomatic corps were being used only as decorations. In 1900, Chinese soldiers were defeated thoroughly by the Eight Power Expeditionary Forces using machine guns.

By surveying the development history of Chinese firearms, we can find the embryonic form of all the modern weapons in the Ming Dynasty, including land mines, water mines, rocket launchers, machine guns, armored divisions, and so on. But in the Qing Dynasty, it can only be said that ignorance ran through the whole dynasty, which originated from Chinese concern about saving face [2].

1.3.5 Modern China

A substantial gap between Chinese and Western firearms technology formed in the mid-19th century. However, as early as the late 17th century, the different roads that Chinese and Western modern science and industrial development took made such a result inevitable. The Western world was experiencing the “Age of Discovery”, while China closed its doors because of the short-sightedness and ignorance of the feudal monarchy. The policy of isolation which the Qing Dynasty insisted upon for 200 years not only hindered the development of Chinese firearm technology, but also made China fall behind the West in many other fields of science and society. All these moves set the tone for the relationship between China and Western world for the next several hundred years [3].

1.4 Solid Propellants

At present, scientists all over the world are competing to research and develop low signature and gelled propellants, and they have made great progress. R&D on solid propellants in China is lagging behind somewhat compared with the rest of the world.

R&D on solid propellants in China began in the early 1950s. First, researchers imitated Soviet general double-base propellants, for instance diacetyl. Then they designed and developed a double-base platform that had intermediate energy and was smokeless. They also designed a high performance modified double-base and composite propellant, as well as relatively complicated engine propellant charging systems, such as propellant cladding. Over the past 40 years, China has made significant

progress in the field of solid propellants. All of the different kinds of propellants used in the world are researched and developed in China, and a series of better performing propellants have been produced and used on strategic missiles and tactical missiles [4].

1.4.1 Modified Low-signature Double-base Propellants

Since the middle of the 1960s, China has carried out research on screw-compressed modified double-base propellants and has produced a series of modified double-base propellants, including P15, 06, GP -19 and so on. These achievements laid the technical foundation for R&D of high burning rate propellant, high energy propellant, and intermediate energy smokeless propellant. Some new propellants, such as 171-25, 171-30, and GR-35, have been developed and widely used in various weapons. In order to meet the requirements of charging for the strategic missile engines, China researched and developed the formulas for high energy casting modified double-base propellant and carried out large scale tests using the $\text{Ø}300$, $\text{Ø}480$, and $\text{Ø}1000$ engines. The results show that the energy characteristics of Chinese propellants have reached the international advanced level. In recent years, scientists have performed R&D on cross-linked modified double-base propellants used in tactical missile [5].

1.4.2 Deterred Low-signature Double-base Propellants

China has adopted the same technical approaches to developing deterred low signature double-base propellants as other countries. At present, China has developed many new materials, including GAP, GL-20, ADN, ammonium nitrate, and so on, and carried out research on propellant formulas like GAP/AN, GAP/HMX, NEPE/AN, and GL-20. Among them, the theoretical specific impulse of GAP/AN propellant is close to 2,450 N. s/kg, which has reached or even exceeded the highest specific impulse in the world [5].

1.4.3 The Gap between China and the World

From the viewpoint of current applications, the development of future solid propellants will involve the following: reducing the cost of high performance and high reliability; reducing environmental pollution; and researching and developing low signature propellants, deterred propellants, and variable energy propellants. Although the research into solid propellants has advanced greatly, the gap between China and the rest of the world is still very large. So far, there are relatively few domestic and international research papers on insensitive propellants, so the research about insensitive propellants, especially about oxidizers in insensitive propellants, should be emphasized.

Li Hongzhen et al. studied the synthesis process of the 3,3'-dinitro-4,4'-azofurazan (DAAzF) and 3,3'-dinitro-4,4'-azoxyfurazan (DAAF), which are two kinds of compounds. The physical and chemical properties, thermal stability, detonation properties, safety, and other aspects of these two compounds were also outlined. In terms of security, the drop hammer impact sensitivity H_{50} of DAAzF and DAAF is similar to 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), while having insensitivity to sparks and friction; therefore, these two compounds are expected to be used in a new generation of insensitive explosives; their performance parameters are shown in Table 1.1 [6].

Table 1.1: Property parameters of several high explosives

	Project test	DAAzF	DAAF	HNS	TATB
Safety experiment	H50 (25kg, type 12)/cm	320	320	54	320
	Spark sensitivity	0.36	0.36	-	-
	Friction sensitivity (BAM)/kg	36	36	-	-

Note: BAM is an instrument developed by Germans to test the friction sensitivity of propellants.

The modified double-base propellants used in other countries' equipment are all under research in China, such as modified high-energy low-smoke double-base propellants and nitrate ester plasticized polyether propellants (NEPE). China has achieved many breakthroughs in the development of modified low-smoke double-base propellants with a measured specific impulse between 2,158 N. s/kg and 2,207 N. s/kg, and some of them are being applied in different models. But there is still a very large gap between China and the rest of the world in the propellant field. Firstly, in China, the development of raw materials cannot satisfy the requirements of propellants. Secondly, the energy levels of current propellants are too low, with theoretical specific impulses less than 2,450 N. s/kg. Thirdly, the means of testing the propellants' smoke characteristics are imperfect. Finally, the relevant standards for the evaluation of smoke characteristics are not established. The level of smoke suppression has reached 60~80% in the world, but in China, this technology has just begun [7].

The development of practical technologies for new propellants combined with different models has been slow in China. Although scientists have developed many new propellants like GAP, CL-20, and stable ammonium nitrate, because of the uneven quality of raw materials

and lagging production processes, the comprehensive properties of propellants are not good and cannot meet the requirements for use in weapons. At present, China is at the 1980s technical level compared to the rest of the world. Therefore, Chinese scientists must analyze the development trends around the world and strengthen the research of new materials and new technologies to further improve the properties of low signature double-base propellant [7].

1.5 Space Solid Rocket Motor

More than one thousand years ago, in the Tang Dynasty, China invented the solid rocket, but the modern era of Chinese solid rocket motors began in the 1950s. In 1958, research on composite solid propellants began. Propellant raw materials were synthesized, and formulations and casting techniques were conducted. In 1960, a 65 mm diameter experimental motor was tested, then a 286 mm diameter motor was made in 1962. From then on, 770 mm, 810 mm, 1400 mm, and 1700 mm diameter space motors have been developed. China possesses the capacity of making large-scale motors right now. The design and manufacturing technologies of motors and propellants have progressed tremendously. Motor mass fraction has been improved from around 0.7 to above 0.9. Sea level specific impulse has increased from 2000 N·s/kg to more than 2400 N·s/kg. Presently, a number of institutions conducting motor design and research, raw material preparation, propellant formulation and processing, case/nozzle material development, nondestructive inspection, environmental test and static test facilities have been set up in China [8].

1.5.1 Sounding Rocket Motor

From 1962 to 1966, China developed its first 286 mm diameter sounding rocket motor, in which polysulfide binder with aluminium powder was used as propellant. High strength steel was used as the case material and high strength graphite as the nozzle throat insert material.

During the development of these sounding rocket motors, problems such as combustion instability and grain cracking, etc., were solved. Several flying tests were carried out successfully in 1965. These early achievements laid the foundation for modern solid rocket technology in China.

1.5.2 The Third Stage Motor of Launch Vehicle

From 1966 to 1971, China developed the launch vehicle for China's first satellite DFH-1. The 770 mm nominal diameter solid rocket motor

was developed as the third stage motor of the Long March-1 (LM-1) launch vehicle.

During the development of this kind of motor, problems such as the manufacturing of ultra-high strength steel motor cases, ignition at high altitudes, effects of spinning on propellant burning rate, insulation erosion, and alumina slag in chambers were solved. On April 24, 1970, China's first satellite, DFH-1, was launched successfully. This kind of motor was also successfully used in the launching of China's first scientific experimental satellite, Practice-1.

1.5.3 Retro-motor of Returnable Satellite

In solving the problem of satellite re-entry, several kinds of retro-motors were developed from 1968 to 1988. These motors are spherical. CTPB was used as a propellant first, then HTPB. An annular igniter was located in the aft dome. The spinning rate of the motor was 60 rpm.

During the development of these kinds of motors, several technical difficulties were worked out, including high-strength steel/titanium alloy spherical chamber case shaping, umbrella finocyl grain mandrel designing, the propellant casting process, and aft-end ignition in high altitude. The returning satellite traveled in orbit for 8 to 15 days before the retro-motor was commanded to ignite. The retro-motors performed normally in all 16 launches after the first successful launch of a returnable satellite in 1975.

1.5.4 Apogee Motor

To meet the requirements of launching synchronous communication satellites, several apogee motors were developed from 1975 to 1987. In these kinds of motors, high strength glass fiber as a case winding material, HTPB as a propellant, and carbon/carbon composite material as a nozzle throat insert were used. The nozzle was contoured with dual arc-shape divergent sections.

During the development of these kinds of motors, problems such as the high strength glass fiber case shaping process, grain structure integrity, and nondestructive detection were solved. These kinds of motors were first used in China's experimental communication satellite DFH-2 in 1984; then the improved ones were successfully used in the communication satellite DFH-2A. The total impulse accuracy (3σ) of these motors had reached 0.7%.

1.5.5 Perigee Orbit Transfer Motor

In the late 1980s to meet the demands of the launch vehicle market both domestically and overseas, two kinds of perigee orbit transfer

motors were developed for the launch vehicle LM-2E. A high-strength glass fiber winding case, high-performance HTPB propellant, three dimensional finocyl grain, and a carbon/carbon composite material throat insert were used in the motor having a diameter of 1400 mm.

This motor performed successfully in the first launching of the LM-2E rocket in 1999. To meet the launching requirement of the Asia Sat-2, a 1799 mm diameter motor EPKM was developed. Its main performance parameters are listed below:

- motor diameter 1700 mm
- motor total length 2930 mm
- motor total mass 6000 kg
- maximum thrust 190 kN
- action time 88s
- total impulse 15600 kN·s
- motor mass fraction 0.907
- specific impulse (vacuum) 2864 N·s/kg

During the development of this kind of motors, some problems such as the erosion of chamber insulation and the effects of motor internal ballistics on spinning conditions, were solved. This motor was first used successfully in the launch of the Asia Sat-2 on November 28, 1995, and then successfully used in the launch of Echo Star-1 on December 28, 1995.

In brief, the solid rocket motor technology has advanced steadily in China. China has a no-failure record of solid rocket motors in space launches. With 38 years of experience in solid rocket motor development, composite propellant rocket motors with a diameter of 1700 mm or larger can be produced in China independently. Technology in this area is still developing rapidly, including organic fiber winding cases, high energy composite propellants, minor torque flexible nozzles with composite material reinforced parts, safe/arm devices, multidimensional weaving carbon/carbon composite nozzle component, advanced nondestructive detection, and static firing tests and measurements [8].

1.6 Latest Research Progress

Energetic materials (explosives, propellants and pyrotechnics) are used extensively for both civilian and military applications. There are ongoing research programs worldwide to develop pyrotechnics with reduced smoke and new explosives and propellants with higher performance or enhanced insensitivity to thermal or shock insults. In recent years, the synthesis of energetic, heterocyclic compounds have

received a great amount of interest. This section will concentrate on recent advances in the research of energetic materials in China [9].

C₆₀ is one of new discoveries in science and a great interest in it now is arising in the fields of physics and chemistry as well as new materials. Wang and Li have done much brilliant research and obtained a great deal of achievements in this field. They elaborated on the applied prospects of C₆₀, especially, in the field of energetic materials [10].

Zhou et al optimized the geometry of hexanitrohexaazaisowurtzitan (CL-20) at the B3LYP/6-31G** level. The population, natural bond orbital and vibrational frequency were carried out. They obtained a possible stable molecular geometry and also discussed the relationship between the bonding behavior and the properties of CL-20 [11].

Chen et al reviewed the progress in the studies on the damage and mechanical properties of energetic materials. They introduced the production and experimental simulation of damage, the damage modes in energetic materials, and the influences of damage on the shock sensitivity, combustion and even detonation properties of energetic materials. They also reviewed the mechanical properties of explosive crystals, the influencing factors of the mechanical properties and constitutive laws including damage, and also made some suggestions for further investigation [12].

Based on experiments, Wang et al investigated the ignition threshold of metal covered energetic material by Nd: YAG laser beam. Finally, the effects of laser spot size and incident angle on ignition threshold were also discussed [13].

Gao et al reviewed the development of acoustic emission (AE) technique and its application in the field of researching energetic materials. From the research of AE features and the performance experimentation, the method and application of AE testing in the field of energetic materials have been analyzed and compared. They obtained the results that AE testing, as a dynamic non-destructive testing technique, has unique reliability and advantages in the research of energetic materials, such as quality control, performance research, the monitoring and evaluation of the inner damage, safety control during processing of energetic materials, etc [14].

Micro-structural aspects of energetic materials can affect the material response to certain stimuli such as shock, and are thus of particular interest from both safety and performance perspectives. Small angle X-ray scattering (SAXS) is a powerful tool for studying structural features of materials. Chen et al employed synchrotron radiation SAXS technique to characterize the micro-structure of loose powder and pressed pellets of the insensitive high explosive TATB. Analysis of the

SAXS data revealed number averaged particle size distribution and porosity in the materials [15].

Xia carried out experiments to research the combustion to detonation transition of new energetic materials and the results showed the cloud of some new energetic mixtures could automatically ignite in air to form a fireball in which combustion to detonation transition then occurred [16]. He et al researched the synthesis process of guanidine dinitramide (GDN) by the reaction of ADN and guanidine salt. Its structure was identified by IR and UV spectrum analysis, and its properties were measured. The properties of GDN were proved to be superior to those of ADN and NG [17].

Based on the SGI graphic station, applying the ISIS operation platform software and MDL chemical reaction data base software, Li et al designed the synthetic routes of RDX and a kind of dummy energetic material. It was proved that the MDL chemical reaction data base software was viable and effective in designing the synthetic routes of energetic materials [18].

1.7 Summary

The invention of gunpowder was a great contribution to world civilization. Gunpowder is one of the four great inventions of ancient China. It not only powered weapons for ancient wars but also laid the foundation for modern explosives. The invention of gunpowder made a significant contribution to technological advancement and industry evolution, and it is still playing an important role in the economy and cultural development of China and the world.

1.8 References

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Chapter 2

Progress in Technology of Chinese Energetic Materials—An Overview

Based on a review of open literature, Chinese energetic materials are competitive internationally for applications ranging from air to underwater. Judging from the attribute of detonation velocity, which is the main criterion of the current approach, Chinese technology advancement appears to be well chartered since the 1960s. Contrasting this short 50 year period of catching up with the rest of the world with more than 500 dormant years since being a pioneer and leader in armament and warfare strategies before the Yuan Dynasty, Chinese progress is remarkable. However, addressing industrial safety, ecological hygiene and health issues on top of integration and generalization of high technologies towards innovation systematically remains a challenging task for the Chinese - and for all other nations.

2.1 Introduction

In the U.S. and Canada alone, blasters use more than 6 billion pounds of explosives and 75 million detonators each year. Coal mining accounts for two-thirds of the explosives consumed, of which more than 80% are ammonium nitrate fuel-oil¹.

Starting with a historical background, this chapter summarizes Chinese progress in energetic materials technology. Information contained herein is based on citations from open literature and is meant for educational or academic use. The objective is to offer a general assessment of Chinese technological attributes and competitiveness in this special technology. A potential benefit is enhancing bilateral

¹ ANFO; History of Explosives and Blasting: <http://www.explosives.org/HistoryofExplosives.htm>

commercial interests. The approach is to classify energetic materials according to application and energy intensity. Both categories can be refined by discussions of their key performance parameters in the context of typical products (when data are available). Medium-energy energetic materials are discussed first.

Medium-energy energetic materials are explosives with detonation velocity between 5000 m/s and 9000 m/s. This includes most explosives. Medium-energy energetic materials are typified by RDX-based systems. Explosives with detonation velocity above 9000 m/s are called high-velocity or high-energy energetic materials. Examples are HMX or CL-20-based systems.

2.2 The Chinese Black Powders—A Historical Note

Black powders, or carbon blacks in a technical context, are recognized as one of China's four greatest inventions. The other three are the magnetic compass, printing by combinative ink stamps, and the brush pen for writing. In historical records, the black powders used as explosives in China are descended from ancient Chinese biomedical research for longevity drugs—possibly created to detoxify and disinfect with the surfactant properties of carbon powders. Traditionally, Chinese medical practitioners were also biochemists, metallurgists, philosophers, and even surgical doctors who were all searching for health-sustaining and illness-curing drugs (similar to medieval doctors in Europe one millennium later). It was during the Tsu'en-Chi'ou Period (the Spring-Fall Period) from approximately 800-500 BCE¹, that the phenomenon of “sublimation of Hg (mercury) by the fire thus invisible” (“得火則飛,不見埃塵”) was recognized². In fact, “Fire Warfare” is one of the thirteen chapters in the famous and pioneering monograph on Bing-Fah (“Rules of Military Strategy”; 208 BCE) of Sun-Wu (Sun-Ze). The unearthed manuscript is in the form of engraved bamboo sticks dating back one thousand years before “Greek fire” (668 CE) [1]. By the 3rd century (229 CE), Zhu Gir-Liang' in alliance with Zhou Yu used “fire-arrow warfare” in combating the overpowering fleets of Tsau-Tsau (the King of Wei) over the Yang-Ze River and won a major victory by the tactic of “total incineration”. Biomaterials such as dried Ai leaves (medical herbs), linen rags, and animal lard were major ingredients of the combustibles of that time. For completeness, we can add to the

¹ http://www.tqxz.com/lssj_readme.asp?id=236

² In “Zhou-Yie Tsan-Tong-Chi” 《周易參同契》：
<http://vm.nthu.edu.tw/history/shows/show01/sung.siege/siege-con04.html>

chronological listing found in the “History of Explosives and Blasting”¹ [1] the pioneering Chinese smoke stack tactics (ca. 800 BCE) and the fire-arrow warfare (ca. 230 BCE).

During the Han and Tang Dynasties, pyrotechnic compound technology evolved from firecrackers and fireworks. By the year 850 CE, As_2S_3 , sulfide, and nitride powders constituted the three-part explosive system. Note that all three are traditional Chinese medicinal ingredients. Therefore, the basic concepts of grenades, shotguns, cannons, and cluster missile warfare were advanced well before the Yuan dynasty, when blast wave phenomena were recognized [2]. Archery was developed in approximately 2500 BCE, when it was established as a ceremonial exercise and a part of social etiquette as well. This corresponds well to the Western Asia development of archery around 3000-2500 BCE. A cannon using black powder as a propellant was built in February of 1332 CE and is on display at the National Palace Museum in Beijing. Details can be seen in Table 2.1, where Chinese scripts are intentionally maintained for Sinologists. We may add that pyrotechnics invented in China spread to Europe through the Silk Road and other channels, notably during the 1200s CE, and to Japan by 1543 during its Jane-Wu Restoration period, also known as the Kenmu Restoration period (1533-1575) [3].

Traditionally, black powder produces around 55% solids by weight. Generally, these solid products are potassium carbonate, potassium sulfate, and potassium sulfide. Currently, many problematic areas of this basic technology are still under research. In China, they include pre-ignition reaction (PIR) of solid S-KClO₃-based compounds or KClO₄-M (M for metals) systems in terms of lattice relaxation kinetics and mechanisms leading to rapid mass transport for explosion. Currently, nano-graphenes, nano tubes [4] and fullerenes are replacing graphite flakes and amorphous clustering of carbon black ashes.

It is worth noting that Song Yingxing (1587-1666), a Chinese scientist and technologist during the Ming dynasty, wrote the chapter “Chi and Sern” in his book titled “On Chi” 《論氣-氣聲篇》 [2]. This was an unprecedented essay dealing with all kinds of Chi, described as propagating waves that can give out sounds, including blast waves. Sun became famous in China only after his death. British sinologist and historian Joseph Needham praised Song Yingxing as “the Diderot of China”, comparing him to the famous French encyclopedist Denis Diderot, for his illustrated encyclopedia published in 1637 CE. He has also been compared to Charles Darwin. This authoritative work embraces all branches of Chinese science and technology, tracing it up to about the

¹ <http://www.explosives.org/HistoryofExplosives.htm>

Warring Time of China (before 500 BCE). His concise descriptions of tools and equipment, materials (including energetic materials and tactics), and processing and production methods, in addition to herbal medicine, crafts, agriculture, and transportation, show that he was a self-educated genius like Leonardo da Vinci. With the recovery of his lost originals, the contributions of early Chinese inventions, with special reference to black powders, firearms, grenades, and missiles, etc., have been firmly established (see Table 2.1 and Figures 2.1 and 2.2).

(a)



(b)



Figure 2.1: (a) First seismoscope invented by Chang Hern; (b) First mobile stencil system, i.e., of movable characters for printing.

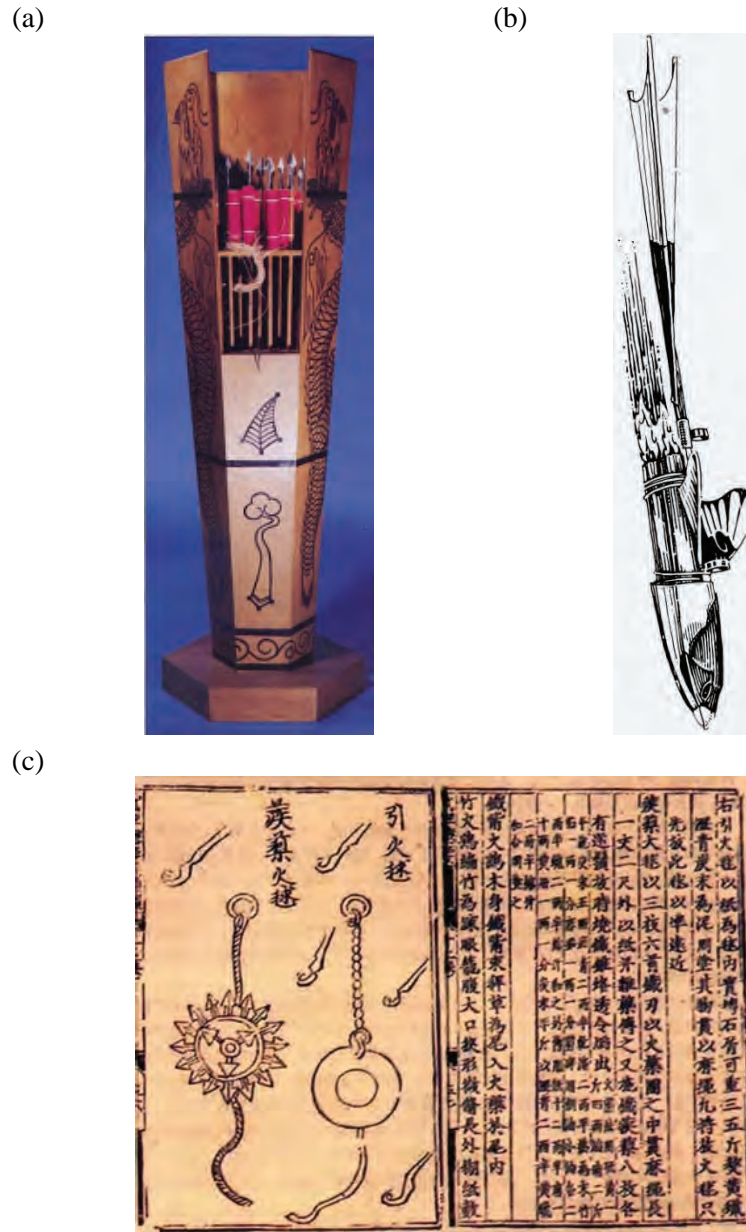


Figure 2.2: (a) A miniature mimicking cluster rockets system; (b) Flying Crow – a Firing Dragon warhead for naval warfare; (c) Design book exhibiting the fused “Gee - Li-Hoh-Chiou” with formulation - the world first “grenade” with both blast and incineration power

Table 2.1: Pioneering energetic technologies invented in ancient China [a]

Technological Innovation	“Original note” (in Chinese classic verse), 《Monograph,〈Chapter, (Date/annotation)》	Chinese chronicle dating (Western calendar year)
Archery [b]	《尚書》〈帝堯篇〉 Appeared in the earliest book “Shon-Shu: King Yao Chapter”	(ca. 2500 BCE)
Smoke tactics [c]	“有寇至舉烽火為信”《周史記》；《明·張居正·帝王圖鑑說》〈戲舉烽火〉 “When enemy comes burn smoking fire for signaling.”	Ending of Western Zhou dynasty (781-771 BCE)
Seismoscope [d]	張衡:地震儀 Invented by Chang Hern	Figure 2.1 (ca. 50 BCE)
Firing arrow warfare	諸葛亮率兵攻打陳倉（今陝西寶雞市東）。魏國守將郝昭指揮士兵用“火箭”向架雲梯攻城的蜀軍怒射，雲梯燃燒，蜀軍受挫。（蜀漢建興七年） Devised by General Hao Zao of Wei Kingship in the township of Chen-Tsong as anti-siege warfare to defeat the army of Shuh Kingship successfully.	Three-Country Period (1229 BCE) (Note: almost 500 years earlier than the “Greek-fire” being used in battle by Greeks in 668 BCE [e])
Blast arrow warfare and archery squad	〈火箭法〉：“施火藥於箭首，弓弩通用之具”《武經總要》；吳越國王進（呈）射火箭軍士《宋史·太祖本紀》970（開寶三年）；976（開寶九年八月乙未朔） As gifts to the emperor recorded in the “Bibliography of Armaments” of Song Dynasty in two accounts (970, 976 BCE)	Late Tang Dynasty and Sun Dynasty
Smoke and phylogenic devices	毒藥煙球，蒺藜火球，火炮火藥戰術及火藥配方記載《武經總要》（宋仁宗） Arsenide smoking balls, “Gee-Li--Hoh-Chiou” (Fig.2.2.2c), cannons/firearms, warfare explosives and formulae for explosives or propellants in records of “Bibliography of Armaments” of Song Dynasty.	Early Northern Sung Dynasty
Ash bomb device	“霹靂砲”（北宋欽宗靖康元年）（1126 CE）；	Late Northern Song Dynasty

Tunnel blast device	“震天雷” (南宋理宗) The “Aerial thunderballs”	Mid Southern Song Dynasty
Bamboo muzzle blast guns	南宋末年，壽春府製造「突火槍」：竹筒裡放火藥，並放入「子窠」轟擊 Bullets in bamboo cylinder and fire with explosives.	Late Southern Song Dynasty
Description of blast wave of high explosives	“守兵百人 皆糜碎无余，楹栋悉寸裂，或为炮风扇至十余里外。”《癸辛杂记》(宋代周密)A devastating blast in a siege smashed 100 soldiers; no one survived. Wooden columns are cracked and the blast “wind” sent debris 10 km away.	Song Dynasty
Cannon squad warfare	蒙古大軍攻金，使用火炮攻擊蔡州〈今河南汝南〉，亡金。Mongols used cannon to attack Jin at the fortress Tsai; Jin Dynasty perished.	1232 CE (Pro-Yuan Dynasty)
Bronze cannon artifact	一尊 “至順三年二月吉日製”明代銅炮(北京故宮博物院藏) Display at Beijing National Palace Museum. Engraved with: “Made in Feb., 1332.”	1332 CE
Essay on Chi, etc.; Chi and sound were both recognized as propagating energy waves	崇禎十年西元 1637 年宋应星著 《天工開物》；《論氣-氣聲篇》；《談天》等 Song Inn-Shin (1587-1666 CE) published “Tian-Gung-Kai-Woo” (“With heavenly skill, artifacts are created”); Energy and Sound chapter in the essay of “Lueng-Chi-Chi-Sern Chapter”: On Energy Flow; “Tan-‘Tien’”: On Astrology, etc.	1637 CE [d]
Warfare of cluster rockets and two stages designed for propelling and blast	“火弩流星”一次可發射十支箭; “一窩蜂”一次可發射三十二支箭; “四十九飛廉”一次可發射四十九支箭; “百虎齊奔”一次可發射一百支箭; “震天雷炮”使用火藥燃燒之力量推進力; “神火飛鴉”紙作成飛鴉外型，以第一節火藥飛行至敵方，再以內部裝滿之第二段火藥殺傷敵人《茅元儀·武備志》；《火龙经》 Giant bows firing blazing arrows in clusters of 32, 49, and 100; self-propelled flying kite	Mid 15th Century CE, Figure 2.2, before late Ming dynasties [e]

	carrying timed incineration bombs (Fig.2.2.2b). Appeared in both “Principal of Firing Dragon Tactics” (Huoh-Lung-Jin), and “Records of Armaments” by Mao Yuan-Yi.	
Firing Dragon warhead for naval warfare	16 世纪中叶，人们又发明一种新式火箭，名叫“火龙出水”《茅元儀·武備志 “Principles of Firing Dragon Tactics – Naval Warfare” – Appeared in “Records of Armaments” by Mao Yuan-Yi	Figure 2.2, Mid 16th Century

Partial Bibliography (in Chinese):

[a] Energetics application and development:

- <http://epaper.nstm.gov.tw/chinascience/I/i4-2.htm>;
- The Fire Dragon strategy: http://www.tqxz.com/lssj_readme.asp?id=236;
- Discovery of Gun powder: http://www.freepyroinfo.com/pyrotechnic_files.html.

[b] Yueh N, Decipher of Shia-Shang-Zhou Chronology Engineering, Hai-Nan Publ., Hai-Kow, 2007. 28-29.

[c] The chronicle records of Zhou Dynasty.

[d]History: <http://history.cultural-china.com/en/50History6396.html>;

Gunpowder: <http://kaleidoscope.cultural-china.com/en/136Kaleidoscope1.html>

[e] Fire arms: <http://vm.nthu.edu.tw/history/shows/show01/sung.siege/siege-con04.html>

2.3 Industrial Energetic Materials

Industrial energetic materials, or industrial energetics, refer primarily to smokeless explosive powders. Following ancient techniques, they are mainly mixtures of energetic chemical compounds, bonding agents, plasticizers, catalysts, and other modifying additives. They produce negligible smoke when fired, while burnt black powder will leave a thick, heavy fouling residue that is hygroscopic and causes the rusting of the barrel. The combustion products of industrial energetic materials are mainly gaseous. Nitrate powders not exhibiting these fouling properties have made modern auto-loading firearms, with their many moving parts, feasible. Despite its name, true smokeless powder is still under development. Conventional industrial energetic materials are formally classified under division 1.3 of the UN Recommendations on the Transportation of Dangerous Goods—Model Regulations [5], regional regulations such as ADR (Accord européen relatif au transport international des marchandises dangereuses par route), and national regulations such the U.S. ATF (Bureau of Alcohol, Tobacco, Firearms and Explosives). This chapter is arranged as follows: 2.3.1 general class, and 2.3.2 high-energy class. The development of energetic materials with detonation speeds below 5000 m/s will not be discussed. They are covered at length elsewhere, e.g. [6]. Medium-energy energetic materials, which pertain to general applications are discussed next.

2.3.1 General Application Class (Detonation Velocity between 5000 and 9000 m/s)

All energetic materials are, in effect, C-H-N-O based systems so they cannot be used as a criterion for systematic study. Here, we will pay attention to the ones that have detonation velocities above 5000 m/s. They will be discussed by order of physical states from solid to liquid phases and for applications from underwater to air borne explosions. The discussion of notable features developed from conventional designs, namely dual charges (or, double-base charges), will also be minimized so that an outlook covering a broad spectrum of developments may be gained from a few typical cases. Accordingly, RDX based system for underwater applications will be discussed first.

2.3.1.1 Dual Charge Design Based on RDX for Underwater Applications

While moisture is a limiting factor for most energetic materials, it is the prevailing condition in this category of energetic materials. Since RDX powders are toxic by inhalation, encasing the high explosive with different cladding system for protection against environmental aging and impact sensitivity are logical design upgrades. However, many interface problems may arise from such composite system and impose performance challenge. Advancing from monolithic energetic materials in the 1970s [7], studies of dual-charge systems and their configurations for optimized energetic effects and augmented safety issues were initiated in the 1980s, and implemented in the 1990s, in harmony with the French Insensitive Munitions Policy (IM Policy) advanced in 1987 and the U.S. MIL STD-2105B/C for hazard assessment tests for non-nuclear munitions. In addition, the efficient shock wave energy per unit mass, and its decay with distance, and the bubble energy, etc., are equally significant but difficult to compute efficiently since wave speed in hydraulic and gas media belong to different scales of magnitude.

Projects were carried out to study reaction kinetics and energy release characteristics of duplex charge designs in connection with underwater engineering projects. A solution for a dual charge with different layouts has been a key issue. Formulations and configuration designs of dual charges have been addressed [8]. Rao et al. [9] compared thermophysical performance characteristics of TNT, i-RDX (insensitive RDX), RDX-Al, and Single Event Fuel Air Explosive (SEFAE¹) for underwater applications. They concluded that the pressure attenuation of

¹ SEFAE is a chemical or non-explosive initiation of detonation in which simultaneous fuel dispersion and combustion as a single event occurred in a heterogeneous system of atomized fuel air and chemical agents rather than delayed onset of detonation initiated by fuses.

SEFAE, and RDX/Al, is lower than the pressure attenuation of TNT and i-RDX. However, the shock wave energy, bubble ripple time, and bubble energy of SEFAE and RDX/Al are higher than those of TNT and i-RDX. The energy output of the former two explosives differed from the latter two mainly due to the aluminum powder catalysis effect as well as the performance of bonding agents. In this connection, molecular dynamic simulations have been used to improve the polyurethane thermoplastic elastomer propellant design on the basis of different types of azide bonding agents. Special reference is made to the assessment of miscibility and elastic modulus [10].

Integrating insensitive munitions (IM) technology for safety enhancement and dual-charge on the basis of GH-1 and GUHL-1 with different layout designs for underwater applications has been carried out by Niu et al. [11]. For shallow underwater explosion tests, the GH-1 was composed of RDX (cyclotrimethylenetrinitramine/bonding agent (80/20). GUHL-1 was composed of RDX/AP/Al/bonding agent (17.6/42/26.4/14). The results were compared with their counterparts for benchmarking studies. It was concluded that a duplex charge is able to fine tune an explosive load near the testing point and reduce the shock wave energy propagation loss. In this context, the maximum chemical reaction time contributing to the underwater blast effect included the assessment of: 1) detonation wave velocity, 2) target fragmentation, 3) shockwave effect, and 4) water-hammer effect. Of note is the underwater demolition or fabrication process, e.g., controlled slab cuttings.

2.3.1.2 JMZ Based on PET, NC, and RDX System

Optimization of the thermal-physical parameters of the new JMZ¹ design has been reported by Huang et al. [15]. TG and DTA test results showed that the low pressure performance of the new product was similar to a high RDX content propellant. Under high pressure, it behaves like conventional products with more favorable ignition and propagation properties. Two stages of reaction kinetics of polyethylene terephthalate (PET) can be noted: 1) the volatilization and decomposition of nitrate plasticizers (NG-TEGN) and NC in the first stage and 2) the decomposition of nitramine and PET where there is RDX present. The particle size of RDX will affect activation energy and exothermic conditions. Changes in size from 50 nm to 10 nm will conspicuously induce faster reaction at the first peak. Hsu et al. [16] followed with the non-stoichiometric design of PET composition for improving the mechanical properties of the new propellant.

¹ A proprietary high energetic high mechanical strength explosive material system of coded compounds.

2.3.1.3 Explosive Cladding, Densification, and Fragmentation

Building on explosive fabrication techniques developed in WWII in the Eastern Bloc, interest in high-energy-rate explosives surged in the 1980s [17]. Thermal-, physical-, and material-based explosive cladding became one of the notable high-energy rate manufacturing processes. A cladding plate is driven by detonation pressure to strike and bond onto the base plate in a pre-engineered energy release manner based on hardware configuration design so that both plates become an integral near-net or a net-shaped forging product characterized by a defect-free interface or metallurgical bonding. This is due to heat and kinetic energy being developed by pre-designed controlled detonation and shock wave propagation simulations based on hydrodynamic and quantum dynamics code developments. Babbitt bearings of copper-clad steel systems have been used in the past for railway wheels and heavy diesel engine shafts. Having a low friction cladding surface, Babbitt bearings are used on excavation, demolition, waste treatment equipment, etc., in China. Blast-resistant design belongs on the opposite end of the spectrum. Compound structures built with laminated cellular composites for shock load resistance were investigated. Formulation of plastic explosives for a freezing environment using low temperature bonding agents, etc., has been reported. Plastic working of Hadfield steel (high Mn steel) casted preforms is an enterprising development derived from classic applications that are constrained by working with malleable stocks. Surface hardness can thus be increased from 170-190 HB to 260-280 HB and then to 310-330 HB in two steps. A hardening depth of 30 mm can be reached and has been exploited with RDX-based detonators [18]. Improving uniformity, tolerance, reliability, and applicability as well as reducing toxicity and development costs are also discussed. It was reported that good ITO (Indium Tin Oxide) crystals can be produced by compacting raw materials mechanically to 50% of their theoretical density at 800°C before exercising explosive compaction [19].

2.3.1.4 SHS Applications

An important variation of explosive cladding or densification is the self-propagation and high temperature synthesis (SHS) process. For the application of lost-form casting, high purity powders of titanium (300 mesh, 99%), carbon (300 mesh, 99.8%), aluminum (460 mesh, 98%), and iron (270 mesh, 97%) were mixed and granulated by compressing them to 240 MPa and then packaging them in Zn foil. The lost form was made of 4-benzoethylene for low-carbon steel casting [20]. The cavity at the core of the lost form was coated with hard face material and filled with SHS granules and protected with a layer of porous refractory

coating before being placed into a dry sand die box. Filling the die with 1550-1600°C molten steel caused SHS to be triggered. The Ti-C-Fe alloying system synthesized was subjected to SEM, XRD, and DSC-TGA examinations for TiC, Fe₃C, and Fe₂Ti for stoichiometry. In this case, the hard coating was rated to 54-59 HRc.

2.3.1.5 Nano-powder Production

Both civilian and military explosives contain metal powders in order to modify performance. While fine-powdered aluminum increases the muzzle blast effect, aluminum or zinc increases the fire effect¹ [21]. Table 2.2 lists a few nano-powders produced by detonation processes that often include both decomposition and synthesis. Using high density emulsion explosives, the MnFe₂O₄ series of nano-particles were assessed by phase, morphology, and thermal characterization. Composition optimization was approached by reverse engineering, i.e., through residuals analysis. For instance, ammonium nitrides can serve as an indicator for incomplete combustion as verified by TEM, XRD, and DSC (differential scanning calorimetry) examinations. Yang et al. [22] examined ZnTiO₃ powder processing conditions through AP (ammonium perchlorate) thermal fragmentation in connection with the catalytic effect. A parallel study was performed by Wang et al. [23] for high density (e.g., of 10 w% max. at 1.55g/cm³) MnFe₂O₄ powders (20-25 nm class) produced using RDX modified emulsion detonators. The effects on the ZnTiO₃ nano-powders were examined. Superhard nano-powders, such as diamond-like crystals (DLCs) or ultra-fine carbon (UFC) crystals, produced by explosions involve a complex high-rate manufacturing process that involves sono-fragmentation, rapid synthesis, fast annealing, controlled crystallization and high-rate compaction. Combinative reaction kinetic mechanisms based on formulation and density control for added value was suggested. Figure 2.3 shows the UFC formation mechanism. Chen [24] investigated the production of UFD of submicrometer particles using a detonation method. With Cu salts (DBC, CNI, NT-Cu, B-Cu, S-Cu, and A-Cu) and grapheme powders in RDX-CMDB as combustion modifiers [25], phase changes in Al₂O₃ powders were examined as a means for both product and process performance testing. Li [26] experimented with producing nano SrAl₂O₄ powder with phosphor properties on the basis of Eu²⁺ and Dy³⁺ content.

2.3.1.6 Plastic Explosives: TEGDN and PETN

TEGDN (CH₂OCH₂CH₂ONO₂) is a low sensitivity plasticizing energetic material for reducing the influence of explosion pressure

¹ Explosives: <http://www.economy-point.org/e/explosive-36287.html>

loading on flame propagation speed in a dynamic atmosphere. It is a popular propellant component. Many experimental-empirical models have been proposed for TEGDN's reaction kinetics behavior, since the conventional TG-DTG curves characterize it as a two-stage decomposition process, as PETN ($C(CH_2N)_2$)₄ also does [27]. However, O-NO₂ should be a fragment during the first stage of decomposition, as in PETN, but it has not been identified as such. It has been speculated that backbone dissociation would occur prior to linear nitramines [28]. Applying TG-FTIR experiments, they reported that the thermolysis process of PETN is similar to that of TMETN in that NO₂, CH₂O, and O-NO₂ will appear first, followed by CO and NO in the second decomposition stage due to the interactions of CH₂O and NO₂ fragments. Tseng et al. [29] applied the Density Function Theory (DFT) method to quantify bonding entropy and free energy through HOMO-LUMO assessment, etc., for the purpose of validating the reaction kinetic model and parameters pertaining to the named product. Yi and Hsu et al. [30] tested its temperatures as well as weight loss for catalyzed TG0604 (TN+TEGDN) in ambient conditions.

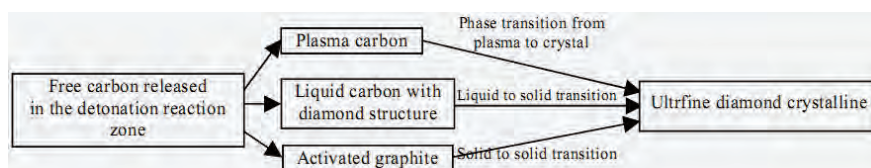


Figure 2.3: UDC reaction kinetics pathways by supercritical flow extraction and crystal growth control [24]

2.3.1.7 Wax Binder Effects on TATB

An increase in weight percentage of the insensitive explosive TATB (triaminotrinitrobenzene) is known to increase the threshold temperature of detonation of HMX. Gao et al. [31] used a 3% wax binder as a modifier and tested it with two major organic constituents (or impurities) of TATB: TCTNB (2,4,6-trichloro-1,3,5-trinitrobenzene) and TCDNB (2,4,6-trichloro-1,3-dinitrobenzene). The detonation velocity and pressure of TATB, TCTNB/wax (97%/3%) and TCDNB/wax (97%/3%) have been measured by ionization probes and a manganin pressure gauge. Detonation parameters and the equilibrium composition of detonation products at the C-J state have been computed by means of the VLWR

thermal dynamic code. The test results showed that the detonation velocity and pressure were 7452 m/s and 24.40 GPa for TATB, 6890 m/s and 20.28 GPa for TCTNB, and 5973 m/s and 15.30 GPa for TCDNB. The relationships between wax addition and the performance of TATB, TCTN, and TCDNB were established.

2.3.1.8 Novel Emulsion Explosives and Their Applications

Emulsion explosives are widely used in the mining industries of the U.S., Canada, and Australia. For civilian applications, formulations with a 12–15 mm explosion critical diameter and 260–300 ml brisance, detonation speeds generally fall between 3200–5000 m/s. In China, emulsion explosives are grouped into powdery emulsion explosive, expanded ammonium nitrate (AN) explosives, modified AN explosives, water gel explosives, and propellant emulsion explosives. However, there are still many novel variations created by exploiting nano-technology, such as nano-porous products. Dual emulsification for improving performance, thermal cycle stability, and shelf-life problems is a key point.

In one case study, Huang et al. [32] reported that a high energy emulsion explosive was prepared by mixing the explosive components of AN with ethylenediaminedinitrate (EDDN) and composite fuel oil containing molecular emulsifier through emulsifying techniques. This may improve detonation speed, critical diameter, explosive power, and intensity to a detonation velocity of 5800 m/s, a critical diameter of 12 mm, a brisance of 17.2 mm, and a power of 360 ml. The resulting explosive also exhibits stable storage capability and can withstand the temperature cycle test 32 times. In addition, the upgraded explosive possesses excellent resistance to water: the detonation performance changes little after being submerged in water for 24 hours. Therefore, it can be applied favorably in mining, heavy construction, or demolition projects, and emulsification can be readily done in the field.

With over 20 years of research and development, the improved high energy emulsion explosives in China are exceeding the GB18095-2000 standard for performance, gas toxicity, second-class coal mine safety requirements, and cost reduction. The ARY#1 series of modified class 1 rock explosives with an emulsifier of PCE in lieu of SP-80 and density above 1.20 g/cm³ are designed to offer improved shelf-life. Geng et al. [33] have discussed improved products for class 2 explosives. One effort has been to reduce toxic fumes by replacing TNT in formulations for mining applications. After the implementation of new standards and regulatory policies for the mining industry in 2007, 50% of small mining enterprises have been closed down. Years of upgrading quality standards are still expected [34].

2.3.1.9 FAE Systems for Air-borne Applications

Due to advancements in FAE technology since the 1960s, energetic materials have improved from the gel type to single event-FAE, or thermobaric explosives, or composite fuel (CF), to dual-event FAE and beyond. Current intensity can exceed 6500m/s explosion speed and 15 GPa with pressure over 128 MPa for 10 m for 6s, or exceed TNT-B capacity by 90% [35].

2.3.2 High Energy Application Class (Explosion Wave Speed above 9000 m/s)

2.3.2.1 HMX System

In the production of RDX by the acetic anhydride method in 1941, a chemical was found in the RDX that could change the properties of RDX. After purification, this RDX homologue was found to be an 8-ring molecule ($C_4H_8O_8N_8$), so it was named octagon, or 1,3,5,7-4-nitro-1,3,5,7-tetraazacyclo dodecane-octane, abbreviated as HMX, also known as HMX gold (Otto Gold) [39].

However, in the preparation of RDX using the acetic anhydride method, the products contain only about 10% HMX initially. In pursuing a more efficient RDX-HMX production process, Chinese high energy material chemists have developed a small molecule synthesis approach. It is an integrated technology approach that is comprised of the nitrourea method (urea method), the TAT method, and the DADN law. This new method has improved the production of acetic anhydride in many ways. For example, by using paraformaldehyde and acetic anhydride as stabilizers, the yield can be increased from 50% to 80%. Using this method the output of HMX is usually a mixture of various crystal types, but stability is poor.

While it is obvious that the aluminized RDX-HMX system and its analogs are the backbone of high energy solid propellants or explosives for advanced energetic systems, the high production costs of the demanding purification process prevent its use in regular warheads. But it is increasingly used in missile warheads and anti-tank weapon charges, as a solid rocket propellant, and as a nuclear detonation charge. In this connection, the electron transport and bond fragmentation pathway is an important issue. Currently, molecular dynamics as well as mass spectroscopy have been applied to enhance the understanding of its variants. The addition of metallic nano-powders may enhance the detonation properties in both HMX and RDX.

2.3.2.2 CL-20 (HNIW) and NEPE System

CL-20 (hexanitrohexaazaisowurtzitane) was first synthesized in the 1980s by the China Lake Group [42]. An optimized formulation scheme for this high energy density energetic material with a cage-type molecular structure has been pursued in China since around 2000 in search of improved energetic properties. The MD simulation approach has been developed for five polymer bonded explosives (PBXs) using CL-20 as a basis. A high energy density compound (HEDC), and five polymer binders (Estane 5703, GAP, HTPB, PEG, and F2314) were evaluated. Phase change issues were reported by Xu et al. [45].

In parallel, the crosslinked nitrate ester plasticized polyether (NEPE) has been investigated for being one of the best solid missile propellants owing to its high energy and low temperature structural properties. NEPE uses NP-1 to bind HMX and AP as well as Al powder. Combining CL-20 for high pressure applications up to 6~7 MPa was found to offer good results. In order to improve mechanical properties, Luo et al. [46] reported that using tripolyisocyanate (#22) as a liner produced the best results among M APO, HX-752, and T313 for anti-aging assessment at 7MPa [47].

2.3.2.3 DNTF System

Having detonation wave velocities of about 10 km/s, DNTF (3,4-dinitrofurazanfuroxan) and PETN (pentaerythritol tetranitrate) are more sensitive to pressure and temperature than TNT. They have TNT equivalent factors around 1.66 and 1.68, respectively. DNTF replaces NG in CMDB for improved propelling capacity in some cases.

As a novel high energy density material, DNTF has been proven to be better than HMX and vicinal CL-20 in terms of physiochemical and detonation properties. It possesses high energy, low melting point, good thermal stability, and moderate sensitivity. Having a detonation velocity of 9250m/s and a density of 1.937g/cm, this energetic material can also form a eutectic mixture with TNT in liquid phase carriers of different melt cast explosives. Therefore, it has broad application possibilities, e.g., solid rocket propellants, warheads, and explosive networks.

2.3.2.4 Boron and Fullerene Modified High Energetic Solid Fuels

Renewed developments of boron in high performance propellants for solid fuel engines in low pressure applications started before 1990 (Chi, 1991 [50]). For its advantages in bonding strength, smokeless combustion, low materials cost and reduced ignition delay under high pressure, coated boron powders have received good attention before 2000 in China. One critical problem was to overcome the formation of detrimental surface oxidants, e.g., B_2O_3 , H_3BO_3 , in supersonic jet.

To take advantage of an extremely large surface area to facilitate fast reaction and its cage configuration for superior structure rigidity compared to nano tubes, syntheses of fullerenes and modified fullerenes in the fields of novel energetic materials and energy storage systems began in the 1990s after the debut of C₆₀ in 1985. Investigations cover aspects of enhancing catalytic actions by implanting transition metals, retarding detonation speed, reducing pressure exponent for burning speed retardation, improving friction and aging properties to enhance thermal stability. Great attention has been paid to NEPE energetic systems [46, 47, 54]. The development of (BN)_n systems in lieu of (C)_n systems advancing from BN and carbon nano tube technologies (BNNTs and CNTs technologies) are of international interests [55-57]. Currently, more theoretical rather than experimental results are appearing [56, 57]. Since fundamental design issues are still pending for further research, reports pertaining to integrated product level are rarely seen [58]. However, research on exotic components is quite active [59].

Table 2.2: Detonation sintering of nano-powders through detonator and process designs

Product	Technology description	Citation
ZnTiO ₃	With 5 w% of 100nm ZnTiO ₃ spherical, particles the low and high decomposition temperature of AP reduced by 18.3°C and 25.1°C, respectively. The higher w% of ZnTiO ₃ tends to enhance reaction kinetics while it deters low temperature decomposition.	[22]
MnFe ₂ O ₄ , LiFe ₂ O ₄ , LiZn ₂ O ₄	Powders and residues produced by different density classes of RDX modified emulsion explosives are analyzed.	[23]
UFD/Graphene	Both graphene and Cu salts are considered RDX-CMDB additives. Kinetic pathways inferred (Figure 2.3).	[24]
γ-Al ₂ O ₃ and α-Al ₂ O ₃	Use Al(NO ₃) ₃ ·9H ₂ O and modified RDX for controlled synthesis of products of different phases (Figure 2.4d).	[25]
Rare earth compounds	Produce nano SrAl ₂ O ₄ with phosphorous properties due to Eu ²⁺ and Dy ³⁺ dopants	[26]

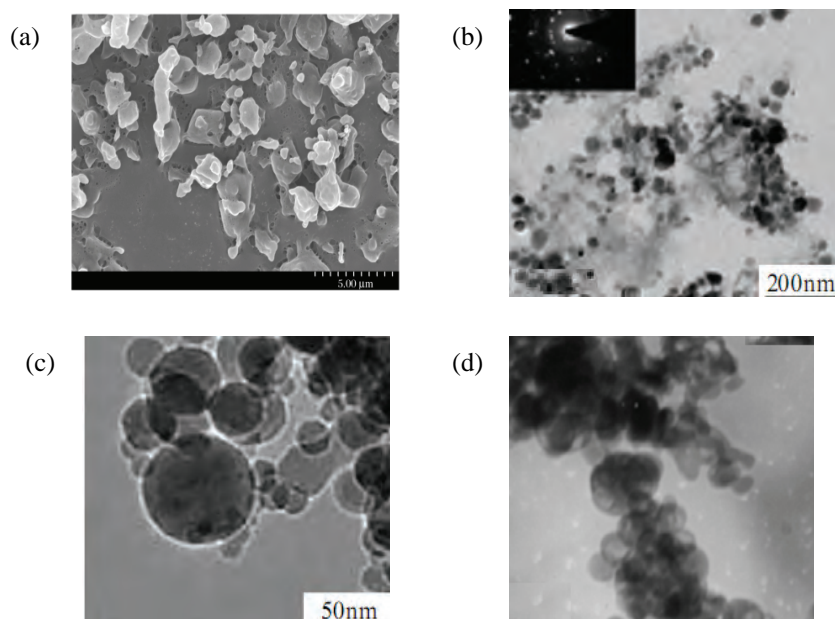


Figure 2.4: Products produced by detonation process: (a) UDC flakes [24]; (b,c) ZnO, TiO₂ powders [25]; and (d) Al₂O₃ [26]

2.4 Results and Discussion

The classification of energetic materials by Economy Point under explosives¹ is well taken. However, it is misleading when they note that, “The Byzantiner knew already in the year 671 a mixture from rosin, sulfur and saltpeter, Greek fire mentioned and invented from Kallinikos from Heliopolis.” The artifacts and historical records, by population density, continuity, and trends unmistakably point to the fact that China was the inventor not only of black powders but many warfare tactics, along with warheads and pioneering means of deployment far before the Yuan Dynasty (1271–1368 CE). A short but comprehensive list is included in Table 2.1.

The reason for China’s earlier weakness in energetic sciences and technology is that the Yuan Dynasty enacted a law in 1330 which forbade the Chinese to possess any weapons or explosives. Moreover, the powerful Ming Dynasty succeeding the Yuan Dynasty in China was also extremely stern on this point, because the first legitimate heir to the

¹ <http://www.economypoint.org/b/black-powder.html>

throne disappeared. Therefore the Ming emperors (1368-1644 CE) always had a fear of rebellion. As a result, theory rather than experimentalism was encouraged. Instead of metallurgy or materials science and technology, philosophy and alchemy became the mainstays. Unfortunately, such a dormant state lasted more than 500 years, while Europeans were exploiting the explosive warfare they had learned from the Mongols, who in turn were taught by the high monks and Han craftsmen. Therefore, the ingenuity of Chinese culture has lasted. The narrator of Economy Point on black powder also failed to recognize this implicit element.

2.5 Concluding Remarks

Chinese industries are competitive internationally up to high energetic systems for applications both above and below water. Vigorous fireworks and demolition industries attest to China's revival in energetic science and technology.

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Chapter 3

Science and Technology Trends

Advancements in science and technology (S&T) research are critical to the growth of any country, including China. This chapter examines S&T trends in China compared with other major countries in the world and then focuses on the research trends, research institutions, and key researchers in the field of energetics in China.

The percentage of global research contributed by each individual country and how these values have adjusted over the last decade (Figure 3.1) show that China contributes 20% of the world's research. This is approximately the same as the number contributed by the United States, twice as much as Japan's contribution, and over five times as much as Germany. This is a growth of over 6% over a period of 5 years (in 2002, China contributed only 14%). In the same period of time, the percentage of global researchers decreased by 3% in the United States and 1% in Germany and Japan [1].

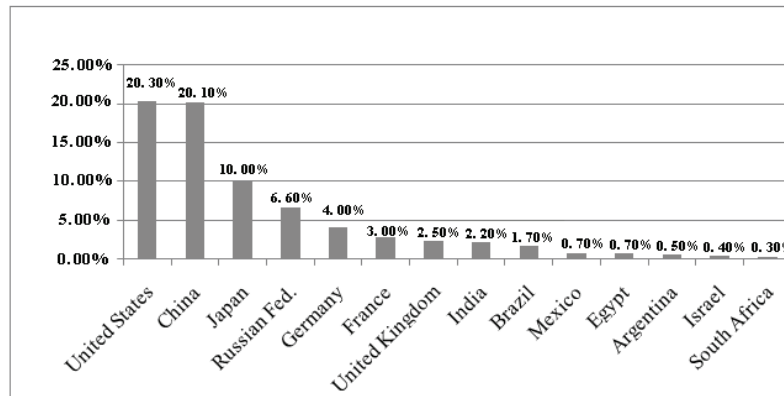


Figure 3.1: Shares of world researchers: 2007 (%) [1]

If we examine researcher density, the United States and Japan both have nearly 5000 researchers per 1 million inhabitants, while China has about 1000. This is due to a large part because of the overwhelmingly large impoverished population in the western Chinese provinces.

China is still behind the United States and Japan in terms of monetary contributions to R&D, with the United States contributing over three times as much as China (see Figure 3.2). However, China's monetary contributions rose to 9.2% from only 5.0% in the last five years, whereas the United States and Japan both dropped slightly in the same period [1]. It is not unreasonable to expect that this trend will continue and that China will surpass Japan and ultimately achieve values in the vicinity of the United States.

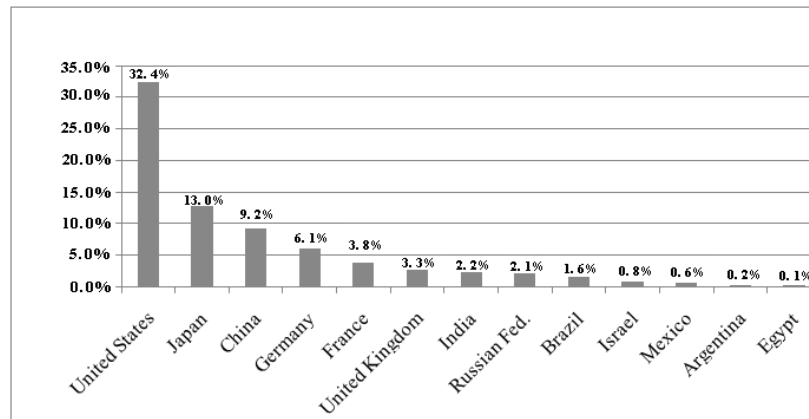


Figure 3.2: Shares of world R&D expenditure (GERD): 2007 (%) [1]

In terms of Gross Domestic Expenditure on R&D as a percentage of Gross Domestic Product, China follows the United States and Japan. China commits 1.5% of its GDP to R&D, whereas Japan and the United States commit 3.4% and 2.7%, respectively. However, 1.5% is significant, given that the value was merely 0.5% in 1996. In fact, China has shown more growth in this regard than any other country over the last decade.

The last comparison is where R&D investment is coming from and which sectors are receiving it. Figure 3.3 indicates the percentage of R&D investment that comes from each sector in China, United States, United Kingdom, South Korea, and Germany.

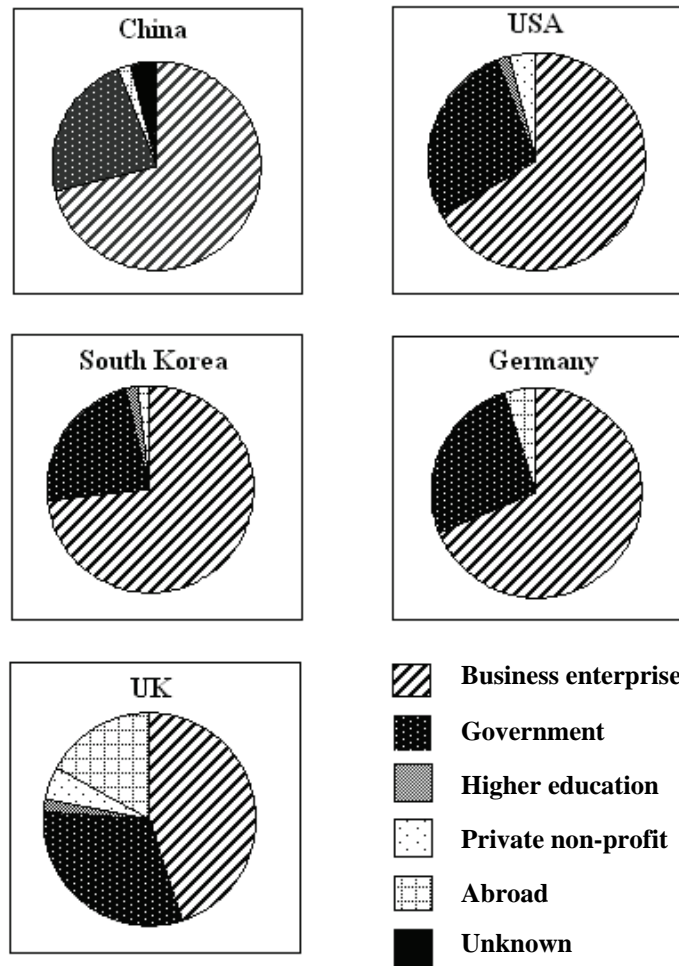


Figure 3.3: UNESCO gross expenditure in R&D (GERD) by source of funds: 2007 [1]

Figure 3.3 shows that that these representative high-tech countries are similar in terms of investing sectors, with a couple of exceptions (notably the United Kingdom and its large funding from abroad). The main difference between China and the United States is that, whereas U.S. energetics research receives funding from the higher education and non-profit sectors, China receives little higher education and non-profit funding.

Figure 3.4 gives a breakdown of the sectors that are receiving the most funding for R&D. Again there are no significant differences between these countries. In comparing China to the United States, the

Chinese government provides nearly twice as much funding (as a percentage) for energetics research as the U.S. government provides. This is partly because the higher education sector in China provides little funding for energetics research. This is also far below the average of the other countries.

The data show that China is rapidly becoming a world science and technology power. In terms of researchers, research institutions, and funding, China is gaining ground as a direct result of government policies and the economic growth and success that it has enjoyed for the last decade.

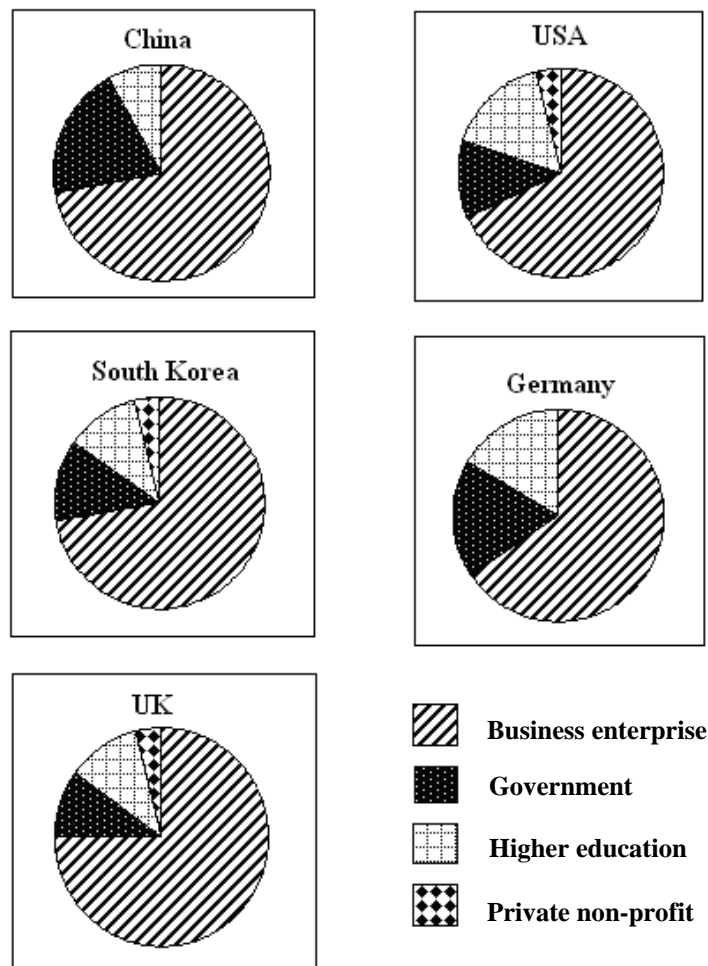


Figure 3.4: GERD by Sector of Performance: 2007 [1]

3.1 Energetics Research

In China, most work in the energetics field is published in journal articles, books, and conferences or symposiums. Consequently, all the data in this section are based on a survey of Chinese research publications conducted by the authors. The energetics field consists of any research publications relevant to energetic materials (explosives and propellants). These publications can be divided into many categories. Research involving the properties of certain substances and their benefits or detriments has been divided into crystal properties, chemical interaction and properties, and thermal properties. Research involving modeling and simulation is placed in its own category. The largest segment of research is categorized into manufacture, preparation, and characterization. These categories represent the production functions of the energetics field. Next, synthesis is an important category as it involves the creation of new energetic materials. Combustion involves combustion processes as well as detonation processes. Weapons and nanoenergetics merit their own category as they are more fitted as branches of the field. Lastly, experimental methods involve research on novel methods of handling energetic materials.

Figure 3.5 shows trends involving specific research in the field since 1998. From Figure 3.5, we can conclude that there has been a decline in interest in the study of chemical interaction and properties. Furthermore, thermal properties seem to be the most relevant and the most researched category out of these material properties categories.

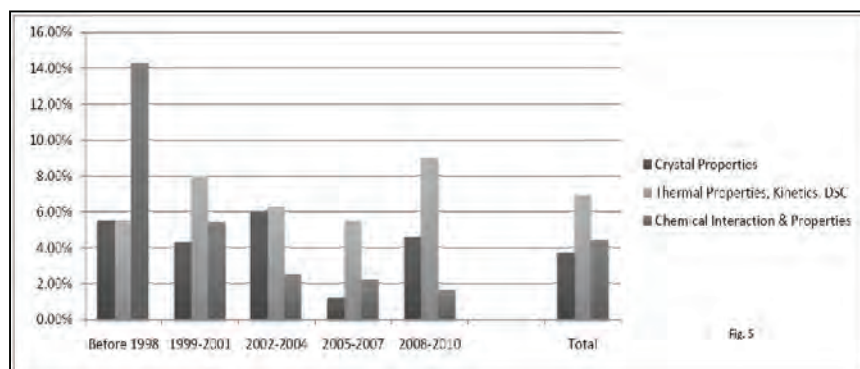


Figure 3.5: Trends in energetic research since 1998

Figure 3.6 shows the change in specific research topics over the past 10+ years. The topic of modeling and simulation has been the subject of

consistently strong research, which is true in most engineering fields, as it can provide great benefits during research. The topic of synthesis is also greatly researched in China. Synthesis provides great interest due to its promise of novel materials. In the past three years, there has been an increase in research in this area. Lastly, the topic of combustion has seen an increase but also a decline in the past 10+ years.

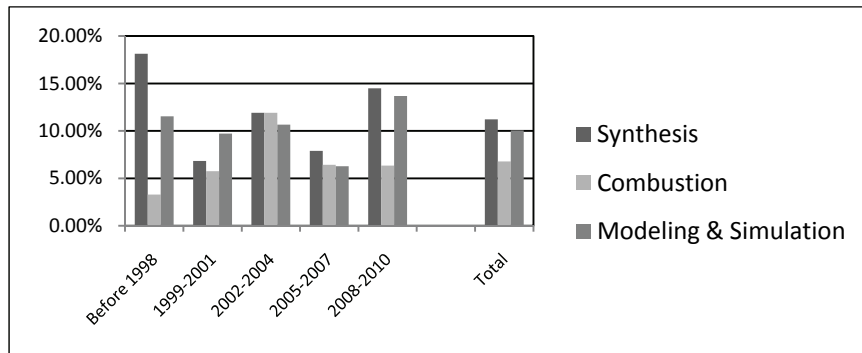


Figure 3.6: Trends in energetic research since 1998

Figure 3.7 shows the last of the categories: weapons, nanoenergetics, and experimental methods. Weapons are a concern, as they provide a country with great power when consistent research is being pursued. Recently, there has been a decline in weapons research. However, China has dedicated an average of almost 10% of its research to weaponry.

Unlike weaponry, which has been a consistently necessary part of research, nanoenergetics is a newly emerging field that offers great promise. Before 1998, nanoenergetics research was nonexistent. Recently, it has started to stimulate more research, and China has dedicated 3% of its research to this subfield in the past three years. Lastly, experimental methods have declined in recent times.

From an analysis of journal articles (Figure 3.8), it was determined that the four leading Chinese institutions that publish research in the field of energetics are: Xi'an Modern Chemistry Research Institute in Xi'an; Beijing Institute of Technology in Beijing; Nanjing University of Science and Technology in Nanjing; and China Academy of Engineering Physics in Mianyang. Other key institutes and research universities include North University of China in Taiyuan and National University of Defense Technology in Changsha.

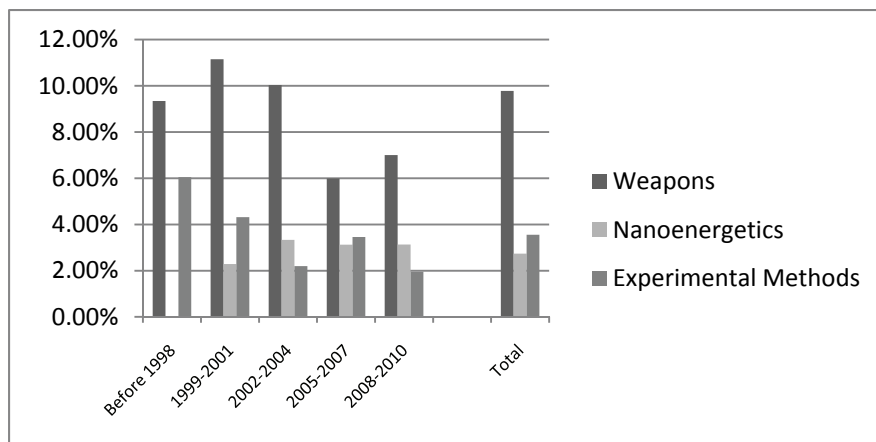


Figure 3.7: Trends in energetic research since 1998

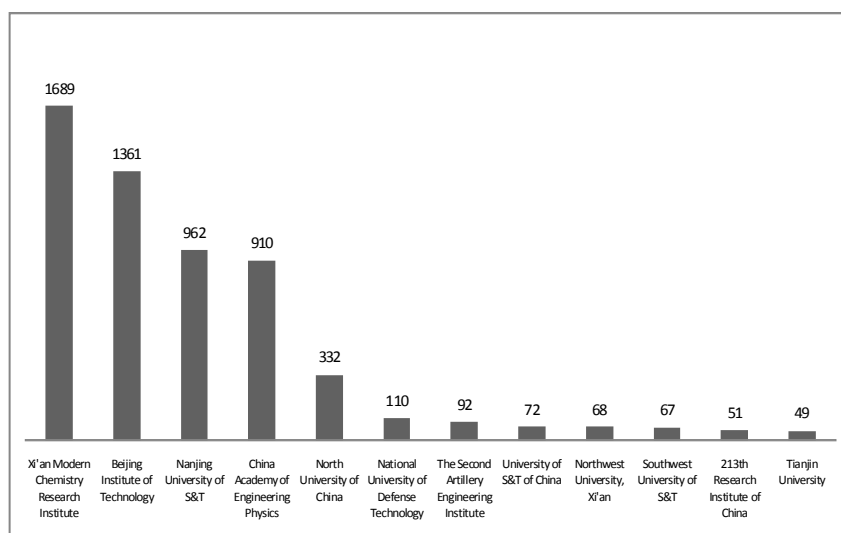


Figure 3.8: Journal contributions

3.2 Xi'an Modern Chemistry Research Institute

The Xi'an Modern Chemistry Research Institute, also known as the 204 Institute, is China's largest research center for chemical energetic materials. It was founded in 1984 and is located in the Electronic

Industry Park of the High-Tech Industry District of Xi'an, Shan Xi Province. The center is mainly engaged in the research and development of organic chemistry, applied chemistry, polymer materials, fine chemicals, electronic devices, and analysis and testing technology.

The Xi'an Modern Chemistry Research Institute is subordinate to the China North Industries Group Corporation (CNIGC), which is the major research and production base of weapons and military supplies for the Chinese army. The institute has the right to offer M.S. and Ph.D. degrees. It was also one of the first 100 research institutes to be authorized for import-export operations, and has been approved by ISO9001-2000. It now has total assets of 506 million RMB (US\$72 million).

3.2.1 Areas of Research in the Xi'an Modern Chemistry Research Institute and Achievements

Armed with advanced analysis and testing instruments as well as international online retrieval terminals, the Xi'an Modern Chemistry Research Institute is a leader in the structural identification of substances, component analysis, thermal property analysis, information retrieval, and blasting engineering services.

Two of the centers at the Xi'an Modern Chemistry Research Institute are the National Defense Key Laboratory of Propellant and Explosive Combustion, whose focus is on the research of propellant mechanisms and combustion theory, and the Physics and Chemistry Test Center of Explosives and Propellants in the Ordnance Industry, whose function is to measure and analyze explosives and propellants.

In recent years, the institute has committed itself to the research and development of high technologies and hi-tech products, including substitutes for ozone-depleting substances, fluorination catalysis technology, photoelectric display materials, new types of pharmaceutical intermediates, fine chemicals, and civil blasting supplies among others. It actively accelerates the industrialization progress of scientific results and the combination of technologies and economic development.

Since the reform and opening up of China, the institute has won numerous awards, including the National Invention Award, the National Award for Progress in Science and Technology, and the Provincial/Ministerial Level Award for Progress in Science and Technology.

3.2.2 Research Projects

The Xi'an Modern Chemistry Research Institute now has around 2000 staff members, including 1200 engineering technicians, 230 researchers, associate research fellows, and senior engineers. The institute has a joint publication with the Association of Chinese Ordnance called the *Journal of Explosives and Propellants*, which

provides a platform for the academic dialog on explosives and propellants. The institute has three Ph.D. programs whose research orientations focus on energetic composites, high energy density material, and the engineering application of energetic composites. Table 3.1 provides a brief overview of recently conducted projects.

3.2.3 Facilities of the Institute

The Xi'an Modern Chemistry Research Institute covers an area of 6000 square meters. It is equipped with the most advanced facilities worth approximately 30,000,000RMB (\$4,285,714). Their equipment includes a laser particle size analyzer, Fourier transform infrared spectrometer, X-ray photoelectron spectroscope, X-ray diffractometer, inductively coupled plasma atomic emission spectrometer, gas chromatographer and mass spectrometer, dynamic mechanical analyzer, scanning electron microscope, modulated differential scanning calorimeter, thermogravimetric apparatus, microcalorimeter, and atomic absorption spectrometer.

Table 3.1 Recent research projects

Project Title	Research Funds	Anticipated Target
Nanometer Materials and Explosive Technology	200,000 RMB (\$28,571)	Research and produce 3–5 new nanometer materials, analyze the influence of nanometer materials on solid propellants.
Application and Synthesis of High Energy Ionic Compounds	180,000 RMB (\$25,714)	Synthesize a high energy ionic compound for explosives and evaluate its application to solid propellants.
Combustion Law and Mechanism Research of New Type of Propellant	200,000 RMB (\$28,571)	Research the combustion behavior and the mechanism of propellant; discover the hypostasis of combustion and put forward a new theory.

3.3 Beijing Institute of Technology

The State Key Laboratory of Explosion Science and Technology (SKLEST) was founded by the State Planning Commission at the Beijing Institute of Technology in 1991. Founded in Yan'an in 1940, the Beijing Institute of Technology (BIT) is a national key university. BIT is an

open, international, and research-oriented university of science, engineering, and the humanities. It was one of the first universities in China to run a graduate school and has received privileged funding from the central government. BIT is also one of the national Project 211 universities receiving preferential support from the state. In 2000, BIT was listed in Project 985, giving it priority for development by the Commission of Science, Technology, and Industry for National Defense (COSTIND), the Ministry of Education (MOE), and the Beijing Municipal Government. Under the administration of the Ministry of Information and Industry, BIT ranks among the best universities in China for its high education and research performance, strong faculty, and distinctive academic programs.

The Beijing Institute of Technology, in carrying out its scientific and technological work, insists on innovations and attaches great importance to bringing the comprehensive advantages of multi-disciplinary study into full play. With the goal of developing a first-class, world-renowned research oriented university, BIT has created a favorable environment for teaching and research. There are over 3500 faculty and staff, including eight academicians of the Chinese Academy of Sciences and the Chinese Academy of Engineering Sciences, 1200 full and associate professors (including researchers and senior engineers), 362 supervisors of doctorate programs, 17 experts with outstanding contributions at the national level, and 55 recipients of special subsidies from the central government. Now BIT has four National Key Laboratories, four National Key Disciplinary Laboratories, two Key Laboratories of Ministry of Education, and four Beijing Municipal Key Laboratories.

BIT's scientific and technological funds have experienced stable growth, reaching 420 million RMB (US\$62 million) in 2003. Major sources and channels of research funds are the National Natural Science Foundation, the National Social Science Foundation, the National High-Tech Research and Development Plan of China, the National Key Basic Research Development Program, cooperation with enterprises, etc.

BIT values international communication partnership with the world's leading universities and has instituted strategic plans for regional cooperation and industry collaboration. So far, BIT has established collaborative programs with universities such as the Hong Kong Polytechnic University, Mississippi State University, Tokyo Institute of Technology, Purdue University, and the University of British Columbia.

3.3.1 Energetics Research in the SKLEST

The State Key Laboratory of Explosion Science and Technology (SKLEST) is a unique state key laboratory in the field of explosion science and technology. SKLEST was founded in 1991 and opened to the

public in 1996. It was approved by the Ministry of Education in 1998 and by Ministry of Science and Technology in 2003. The mission of SKLEST is to solve research problems of science and technology for national defense weapons equipment and social safety. SKLEST has 87 staff, of which 44 are professors and 22 are associate professors. The laboratory has two Members of the Chinese Academy of Engineering.

SKLEST's research areas are focused on the theory and applied technology of energetic materials, detonation and explosive technology, impact dynamics of materials and construction, damage theory and protection technology, explosion safety theory, and assessment methods. SKLEST is involved in the disciplines of aeronautics and astronautics, mechanics, material science and engineering, and mining engineering. SKLEST hosted the 2007 and 2009 International Autumn Seminars on Propellants, Explosives and Pyrotechnics; the 7th International Conference on Shock and Impact Loads on Structures; the 2008 International Symposium on Safety Science and Technology; the 4th National Conference on Calculate Explosion Mechanics; and the 8th Conference on Material Dynamics.

3.3.2 Research Capability

SKLEST covers an area of 8000 square meters. It is equipped with advanced facilities worth approximately 59,270,000 RMB (US\$8,500,000). SKLEST's equipment includes a Zeta Pals particle size analyzer, surface tension analyzer, velocity meter, magnetron sputtering coating machine, multi-beam velocity system, two-stage light gas gun, split-chassis Hopkinson tie bar, high-speed digital camera, high-speed digital imager, high-speed motion analysis system, high-speed motion analyzer, solid-state laser, lithography machine, nuclear quadrupole resonance system, infrared spectrograph, thermal infrared imager, mixture explosion performance testing equipment, laser high-speed photography recorder, laser Raman analysis systems, laser particle analyzer, accelerating rate calorimeter, rheological measurement system, and six-channel instantaneous optical pyrometer.

There are five divisions in the SKLEST. The research areas are Theory and Applied Technology of Energetic Materials, Detonation and Explosion Technology, Impact Dynamics of Materials and Construction, Damage Theory and Protection Technology, Explosion Safety Theory, and Assessment Methods.

Division 1: Theory and Applied Technology of Energetic Materials

The Division 1 research team consists of 17 staff, of which 11 are professors and six are associate professors. Prof. Xu Geng-guang (徐更光),

a Ph.D. supervisor and an academician of the Chinese Academy of Engineering, is the leader of the research team and is one of the founders of applied theory and technology of high-energy mixed explosives in China. His research areas include the numerical simulation of detonation parameters, formulation design, composite explosives, and thermal decomposition of the kinetics of explosives. He has published more than 100 papers and has won the National Prize for Progress in Science and Technology. His research on 11 composite explosives and their propellant charge techniques has contributed greatly to the development and innovation of weapons.

Division 1 conducts research on molecular structure, design theory, and controlling technology of critical processes of energetic materials, including high-energy explosives, propellants, powders, pyrotechnics, and primary explosives; passivation and sensitization mechanisms and modifying technologies of energetic materials; the macroscopic and microcosmic physical cluster and rheological theory of energetic materials; the combustion and engineering calculation of detonation parameters; basic physical chemistry data for energetic materials; the kinetic theory and the technology of the invariability and security of energetic materials; design theory and the technology of the charge techniques of rocket engines and warheads; and preparative techniques for and characterization of ultra-fine energetic materials.

Division 2: Detonation and Explosion Technology

The research team of Division 2 is composed of 12 staff, of which six are professors and two are associate professors. Prof. Jiao Qingjie (焦清介), a Ph.D. supervisor at BIT, is the leader of Division 2. His research areas focus on the security and reliability of explosive systems and their design technology. He has published about 100 papers related to the reliability of detonation and explosive systems.

Division 2 conducts research on condensed phase, gas phase, multiphase, and multi-dimensional detonation and combustion theories; initiating and ignition theory; the mechanisms, criteria, and model analyses of DDT (deflagration to detonation transition) and SDT (shock to detonation transition); propagation of combustion waves and detonation waves and the interaction between them; Eigen relations and the state equations of energetic materials; physical models and digital simulation of combustion and detonation; the mechanisms of energy transition, transformation, and the design of ammunition exploding series; the mechanisms of chamber explosion and analysis of launching safety; flameout and the self-explosion mechanism of propellants;

experimental technology of combustion and detonation processes; design theory and engineering application technology of blast safety for earthwork and building and construction; and blast processing technology.

Division 3: Impact Dynamics of Materials and Construction

The Division 3 research team is composed of 22 staff, of which ten are professors and six are associate professors. Prof. Huang Fenglei (黄风雷), a Ph.D. supervisor at BIT as well as a specially engaged professor in the Ministry of Education's "Cheung Kong Scholars Program", is the leader of Division 3 and a subeditor of the *Journal of China Ordnance*. He has published 122 papers and five monographs and has five patents. He is the vice-director of the Chinese Society of Theoretical and Applied Mechanics and the director of the China Ordnance Society. He has dedicated himself to research on explosions and shock waves, condensed explosive detonation products, mechanisms of explosives, and the damage effects of explosives. Prof. Huang won second place for the 1995 National Prize for Progress in Science and Technology for his research on solid explosives initiation under shock waves and second place for the 2008 National Prize for Progress in Science and Technology for the study of the risk of solid propellant detonation.

Division 3 conducts research on the dynamic behavior of various materials and structures under explosion and high-speed impact load; microscopic and macroscopic damage and destruction theory; Eigen relations and state equations of materials; the formation mechanisms of fragments, jets, explosive formed penetrators, and plasma; experimental technology; and digital simulation during impact.

Division 4: Damage Theory and Protection Technology

The Division 4 research team consists of 16 staff, of which 8 are professors and 3 are associate professors. Prof. Feng Shunshan (冯顺山), a Ph.D. supervisor at BIT, is an expert in National Security and in fire extinguishing for the Ministry of Public Security. He is the leader of the Division 4 research team as well as the director of the Explosion and Security Professional Committee of the China Ordnance Society and vice-director member of the Ammunition Society. He has won 12 science and technology progress awards, has 8 patents, and has published 160 papers. He proposed a new design method for smart munitions. His invention of an ammunition interceptor was used for air security during the 2008 Beijing Olympic Games.

Division 4 conducts research on vulnerability theory, models, and criteria of various targets and structures; interaction theory of various damage units and media; damage mechanisms of targets and structures; terminal ballistics and terminal effect theory of warheads; target damage and structure protection technology; new principles, concepts, and technology of damage and protection; simulation and measurement of damage and protection; and digital simulation technology of damage processes and terminal effects.

Division 5: Explosion Safety Theory and Assessment Method

The Division 5 research team is composed of 16 staff, of which 7 are professors and 3 are associate professors. Prof. Bai Chunhua (白春华) is a Ph.D. supervisor and the leader of Division 5 as well as the director of SKLEST. He is a member of the editorial board of the *Science & Technology Review*, the *Journal of China Safety Science*, and the *Journal of Explosives and Propellants*. He has published more than 150 papers and 3 monographs, 12 patents, and has won 4 province-ministry class awards.

Division 5 conducts research on the detection of flammable, explosive, and toxic materials; identification, analysis, and evaluation of major hazardous sources; accident mechanisms and preventive technology; safety evaluation and detection technology for systems; information systems for safety management; digital simulation technology of safety accidents; and new principles, concepts, and technology for weapons system safety.

3.4 Nanjing University of Science and Technology

Located in Nanjing, the Nanjing University of Science and Technology (NUST) is one of the national key universities under the Ministry of Industry and Information Technology. The university developed from the Institute of Military Engineering of the People's Liberation Army and was established in 1953. It is the highest institution of military technology in China. The university changed to its current name in 1993. The university has become a multi-disciplinary university incorporating science, engineering, liberal arts, economics, business, management, law, and education for coordinated development. NUST has an area of 2,078,000 square meters and a total value of fixed assets equaling 1,400,000,000 RMB (US\$200 million). The university has a complete logistics service system, 56 labs, various teaching and research apparatuses, and equipment valued at 499,000,000 RMB (US\$75 million).

The present number of faculty members is 3,099, including 1,508 full-time teaching and research personnel, 1,164 senior teachers, 214 doctoral tutors, and 5 academicians of the Chinese Academy of Engineering. The university is a place for education as well as technology research. Currently, it has more than 30 research institutes. The university has conducted exchange and cooperation with educational and technological institutions at home and abroad, having established sound cooperative relationships with universities and research institutes including Saint Joseph's University in the U.S., Fukuoka Institute of Technology in Japan, the Technical University of Munich in Germany, and AJOU University and Soonchunhyang University in Korea. On May 18, 2010, the *25th International Conference on Ballistics*, which was co-hosted by NUST and Chinese Ordnance Society, was convened at the Friendship Hotel in Beijing, China. This was the first meeting of its kind to be convened in an Asian country.

3.4.1 Energetics Research in the School of Chemical Engineering

The School of Chemical Engineering is directly affiliated with Nanjing University of Science and Technology, its predecessor being the Explosives & Propellants Division of the Artillery Engineering Department of the Institute of Military Engineering for the People's Liberation Army (Ha'erbin Military Institute for short), which was established in 1953. There are now more than 2,500 registered students of various specialties in the School of Chemical Engineering, including 260 Ph.D. students, 600 master's students, and more than 1,600 undergraduate students. The School of Chemical Engineering has developed a broad range of disciplines and has exhibited strength in such fields as chemistry, chemical engineering, materials, environmental science, biology, and safety engineering. It has also adopted distinctive programs in military engineering, civil explosives equipment, materials, and chemical engineering.

The Applied Chemistry Department in the School of Chemical Engineering consists of disciplines and specialties such as applied chemistry, military chemistry, and special energy engineering and pyrotechnics. The special energy engineering and pyrotechnics is an important discipline under the administration of the Commission on Science, Technology and Industry for National Defense. It annually undertakes over 300 top-level national, provincial, and ministerial subjects for study, and its annual scientific research fund amounts to more than 80 million RMB (US\$11.75 million). The department mainly engages in the research of synthesis and characterization of energetic compounds, the synthesis and characterization of energetic nitrogen

compounds and the derivatives thereof, the design and preparation of pyrotechnic agents and functional materials, research and application of the special combustion effects of pyrotechnic materials, combustion and explosion physics of energetic materials, ignition and detonation technology of energetic materials, reliability and failure analysis of initiating explosive devices, spectrum telemetry and remote sensing technology, micro-systems and chemical chip technology, fast solid-phase chemical reactions, and applied electrochemistry. Every year, the school invites scholars of international standing to give lectures and academic seminars.

3.4.2 Research Capability in the School of Chemical Engineering

The Applied Chemistry Department now has 23 staff members, including 10 professors and researchers and 6 associate professors and researchers.

Dr. Zeshan Wang (王泽山), academician of the Chinese Academy of Engineering, is a Ph.D. supervisor at the Nanjing University of Technology and Science. He is also the leader of a research team in chemical engineering and technology in the Applied Chemistry Department and has published over 80 papers, 9 books, and 19 national defense secret patents related to energetic materials. His research focuses on pyrotechnics. As an expert in energetic materials, he has won first place for the National Award for Technological Invention for his invention of low temperature technology for propellant combustion, which highly increased the emission efficiency and power of propellants; the first place award for National Science and Technology Progress for his invention of propellant waste recycling, which has improved security and economic benefits; and third place for the National Award of Technological Invention based on his technique for developing high loading density gun propellant charges. Recently, Dr. Wang undertook two projects in national defense science with a research funding of 2,000,000 RMB per year.

Dr. Zuliang Liu (刘祖亮) is a Ph.D. supervisor. He is an expert researcher in the area of energetic materials and chemical technology and has published 80 papers. He has participated in 17 research projects and has the benefit of a State Council Expert Special Allowance. He has been granted 16 patents, including one Gold Award from China's Patent Office and two awards for State Top 10 patents. His research areas include continuous automated production technology of industrial explosives used for construction, mining, and quarrying; preparing technology of energetic materials; and the technology development of

both civilian- and military-use explosives. Recently, he has undertaken the projects of ammonium nitrate explosive industrialization and seismic charges containing gun propellant.

Dr. Chunxu Lu (吕春绪), a Ph.D. supervisor, is a famous scholar and expert in the research area of energetic materials in China. His invention of expanded technology for ammonium nitrate and its application is famous as a great innovation in the field of industrial explosives. This technology is treated as a national-level promotion program that has made a great contribution in terms of both social benefits and economic benefits. He was once the vice president of Nanjing University of Technology and Science and was twice invited to lecture at Tokyo University. In 1994, as a senior scholar, he went to Stockholm University, Sweden, to conduct cooperative research. Now he is the chairman of the China Civil Explosive Materials Distribution Association and vice president of Jiangsu Chemical Industry Association. He has received the National Science and Technology Progress Award, the Award for National Science and Technology Invention, and the Gold Award for the Top 10 Chinese Inventions. He has published 17 textbooks and 140 papers, of which 31 are represented in Science Citation Index (SCI) and the Engineering Index (EI).

3.4.3 Energetics Research in the NSSPERC

The National Special Superfine Powder Engineering Research Center (NSSPERC) is one of four national level research centers at the Nanjing University of Science and Technology. Established in 2002, NSSPERC is a research center engaged in the research and development of superfine powder technologies. NSSPERC is composed of three institutes: the Research Center for Superfine Powder and Surface Science Technology, the Superfine Powder Technology Development Center of China North Industries Group Corporation, and the Jiangsu Province Engineering Research Center of Superfine Powder.

NSSPERC mostly conducts research on the application of superfine powder in the military field and the civilian area, the surface modification technology of superfine powder, the application of compounding technique of micro/nano particles in solid propellants and explosives, and security technology for the preparation process of superfine powder.

3.4.4 Research Capability in the NSSPERC

NSSPERC covers an area of 500 square meters and possesses a testing laboratory of nano/micrometer superfine powder established jointly with Malvern Instruments Ltd. NSSPERC is equipped with advanced facilities including a Mastersizer micro-particle size analyzer, a

Zetasizer nano-particle size analyzer, a simultaneous DSC/DTA-TGA thermal analyzer, a surface area and pore size analyzer, plasma equipment, an upright microscope, and a high speed hammer mill.

NSSPERC has over 40 staff including professors, associate professors, research staff, senior engineers, and post-doctoral researchers.

Dr. Fengsheng Li (李凤生), director of NSSPERC, is a professor at NUST. He has been working for a long time on the design and manufacturing technology for new propellant and superfine materials and the industrialization, design, and production of gun propellants. He involved himself with research on the effects of nanometer materials and micro-nano composites on the burning rates, pressure exponents, and manufacturing technology of solid propellants. He has invented many techniques for the manufacture of nano- and micro-materials and micro- and nano-composites. Dr. Li was conferred the title of Outstanding Scientist with Prominent Contributions by the government of China. He has received second and third places for the National Award for Technological Invention, first place for the National Science and Technology Progress Award, the National Science Conference Award, and over 10 province/ministerial awards. In addition, Dr. Li has won 31 national patents, among them for his technique for the preparation of nano/micrometer composite materials. He has also compiled 10 books, including *Application and Manufacture Technology of Special Superfine Powder*; *Design and Manufacture of Advanced Propellants*; *Nanometer Functional Composite Materials and Applications*; *Technology of Solid Propellants*, and *Nano-Material Applications*. He has published 290 papers in leading academic journals in China and abroad. Presently, he also works as a Committeeman of the High Energy Materials Society of India, the Director of the Science Committee for Zoology and Environment Materials in Jiangsu province of China, Administrative Director of the Particles Technology Society of China, and a Committeeman of the Fine Chemical Engineering Committee of the Chemistry Engineering Society in China. His research achievements have been applied to the manufacturing of new weapons in the military field. Recently, Dr. Li has taken charge of several projects concerning technology for preparing micro- and nano-materials and their application in solid propellants and explosives and new techniques in preparing energetic materials. The total research funding has reached the amount of 10,000,000 RMB (US\$1.5 million).

Dr. Hongchang Song (宋洪昌) received his Ph.D. in energetic materials in 1986. His research area covers structural design and the theoretical study of solid propellants, including combustion

characteristics of aluminum-magnesium fuel-rich propellants at low pressure as well as the surface modification technology of superfine powders and their applications. Dr. Song has won first place for the National Science and Technology Progress Award, second and third places for the Province Level Science and Technology Progress Award, and has five national patents. He authored a book titled *Fundamentals of Propellant Design*. He has published several academic papers, four of which are represented in SCI. Currently, Dr. Song is undertaking three research projects: combustion model of solid propellant and technology of burning rate prediction; surface modification technology of military oxidants and its application; and prescription and property of fuel-rich propellants. His research funds total 300,000 RMB (US\$45,000), 60,000 RMB (US\$9,000), and 100,000 RMB (US\$15,000), respectively.

3.5 China Academy of Engineering Physics

Located near Mianyang, whose nickname is Scientific Town, in the mountains northwest of Chengdu, Sichuan Province, the China Academy of Engineering Physics (CAEP), also known as the Southwest Institute, was founded in October 1958. It is the primary design laboratory for Chinese nuclear weapons. The academy was formerly named the Ninth Institute of the Second Ministry of the Mechanical Industry and also the Ninth Institute of the Ministry of the Nuclear Industry. It was later renamed CAEP. In China, the Ninth Institute is still well recognized. CAEP has multiple branches in Beijing, Jiangyou, Chengdu, and Shanghai. CAEP includes about 12 institutes spread throughout Mianyang, Sichuan Province. Institute 907 is located in Jiangsu, north of Shanghai. It also has four key defense science laboratories and two key laboratories, designated with number 863. Their research areas include theoretical physics, explosives and organic chemistry, shock wave and explosive physics, nuclear and plasma physics, engineering and material sciences, electronics and photo-electronics, radioactive chemistry and chemical engineering, computer science and computational mathematics, and others.

CAEP has over 8,000 researchers, 2000 of which are senior technical staff. Some prominent Chinese scientists used to be leaders of the academy, including Yu Min, Wang Ganchang, Deng Jiaxian, Zhu Guangya, Chen Nengkuan, Zhou Guangzhao, Guo Yonghuai, Cheng Kaijia, and Peng Huanwu. It currently has nine academicians of the Chinese Academy of Sciences (CAS), seven academicians of the Chinese Academy of Engineering (CAE), and a number of outstanding scientists. In the academy, the number of students is around 360. There are 131 advisors for Ph.D. students compared with 224 professors for master's

students. Currently, the academy has 917 graduates with master's degrees and 261 Ph.D. graduates.

3.5.1 Energetics Research at the Institute of Chemical Materials

The Institute of Chemical Materials, also known as the Southwest Institute of Chemical Materials, is one of the twelve research institutes in CAEP spread throughout Mianyang, Sichuan Province. The Institute of Chemical Materials conducts research, development, and manufacturing work in energetic materials, pyrotechnics, and high polymer materials. The institute is equipped with advanced testing devices and manufacturing equipment. It has made a lot of scientific research achievements in the areas of high explosives, insensitive ammunition, new style pyrotechnics, and macromolecular materials. Two of the most important labs in the Institute of Chemical Materials are the Laboratory of Materials Evaluation and Nondestructive Testing and the Laboratory of Physics and Mechanics of Materials.

The Laboratory of Materials Evaluation and Nondestructive Testing (LMENDT) tests and evaluates the qualities and properties of energetic materials, including pyrotechnics and high polymer materials. The lab performs services of material assessments, damage evaluation, and process detection and diagnosis.

The Laboratory of Physics and Mechanics of Materials (LPMM) supports research and the development of new materials. The main function of this lab is research of materials, physics, and mechanical properties in the area of strength theory, damage, and failure modes.

3.5.2 Research Capability

The Institute of Chemical Materials has over 800 researchers, including one academician from the Chinese Academy of Engineering who receives the benefit of the State Council Expert Special Allowance, as well as several academic and technical leaders in their respective areas. Senior academicians and technicians account for 45% of the total staff. Dr. Xiping Long (龙新平) received his Ph.D. in Engineering from the Beijing Institute of Technology. He has received the award for one of the 10 most outstanding youngsters in Sichuan province, the award for scientific development, the award for Chinese Invention Patent, the award for Outstanding Contributor in Sichuan Province, and the benefit of the State Council Expert for Special Allowance for his longtime contributions in the research area of explosion mechanics, pyrotechnics, performance of explosives, and metal dynamic fracture toughness.

Dr. Hui Huang (黄辉) is the director of the Institute of Chemical Materials and is also an advisor for Ph.D. students. His research interest is in the area of energetic materials. He has received several awards, including Advancement in Technology Awards, the award for Outstanding Young Professionals in the scientific industry of national defense, and an award for outstanding youngsters from the Chinese Association of Science and Technology.

CAEP is a research center directly supervised by the State Council of PR China. Hence, most of its research funds come from the Chinese government. The China Academy of Engineering Physics (CAEP) and the National Natural Science Foundation of China (NSFC) set up a joint fund called National Natural Science Associated Foundation of China (NSAF) to encourage scientists in relevant fields to participate in basic and applied research within the scientific and technological programs of CAEP. The funding for experimental projects is about 200,000 RMB (\$30,000) per project, and about 100,000 to 120,000 RMB (\$15,000–\$17,000) per project for theoretical projects.

3.6 North University of China

The North University of China (NUC), formerly known as the North China Institute of Technology (1993–2004) and the Taiyuan Institute of Machinery (1958–1992), is located in Taiyuan, Shanxi Province, China. NUC is a multi-disciplinary institution of higher education that is managed jointly by the Commission of Science Technology and Industry for National Defense (COSTIND) and the People's Government of Shanxi Province. NUC is the largest educational institution in Shanxi Province. It played an important role in the improvement of manpower and weaponry of the Chinese People's Liberation Army.

NUC consists of 15 schools and has been authorized to confer doctoral, master's, and bachelor's degrees. Full-time enrollment is 25,206, including more than 22,858 undergraduates and over 1,400 Ph.D. and masters candidates. NUC's fields of study include engineering, science, liberal arts, economics, management, law, and education. The university features 10 provincial and ministerial key disciplines and houses several state, provincial, and ministerial key laboratories, bases, and research centers. Over the past 66 years, NUC has cultivated scientific research. The fund for scientific and technological development reached 120,000,000 RMB (US\$17,143,000) in 2006. It has achieved tremendous accomplishments in a great number of programs, some of which have won high-level awards.

3.6.1 Energetics Research in the School of Chemical Engineering and Environment

The School of Chemical Engineering and Environment at NUC consists of 3 departments: the Department of Chemical Engineering, the Department of Safety Engineering, and the Department of Environmental Engineering. The Department of Safety Engineering offers Safety Engineering, Special Energy Engineering and Pyrotechnics, Military Chemistry, and Pyrotechnics majors. The school mainly conducts research on fire and explosion prevention technology, technology of initiators and pyrotechnics, variable burning rate propellants, propellants and propelling charge techniques, synthetic technology for explosives, and explosive reactive armor.

The university has 8 provincial and ministerial key disciplines. Three of the most important disciplines in the School of Chemical Engineering and Environment are Artillery, Automatic Gun and Ammunition Engineering, Weapons Systems and Application Engineering and Applied Chemistry. Two of the six laboratories and research centers in the School of Chemical Engineering are the National Ordnance Industry Booster Explosive Testing Center and the Shanxi Technology Research Center of Fire and Explosion Prevention.

3.6.2 Research Capability

The research team of Weapons Systems and Application Engineering is composed of 6 doctorate supervisors, 18 professors, and 27 associate professors, many of them being noted experts in ordnance and aerospace organizations. Prof. Hu Shuangqi (胡双启) is the leader of the research team. He has published over 30 first level academic papers, in which 10 papers are found in the Engineering Index and Index to Scientific & Technical Proceedings (ISTP). He has participated in 20 research projects. Presently, the research funding is about 2,000,000 RMB (US\$300,000). As a Ph.D. supervisor at NUC, he published the book *Combustion and Explosion* and won third place for the National Defense Prize for Progress in Science and Technology for his joint research on high energy hexogen-X boosters with Prof. Zhang Jinglin (张景林), and second place for the Shanxi Province Award of Progress in Science and Technology for his research on a new charge structure for booster pellets. In recent years, over 30 awards for scientific and technological achievements at the national, ministerial, and provincial level have been granted to the discipline. Major research interests include weapon safety engineering, design of weapons systems and their key subsystems, weapons system confrontation technology, precision guidance, and control of conventional warheads.

The research team of Artillery, Automatic Gun, and Ammunition Engineering is composed of 15 doctoral supervisors, 2 members of the China Academy of Engineering, 23 professors, and 23 associate professors or senior engineers. The major research interests focus on weapon structures design and dynamic research, weapons testing technology, warhead structures and control technology, and warhead terminal effect and anti-penetrating technology.

Prof. Chen Guoguang (陈国光) is the leader of the research team. He is a Ph.D. advisor at NUC, and his research area covers guided and control systems of projectiles rockets, technology of smart munitions, control systems of weapons, system kill probability, and technology of long-range rockets. He has participated in over 20 research projects whose research funding totaled 2,580,000 RMB (US\$380,000).

The research team in Applied Chemistry consists of 5 doctorate supervisors, 12 professors, and 10 associate professors. Its research interests include special energy chemistry and applications, synthetic fine chemical products and their applications, functional polymer materials, multiphase fluid mass in the high-gravity field, and ultra-fine powder materials and their chemical reaction. Prof. Cao Duanlin (曹端林) is the leader of the research team. His research area mainly focuses on the synthetic fine chemical technology and its application of special energy for weapons, techniques for loading materials for initiating explosive devices, and manufacturing processes of pyrotechnics.

The National Ordnance Industry Booster Explosive Testing Center was one of the earliest institutes in China to conduct research on booster explosives. The School of Chemical Engineering and the Environment has made a lot of scientific research achievements regarding the energy security of booster technology, the technology of armor and defense, high energy and high strength propellants, synthesis and application of energetic materials, testing techniques of explosive properties, and new initiation techniques of insensitive ammunition. The center won several awards, including first place for the Chinese Defense Science and Technology Award, second and third place for the National Award for Technological Invention, and over 40 Provincial/Ministerial Level Awards for Progress in Science and Technology. The testing center covers 4000 square meters and is equipped with 44 advanced facilities such as a scanning electron microscope, micro-calorimeter, specific surface area analyzer, Fourier transform infrared spectrometer, particle shape and size image analyzer, verification regulation of micron photosizer, Pulverisette 4 vario-planetary ball-mill, and lab spray dryer.

The testing center has a total of 25 staff, including 7 professors, 8 associate professors, and 8 lecturers. Prof. Jinglin Zhang (张景林) is the

director of the testing center. He graduated from Beijing University of Technology in 1964. As a Ph.D. supervisor and an expert in safety engineering, he has published over 30 papers in leading academic journals and has won 15 awards for technology progress, such as the second place for the Shanxi Province Award of Progress in Science and Technology for his research achievements on J0-9C booster pellet, third place for Technology and Industry for National Defense Progress Award for his research on the performance testing system of booster pellet, and the third place of the ministerial level Science and Technology Award for the research of TNT explosive characteristics under heat environment. He wrote several books including security system engineering, combustion and explosion disasters, and shipment of dangerous chemicals. Recently, he has been leading a research project in molecular and particle design technology of booster explosives, which is a sub-project of the 973 National Defense Project.

The Shanxi Technology Research Center of Fire and Explosion Prevention was established for research into the safety of propellants and explosives, weapons system protection techniques, military chemistry, pyrotechnics and weapons systems, and utilization engineering. It is equipped with over 500 devices worth 10,000,000 RMB (US\$1,429,000), including a high speed camera, a laser diffraction particle size analyzer, and a high speed data acquisition and harmonic analyzer. Besides two sub-projects of the 973 National Defense Project, their research currently is undertaking over ten provincial level projects. Total research funding has reached the amount of 35,000,000 RMB (US\$5,000,000), derived mostly from government and national foundations. For example, the research funding is 1,200,000 RMB (US\$175,000) supported by Shanxi Province for the project of simulation models of combustion and explosion processes of gas, liquid, and particles and their testing and evaluation technique. A project on explosion characteristics of gaseous chlorine dioxide and its reaction dynamics received research funding of 290,000 RMB (US\$40,000) from the Natural Science Foundation. During the past ten years, the center has won over fifteen national and ministerial level achievements such as third place for the National Invention Award for the invention of explosion testing equipment of combustible liquids and second place for the Shanxi Province Award of Progress in Science and Technology for improvement in explosive characteristic testing system of columnar explosion mixtures.

The research team consists of 4 Ph.D. supervisors, 6 professors, and 6 associate professors. Dr. Shuangqi Hu (胡双启) is the director of this research center. He is a professor at NUC, a Ph.D. supervisor, and the leader of a project called "Weapons Systems and Application

Engineering”. His research mainly focuses on the Weapons System Safety Engineering and propellants and propelling charge techniques. He has published over 100 papers in leading domestic and international academic journals. He has won seven province-level awards for Science and Technology Progress and three national patents for his research products.

3.7 National University of Defense Technology

The National University of Defense Technology (NUDT) is a key national comprehensive university designated as a State Project 211 and Project 985. It has cultivated senior science and engineering technology talents and commands for the whole army, training senior leaders and engaging in research on advanced military equipment and defense technology. NUDT was originally founded in 1953 as the Military Academy of Engineering in Harbin in Heilongjiang Province. In 1970 the Academy of Engineering moved south to Changsha and was renamed the Changsha Institute of Technology. The Institute changed its name to the National University of Defense Technology in 1978.

NUDT’s main research fields are mathematics, physics, dynamics, aerospace, materials, automatic controls, radar, communication, navigation security, opto-electronic engineering, and management engineering. Since 1978, NUDT has accomplished over 4,000 research achievements such as Galaxy-Series supercomputers, maglev trains, humanoid robots, and core routers, etc., and over 1600 of them have been awarded Science and Technology Progress Prizes by the state, the People’s Liberation Army, and ministries and commissions. Over the past five decades, NUDT has fostered more than 130,000 high-caliber personnel for the country and the People’s Liberation Army. NUDT has also delivered a large number of high-caliber personnel for China’s manned spaceflight program, and 13 of the commanders-in-chief, deputy commanders-in-chief, and chief designers of the seven systems of Shenzhou VI Aerospace Project have graduated from NUDT. NUDT has become an important player in the national innovation system of defense science and technology.

According to the National Subject Evaluation of the years 2002–2004 organized by the Ministry of Education, five programs at NUDT were in the top five nationally, and NUDT’s computer science and technology program ranked first nationwide. NUDT owns three national level key laboratories, including a national high performance computer center, national military laboratory of aerospace propulsion, and national military laboratory of integrated electronic information system. The faculty includes one academician of the Chinese Academy

of Science, five academicians of the Chinese Academy of Engineering, 155 tutors of Ph.D students, 375 tutors of master's students, 1000 teachers with having senior professional technical titles, nearly 400 teachers having doctoral degrees, 19 teachers deemed to be State-level "young and intermediate experts with great contributions", and 200 teachers with enjoying special government subsidies.

With a strong commitment to internationalization, the university has academic ties with over 100 universities and research institutes from 40 countries and regions. It has signed formal collaboration agreements with more than 10 well-known universities, including the University of Paris-Sud 11, Durham University, Moscow State Aviation Institute, Ankara University, and Turkey YILDIZ Technical University. The university invites hundreds of scholars of international standing to give lectures and academic seminars every year, and holds large-scale international academic conferences, such as the Asia Pacific Web Conference in 2001. The university annually sends out more than 300 teaching or research staff as short-term overseas visitors to study, carry out joint research, and pay academic visits.

3.7.1 Energetics Research in the College of Aerospace and Materials Engineering

The College of Aerospace and Materials Engineering of NUDT comprises three departments and one institute: the Department of Astronautical Science and Engineering; the Department of Materials Engineering and Applied Chemistry; the Department of Military Aerospace; and the Institute of Space Technology. It focuses on astronautical science and new materials, and mainly undertakes research on the overall design technology for satellites; rockets; various kinds of aircraft; propulsion technology; controlling, testing, and launching technology; micro-electro-mechanical systems; nano-functional materials and nano-apparatus technology; new materials technology; chemistry and pyrotechnics technology; and other facets of this technological area. The college is oriented to cultivate high-quality talents in engineering technology arenas confronting the national defense industry.

The college has seven first-grade disciplines, which are dynamics, aeronautical space navigation science and technology, materials science and engineering, weapons science and technology, chemical engineering and technology, power engineering and engineering thermo-physics, and chemistry. At present, this college has three Ph.D. programs in the first-grade disciplines, which are dynamics, aeronautical space navigation science and technology, and material science and engineering. It also has three postdoctoral scientific mobile research stations for scientific research in the fields of dynamics, aeronautical space

navigation science and technology, and materials science and engineering. This college also retains a state-level key discipline, namely, aeronautical space navigation propulsion theory and engineering; and four province-level key disciplines, which are materials science, aircraft design, solid mechanics, and hydromechanics.

3.7.2 Research Capability

The College of Aerospace and Materials Engineering currently has a faculty of more than 130 professors and associate professors, and it possesses advanced facilities for teaching, scientific research, and experimentation. Prof. Yang Tao (杨涛) and Prof. Zhang Wei (张伟) are Ph.D. supervisors in the Department of Materials Engineering and Applied Chemistry. Their research area mainly focuses on un-choked ducted rocket engines and their solid propellants, smart munitions, the theory of combustion in rocket motors, and combustion diagnosis and scramjet combustion.

The college has undertaken some important scientific research missions, such as overall flight vehicle technology, advanced propulsion technology, continuous SiC fiber, and technology of preparing nano-materials. It has made achievements in scientific research that include “Alterable Propulsive Thrust Liquid Propulsor”, “ZN-31 High-speed Test Rocket”, “921 Ejection Escaping Emulation System”, “Liquid Propulsor Fault Detection and Diagnosis Technology”, “Silico-carbon Nitrogen Nano-composite Micro-powder and Its Ceramic Composites Preparation and Applied Research”. In past years, this college has won one prize for Important Scientific and Technological Achievement from the National Science Conference, one second place Prize for National Scientific and Technological Advancement, and four third place Prizes, one prize for National Invention, and more than 300 ministerial prizes for Scientific and Technological Advancement. Since the 9th five-year plan, more than 2400 academic papers have been published and more than 600 have been collected by the three international indexing databases.

The Center for Materials Science within the college was established to support research and innovation in new materials for military weapons equipment. The center is equipped with an emission scanning electron microscope, a scanning probe microscope, a transmission electron microscope, a wave surface interferometer, a high-precision Fourier transform spectrometer, a portable spectrometer, a plasma chromatograph mass spectrometer, and devices for Metal-Organic Chemical Vapor Deposition (MOCVD) functional thin film manufacturing.

Figure 3.9 shows the authors with the most publications in the Chinese Journal of Energetic Materials in the last two years. From these statistics, the four leading contributors are as follows:

- Zhao Feng-qi (赵凤起) *interest: Thermal Properties*
- Zhang Tong-lai (张同来) *interest: Crystal Properties, Synthesis*
- Hu Rong-zu (胡荣祖) *interest: Thermal Properties*
- Liu Zi-ru (刘子如) *interest: Chemical Interaction and Properties, Thermal Properties*

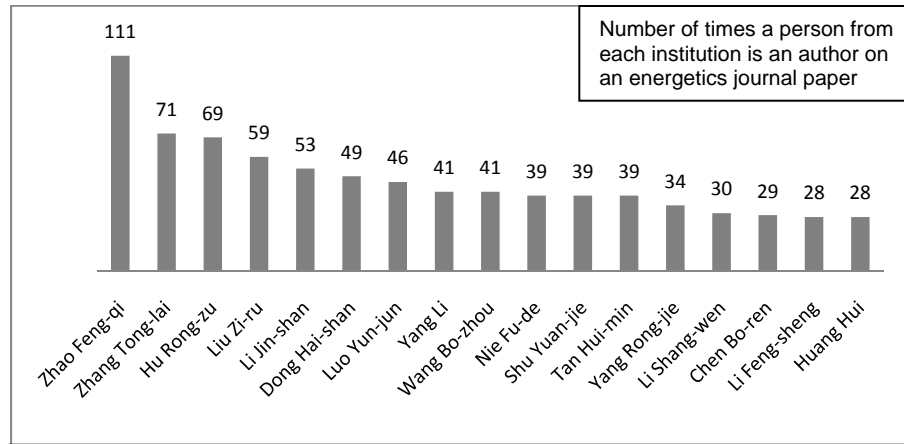


Figure 3.9: Number of publications

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Chapter 4

Synthesis

Synthesis is the alteration and manipulation of molecules in compounds to produce a new product compound through a series of chemical reactions. The substances used for a reaction are known as reactants or reagents. Synthesis requires knowledge of chemistry and material science. Synthesis is important because new chemical compounds can have greater power, energy, and safety.

Because of its potential for breakthroughs, synthesis is an active energetics research field in China, consistently comprising over 10% of all energetics research. Figure 4.1 shows the fourteen-year history of energetic synthesis research publications in China.

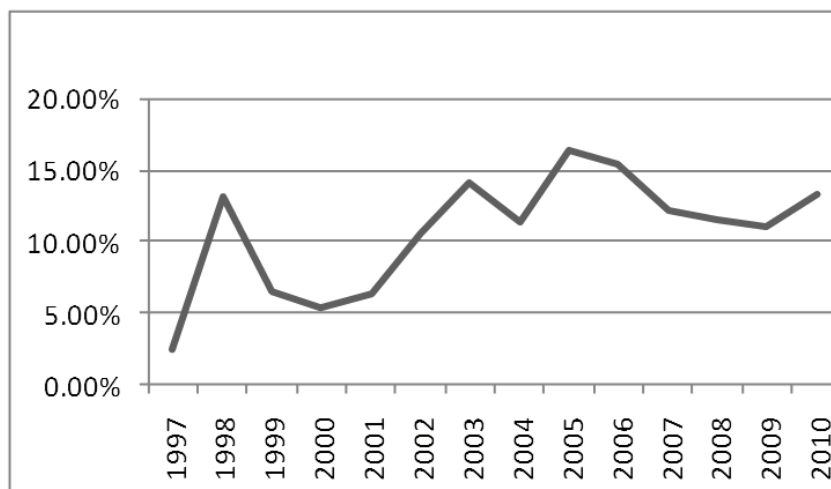


Figure 4.1: Research in synthesis

Examples of energetics synthesis techniques include acetylation (addition of an acetyl functional group), nitration (addition of a nitro group), hydrolysis (splitting of a water molecule), deprotection (modification of a functional group), hydrogenation (form of chemical reduction), N-oxidation (involving a nitrogen-oxygen bond), dimerization (combination of two identical molecules), and condensation (combination of two molecules). One synthesis technique involving substituted diphenyl ethers (SDE) is the Williamson reaction, also known as the Williamson ether synthesis. This is a way to perform the synthesis of ethers. It occurs when an organohalide reacts with an alcohol, often in an ionic liquid.

An ionic liquid is a solvent that is used as a substitute for water during the synthesis of energetic materials. It can be prepared from a substance such as aluminum chloride and then used as a catalyst as well as a solvent. It has also been found that ionic liquids can affect reaction properties such as reaction time and temperature. Its effectiveness stems from its low combustibility and excellent thermal stability. Use of an ionic liquid can produce a higher synthesis yield.

Just as there are numerous synthesis methods, there are numerous reactors in which synthesis reactions are done. A micro-reactor is an extremely small continuous-flow device in which synthesis chemical reactions take place. There are two inputs to the micro-reactor. Two reactant compounds flow in, mix, and react. It can handle both liquid-liquid and liquid-solid reactions. The separate solutions are pumped into channels through a mixing chamber and the product is continuously collected. Because of the micro-reactor's miniature size, it allows a high surface area to volume ratio which leads to superior heat exchange. Furthermore, the micro-reactor is very efficient, performing mixing at optimum ratios and optimum temperatures.

4.1 Energetics Synthesis Research

Synthesis is a topic of significant research and publications in the energetics field in China. Synthesis research includes the materials, their properties, and the parameters affecting product yield, such as the ratio of components in the mixtures, solvents, catalysts, temperatures and reaction times. The chemical and physical structure is normally characterized by IR, NMR, DSC, and elemental analysis.

Synthesis of energetics such as RDX (e. g. thermal decomposition of RDX [15, 109], coatings [88]) and HMX has been extensively studied [1, 51, 69, 120]. For example, a method of synthesizing HMX using DADN (1,5 diacetyl 3,7-dinitro 1,3,5,7 tetranitrotetrazacycloctane) as a reactant is presented in [120]. In that study, HMX was synthesized in a nitrating

agent consisting of a mixture of dinitrogen pentoxide and nitric acid. The yield of HMX was more than 96%, mp 272, 0~272, 8°C. In [19], researchers studied the synthesis of Zirconium 3-Nitrophthalate and its effect on the combustion of various propellants, including RDX-CMDB (composite modified double base) propellants. In [123], the effects of two catalysts (nanometer PbO and nanometer Bi₂O₃) on the burning properties of RDX-CMDB propellant were investigated. In [94], researchers studied the synthesis of Keto-RDX using urea and a mixture of nitric acid and dinitrogen pentoxide as nitrating agents.

Research has identified alternatives to HMX and RDX, including N-guanylurea dinitramide (GUDN). DSC results have shown that GUDN is compatible with common energetic materials such as HMX and RDX [61]. In [117, 127], researchers investigated mixtures containing HMX and mixtures that produce by-products of HMX. In [16, 25], researchers conducted synthesis and characterization of 1-Methyl-2,4,5-trinitroimidazole (MTNI). The structure of MTNI was characterized by IR, NMR, and elemental analyses. The thermal decomposition performance of MTNI was tested by DSC. The results showed that the detonation performance characteristics were comparable to those of RDX. In fact, MTNI is an insensitive high explosive with friction sensitivity similar to TNT and impact sensitivity similar to Comp B. In [113], researchers studied the syntheses and physical-chemical properties of 1,3,3-Trinitroazetidine (TNAZ). TNAZ, a castable explosive, is more powerful than RDX.

Various researchers [8, 68, 97, 110, 122] have synthesized 1,3,5-triamino-2,4,6-trinitrobenzene (TATB). In [97], researchers studied parameters that affect the particle size of TATB, such as the reaction temperature, the ammonia flow rate, the TCTNB concentration, and the stirring rate. Modified synthesis methods for TATB containing chloride compounds and chloride-free TATB compounds were studied in [68]. New methods for the preparation of energetic materials containing multi-nitro and amino aromatic compounds were also evaluated [68].

DADE was synthesized [85] by the nitration of 2-methyl-4,6-pyrimidindione in nitric acid/sulphuric acid and the hydrolysis of the intermediate 2-dinitromethylene-5,5-dinitro-dihydro-pyrimidine-4,6-dione. The total yield was 83%. DADE was also synthesized by nitration and hydrolysis steps using 2-methylimidazole as the primary substance [81]. Researchers also synthesized and studied emulsion explosives (acrylated Span80 [17]).

Researchers have studied energetic binders, plasticizers, and bonding agents. One study [89] showed that a material called PBAMO is an energetic binder with low sensitivity, a suitable melting point, and low melt viscosity that can be used as an energetic elastomer. The nitrate ester

plasticizers are sensitive explosives easily initiated by friction and impact. In [96], a new highly energetic binder for solid propellants, nitrocellulose azidonitrate glycidyl ether (NCAGE), was synthesized from cotton cellulose pretreated by steam. The primary role of energetic plasticizers in energetic material formulation is to modify the mechanical properties to improve safety characteristics while also increasing the material's specific energy yield [70]. In order to improve the mechanical properties of solid composite propellants, researchers [28] have also synthesized and evaluated new bonding agents, (e. g. 3-propargyl-5,5-dimethylhydantoin).

Researchers [93, 56, 96] investigated the synthesis of hexa-nitro-hexaaza-iso-wurtzitane (HNIW). In [96], synthesis involved tetra-acetyldinitro-sohexaaza-iso-wurtzitane (TADNSIW), the precursor for the synthesis of HNIW. The structure of TADNSIW was determined by FTIR, NMR, and element analysis and a method of debenylation to TADBIW was developed. Another study [14] created TAEIC and showed its use as a low melting point melt-cast explosive. In [47, 48], a new fullerene derivative, 2-(3-nitrophenyl) fullerene-pyrrolidine (mNPF) containing energy-producing groups, was prepared.

The synthesis of energetic salts using imidazole, triazole, tetrazole and pentazole as precursors has been studied [3]. The physiochemical properties of these energetic salts, such as melting point, density, enthalpy of formation and detonation performance, as well as the effect of molecular structure and substituted groups on these properties were summarized. The applications of these compounds in explosives and propellants are also discussed [3]. In [6] researchers investigated three kinds of energetic complexes: $\text{Co}(\text{CHZ})_4(\text{PA})_2 \cdot 3\text{H}_2\text{O}$, $\text{Cu}(\text{CHZ})_4(\text{PA})_2 \cdot 4\text{H}_2\text{O}$ and $\text{Pb}(\text{CHZ})_2(\text{PA})_2 \cdot 4\text{H}_2\text{O}$, all synthesized with carbohydrazide, picric acid, and the corresponding metallic (Co, Cu, Pb) salts. Another study [7] investigated the synthesis, crystal structure, and sensitivity of $[\text{Mn}(\text{IMI})_6](\text{ClO}_4)_2$ as an energetic compound. Another study [9] investigated the application of crystal modifiers in the synthesis of Nitrophenol Potassium energetic salts.

In [75], three new high-nitrogen energetic compounds bis-(ammonium): 5,5'-Azotetrazolate, bis-(guanidinium); 5,5'-Azotetrazolate and bis-(triaminoguanidinium); and 5,5'-Azotetrazolate were synthesized from 5-aminotetrazole, which was used as a starting material. Their structures were assessed by IR, NMR, DSC, the melting point test, and elemental analysis. The results showed that these azotetrazolate compounds possess positive enthalpy of formation, high gas generating abilities with little or no smoke, nonhygroscopic properties, and good explosive performance. They are important ingredients of gas generators,

low signature propellants, pyrotechnics, and high performance explosives [75].

A thermoplastic polyurethane elastomer was synthesized for use in the binder in a novel gun propellant, which uses polyethylene glycol; has good miscibility with nitrate ester, 4,4'-methylenedi(phenyl isocyanate), as the soft component; and ethylene glycol as the hard components [46].

In [77], 3-Hydroxymethyl-3-methyl oxetane (HMMO) was prepared by the cyclization of the raw materials, 1,1,1-tri(hydroxymethyl) ethane and diethyl carbonate. The results showed that the final product, AMMO, is an important energetic oxetane monomer.

A new class of caged hydrocarbon fuels with high energy and high density were synthesized [92] with the expectation that their use in a fuel would result in a net increase in the volumetric combustion value of the current generation of power-plants. These caged hydrocarbons exhibit high density and contain a moderate amount of strain energy, which contributes to the energy output during combustion.

Energetics synthesis research has also studied synthesis methods. For example, researchers [104] studied the use of microwaves to provide uniform heating, reaction rate acceleration, higher chemical yield, and lower energy usage during synthesis reactions. It was found that when compared to conventional heating, the synthesis of the explosive 2,4-DNI using microwave heating produced a shortened reaction time and an improved yield.

Some of the top researchers in China include Yang Li, Mo Hong-chang, Zhang Zhi-gang, Li Na, and Wang Xi-jie. Yang Li, a researcher from the State Key Laboratory of Explosion S&T in the Beijing Institute of Technology, has conducted extensive research on synthesis in conjunction with crystal structures. Examples of his research include the synthesis of nitrophenol potassium salts and the synthesis of compounds containing carbo-dihydrazide and picric acid [6]. Mo Hong-chang and Zhang Zhi-gang, from the Xi'an Modern Chemistry Research Institute, are experts in the synthesis of chemical compounds, including 5-vinyltetrazole and 3,4-epoxybutanol nitrate [4, 11, 21, 26]. Other compounds synthesized include 3,4-diphenylfuroxan and triaminoguanidine perchlorate and 3,4-bis(pyrazine-2'-yl) furoxan [11].

The Xi'an Modern Chemistry Research Institute is a leader in synthesizing and evaluating high energy density materials and their performance characteristics [4, 13, 20–23, 25–27, 29–39, 41, 51]. For example, researchers have investigated [34] various formulations of explosives and propellants, including their synthesis methods, physical-chemical properties, explosive properties, compatibility, and applications. Researchers [35, 36] have also studied novel compounds to suppress flame temperatures and improve control over the burn rate of gun

propellants. The Shaanxi Applied Physicochemical Research Institute, also located in Xi'an, is also strong in the area of energetic synthesis [24, 52]. They have investigated new energetic materials [e.g. 3-nitro-1,2,4-triazol-5-one (NTO)], including synthesis methods, crystal structures, quantum chemistry, thermal behavior, and toxicity [52]. China also has a Key Laboratory for Green Chemical Technology of State Education Ministry within the School of Chemical Engineering and Technology, Tianjin University. They have studied such topics as "Synthesis of HMX from DPT by Green Nitrolysis with Dinitrogen Pentoxide" [1], Green Synthesis of Glycidyl Nitrate [18], and Green Synthesis of 1,2-Propylene Glycol Dinitrate [50].

4.2 References

1. Synthesis of HMX from DPT by Green Nitrolysis with Dinitrogen Pentoxide, He Zhi-yong, [School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing 210094,China], Luo Jun, [School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing 210094,China], Lü Chun-xu, [School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing 210094,China], Xu Rong, [Institute of Chemical Materials, CAEP, Mianyang Sichuan 621900,China], Li Jin-shan, [School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing 210094,China], Chinese Journal of Explosives & Propellants. 2010, 33(2):1-4.

Abstract: In order to achieve a clean synthesis process of HMX, nitrolysis of DPT in two nitration systems was investigated. Nitrolysis of DPT in N_2O_5 /organic solvent systems was investigated to yield little HMX but mainly complex by-products with low melting point, indicating that the solutions of N_2O_5 in organic solvents was not suitable for this process. Nitrolysis in N_2O_5/HNO_3 system was investigated. The effect of reaction time, reaction temperature, amount of ammonium nitrate and ratio of raw materials on the yield of HMX were studied, finding that yield of HMX increases first and then decreases along with the increasing usage of N_2O_5 and N_2O_5/HNO_3 system was suitable for the nitrolysis of DPT because it could give HMX in a high yield up to 58% and purity of 99% under optimized conditions: $n(N_2O_5):n(DPT)=2:1$, $n(HNO_3):n(DPT)=36:1$, react time 30 minute and react temperature $25^\circ C$.

2. Synthesis and Performance of Polyaryloxyphosphazene, Wang Zhi-feng, [Ningbo Branch of Academy of Ordnance Science, Ningbo 315103,China], Cao Ji-ping, [Xi'an Modern Chemistry Research Institute, Xi'an 710065,China], Yao Nan, [Xi'an Modern Chemistry Research Institute, Xi'an 710065,China], WANG Jian-zhong, [Ningbo Branch of Academy of Ordnance Science, Ningbo 315103,China], Chinese Journal of Explosives & Propellants. 2010, Chinese Journal of Explosives & Propellants. 2010, 33(2):61-64.

Abstract: Poly-aryloxy-phosphazene was obtained with aryloxy substituting chlorine atom of the linear poly-dichloro-phosphazene, which was synthesized by solution polymerization of hexa-chloro-cyclotriphosphazene. The polymer was characterized by IR spectrum and analyzed by GPC, DMA, TGA, and thermal conductivity. The results show that the polymer obtained is poly-aryloxy-phosphazene with number-average molecular weight ranging from 38343 to 44625 and dispersion degree ranging from 3.0305 to 4.8857. The peak temperature of the initial thermal decomposition is 374.23°C and of main decomposition reaction is 397.78°C. The weight of the polymer which shows obvious weight loss at the temperature of 461.14°C and 529.95°C could remain 45.40% at the temperature of 565.37°C and then keep constant. It can be expected that the polymer has good thermal stability at high temperature. The glass transition temperature of the polymer is -24.09°C and the thermal conductivity 0.21W/(m·K).

3. Progress of Study on the Synthesis of Azole Energetic Ionic Compounds, Liu Xiao-jian, [School of Life Science, Beijing Institute of Technology, Beijing 100081,China], Zhang Hui-juan, [School of Life Science, Beijing Institute of Technology, Beijing 100081,China], Lin Qiu-han, [School of Life Science, Beijing Institute of Technology, Beijing 100081,China], Li Yu-chuan, [School of Life Science, Beijing Institute of Technology, Beijing 100081,China], Li Ya-yu, [Beijing Institute of Aerospace Testing Technology, Beijing 100074,China], Pang Si-ping, [School of Life Science, Beijing Institute of Technology, Beijing 100081,China], Chinese Journal of Explosives & Propellants. 2010, 33(1):6-10.

Abstract: The syntheses of energetic salts comprising imidazole, triazole, tetrazole and pentazole as precursors are reviewed with 36 references. The physiochemical properties of these new energetic salts, such as melting point, density, enthalpy of formation and detonation performance, as well as the effect of molecular structure

and substituted groups on properties are summarized. The applications of these compounds in explosives and propellants are discussed.

4. Synthesis of 3,4-Epoxybutanol Nitrate, Mo Hong-chang, Gan Xiao-xian, Li Na, Xing Ying, Han Tao, Zhang Zhi-gang, Li Lei, [Xi'an Modern Chemistry Research Institute, Xi'an 710065, China], Chinese Journal of Explosives & Propellants. 2010, 33(1):24-26.

Abstract: 3, 4-Epoxybutanol nitrate was synthesized with 3-butane-1-ol as raw material via two-step reactions, nitration and epoxidation, and characterized by IR, ¹H NMR and elemental analysis. The optimum nitration reaction conditions are as follows: nitrating agent and 3, 4- epoxy butyric alcohol (EBA) in the molar ratio of 1.5:1.0, i.e. [n(HNO₃):n(EBO)=1.5:1.0], reaction temperature is -10°C and the reaction was terminated when temperature began to descend. The yield of nitrating reaction is 65.2%. The purity of the product is 98.2%.

5. Synthesis of 3,4-Diphenylfuroxan with High Efficiency, Xue Yun-na, Yang Jian-ming, Li Chun-ying, Lü Jian, [Xi'an Modern Chemistry Research Institute, Xi'an 710065, China], Chinese Journal of Explosives & Propellants. 2010, 33(1):34-37.

Abstract: 3, 4-Diphenylfuroxan was synthesized using benzil as starting material via hydro amine addition and oxidative cyclization. Its molecular structure has been identified with IR, ¹H NMR, ¹³C NMR and elemental analyses. The effect of the category, dosage, mass fraction of oxidants and reaction temperature on the cyclization were investigated. Under the condition of HClO (mass fraction 7.39%) as oxidant, n(HClO):n(diphenylgly-oxime)=3, reaction temperature 80°C, atmospheric pressure and reaction time 1.5h, the yield of 3, 4-diphenyl furoxan was 92.8%.

6. Syntheses of CHZ and PA Energetic Compounds and Their Effects on Thermal Decomposition of CL-20, Zhang Guo-tao, Zhang Tong-lai, Liu Jun-wei, Zhang Jian-guo, Yang Li, [State Key Laboratory of Explosion Science and Technology, Beijing Institute of Technology, Beijing 100081, China], Chinese Journal of Explosives & Propellants. 2010, 33(1):38-42.

Abstract: Three kinds of energetic complexes, Co(CHZ)₄(PA)₂·3H₂O, Cu(CHZ)₄(PA)₂·4H₂O and Pb(CHZ)₂(PA)₂·4H₂O (CHZ=

carbodihydrazide, PA=picric acid), were synthesized with carbodihydrazide, picric acid and corresponding metallic (Co, Cu, Pb) salts. The molecular formulas of these coordination compounds were derived by using elemental analyses and FTIR techniques. The friction, impact and flame sensitivities of the complexes were tested followed by the standard methods. The effects of the energetic complexes on the thermal decomposition of CL-20 were studied by means of DSC and TG-DTG techniques. The results show that the addition of those complexes make the onset temperature and peak temperature of CL-20 shift to low temperature. The kinetic parameters E_a and A of the first exothermic decomposition process for complexes/CL-20 mixture were calculated by Kissinger's method and Ozawa-Doyle's method. Cu(CHZ)(PA) and (CHZ)(PA) make the E_a value of the exothermic processes of CL-20 decrease from 222.8kJ/mol to 186.6kJ/mol and 183.0kJ/mol.

7. Synthesis, Crystal Structure and Sensitivity of $[\text{Mn}(\text{IMI})_6](\text{ClO}_4)_2$, Ren Yan, [State Key Laboratory of Explosion Science and Technology, Beijing Institute of Technology, Beijing 100081, China], Yan Ying-jun, [Jiangxi Journalism and Publication College, Nanchang 330224, China], Yang Li, [State Key Laboratory of Explosion Science and Technology, Beijing Institute of Technology, Beijing 100081, China], Zhang Tong-lai, [State Key Laboratory of Explosion Science and Technology, Beijing Institute of Technology, Beijing 100081, China], Zhang Jian-guo, [State Key Laboratory of Explosion Science and Technology, Beijing Institute of Technology, Beijing 100081, China], Yu Kai-bei, [State Key Laboratory of Explosion Science and Technology, Beijing Institute of Technology, Beijing 100081, China], Chinese Journal of Explosives & Propellants. 2009, 32(6):15-19

Abstract: An energetic compound $[\text{Mn}(\text{IMI})_6](\text{ClO}_4)_2$ (IMI: imidazolium) was synthesized by reaction of imidazolium with $\text{Mn}(\text{ClO}_4)_2$ in aqueous solution. Single crystal of $[\text{Mn}(\text{IMI})_6](\text{ClO}_4)_2$ was obtained. The compound was characterized by elemental analysis, TG-DTG and single crystal X-ray diffraction analysis. The results show that the crystal belongs to a monoclinic system with $P_2(1)/n$ space group and cell parameters of $a=11.721(2)\text{nm}$, $b=7.2191(13)\text{nm}$, $c=16.402(3)\text{nm}$, $\beta=90.064(3)^\circ$, $V=1387.9(4)\text{nm}^3$; $D_c=1.585\text{g/cm}^3$; $Z=2$; $F(000)=678$, $\mu=0.160\text{mm}$, $R_1=0.0367$, $\omega R_2=0.1372$. The title compound $[\text{Mn}(\text{IMI})_6](\text{ClO}_4)_2$ formed by $[\text{Mn}(\text{IMI})_6]_2^+$ and $(\text{ClO}_4)^-$ belongs to an ionic compound. The central Mn(II) ion is six-coordinated with six imidazole molecules. At a

heating rate of 10K/min, the thermal decomposition process of the title compound consists of one endothermic peak and one exothermic peak with 9.9% residues. The mechanic sensitivity test results show that this compound is an insensitive energetic compound.

8. Synthesis and Thermal Decomposition Kinetics of TATB without Chloride, Ma Xiao-ming, Li Bin-dong, Lü Chun-xu, Lu Ming, [School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing 210094,China], Chinese Journal of Explosives & Propellants. 2009, 32(6):24-27

Abstract: In order to solve the influence of chloride in the traditional synthesis of TATB, taking phoroglucinol as primary material, 1, 3, 5-triamino-2, 4, 6-trinitrobenzene (TATB) was synthesized by nitration with N_2O_5 , methylation and ammonia, and its structure was identified by NMR, IR and MS. The effect of ammonia reaction on the yield and thermal decomposition property of TATB was investigated; the total yield of crude TATB was 92%. High-purity TATB was obtained by organic solvent re-crystallization with yield of 75%. Thermal properties of TATB was analyzed by DSC and TG, the thermal decomposition activation energy and pre-exponential factor of TATB obtained by Owaza's equation are $E_{TATB}=135.28\text{kJ/mol}$ and $A_{TATB}=2.340\times 10^9\text{s}^{-1}$.

9. Application of Crystal Modifier in the Synthesis of Nitrophenol Potassium Salts, Tang Zhan, [State Key Laboratory of Explosion Science and Technology, Beijing Institute of Technology, Beijing 100081,China], Yang Li, [State Key Laboratory of Explosion Science and Technology, Beijing Institute of Technology, Beijing 100081,China], Yan Ying-jun, [Jiangxi Journalism and Publication College, Nanchang 330224,China], Zhang Tong-lai, [State Key Laboratory of Explosion Science and Technology, Beijing Institute of Technology, Beijing 100081,China], Zhang Jian-Guo, [State Key Laboratory of Explosion Science and Technology, Beijing Institute of Technology, Beijing 100081,China], Qian Xiao-jing, [State Key Laboratory of Explosion Science and Technology, Beijing Institute of Technology, Beijing 100081,China], Chinese Journal of Explosives & Propellants. 2009, 32(6):28-30,34.

Abstract: In order to attain the amount of crystal modifier in synthesis of nitrophenol potassium salts, the grained KPA was synthesized with the non-ionic surfactant that containing H in the functional group served as crystal modifier. The surface tension and

data of the surfactant, which will provide theoretical support for the dosage of surfactant, was studied. The grained KPA obtained in different conditions was studied with X-ray powder diffraction and the important growth facet that has more influence on the morphology was analyzed. The results show that the surfactant can reduce the strongest diffraction peaks and affect the dominant crystal facet, so they can control crystal morphology of KPA. Grained crystal can be gained if choosing appropriate surfactant and dosage through measuring surface tension of surfactant.

10. Structure, Thermodynamics and Sensitivity Property of (TAGH) CIO₄, Qi Shu-yuan, [State Key Laboratory of Explosion Science and Technology, Beijing Institute of Technology, Beijing 100081,China], Zhang Tong-lai, [State Key Laboratory of Explosion Science and Technology, Beijing Institute of Technology, Beijing 100081,China], Ao Guo-jun, [East China Research Institute of Microelectronics, Hefei 230022,China], Zhang Jian-guo, [State Key Laboratory of Explosion Science and Technology, Beijing Institute of Technology, Beijing 100081,China], Yang Li, [State Key Laboratory of Explosion Science and Technology, Beijing Institute of Technology, Beijing 100081,China], Chinese Journal of Explosives & Propellants. 2009, 32(6):35-39.

Abstract: Triaminoguanidine per chlorate was synthesized with three aminoguanidine and perchloric acid as raw materials. The crystal structure was determined by X-ray single crystal diffraction analysis. The results show that the title compound belongs to monoclinic system with $P_2(1)/c$ space group and cell parameters of $a=1.0213(11)\text{nm}$, $b=1.4869(15)\text{nm}$, $c=1.0936(11)\text{nm}$, $\beta=102.91(2)^\circ$. The title compound, with formula of $\text{CH}_9\text{ClN}_6\text{O}_4$, is an ionic compound formed by $[\text{C}(\text{N}_2\text{H}_3)_3]^+$ and ClO_4^- . There are a lot of intra-molecular and inter-molecular hydrogen bonds, which make it stable. The title compound was characterized by elemental analysis, FTIR, DSC, TG-DTG. The results show that the title compound lost 99.7% at 457.03°C with a heating rate of $10^\circ\text{C}/\text{min}$. The sensitivity test results show that it has low friction sensitivity and has no frame sensitivity, and impact sensitivity under the sensitivity test conditions.

11. Synthesis and Characterization of 3,4-Bis(pyrazine-2'yl)furoxan, Li Ya-nan, Zhang Zhi-zhong, Zhou Yan-shui, Chen Bin, Wang Bo-zhou, [Xi'an Modern Chemistry Research Institute, Xi'an 710065, China], Chinese Journal of Explosives & Propellants. 2009, 32(6):34-37.

Abstract: 3, 4-bis (pyrazine-2'-yl) furoxan (DPF) was synthesized using 2-cyanopyrazine as raw material, via four-step reactions of oxime, diazotization, denitrification and cyclization and the overall yield was 51.0%. The structures of target compound and intermediates were characterized by IR, NMR, MS and elemental analysis. The mechanism of cyclization reaction was investigated. The affecting factors of reactions were optimized. The optimum reaction conditions of cyclization were listed as below. The ratio of the molar volume to the theoretical value is about 1.10 - 1.25 times for Na_2CO_3 , reaction temperature is 2 to 10°C and reaction time 4h. The yield of DPF is about 75.6% and purity of 99.0%.

12. Synthesis, Crystal Structure and Quantum Chemistry of $\text{C}_3\text{N}_2\text{H}_5^+\text{C}_6\text{N}_3\text{O}_7\text{H}_2^-$, Li Dan, [School of Chemical Engineering/Shaanxi Key Laboratory of Physico-inorganic Chemistry, Northwest University, Xi'an 710069,China], Ren Ying-hui, [School of Chemical Engineering/Shaanxi Key Laboratory of Physico-inorganic Chemistry, Northwest University, Xi'an 710069,China], Zhao Feng-qi, [Xi'an Modern Chemistry Research Institute, Xi'an 710065,China], Yi Jian-hua, [Xi'an Modern Chemistry Research Institute, Xi'an 710065,China], Chang Chun-ran, [School of Chemical Engineering/Shaanxi Key Laboratory of Physico-inorganic Chemistry, Northwest University, Xi'an 710069,China], Song Ji-rong, [Conservation Technology Department, The Palace Museum, Beijing 100009,China], Chinese Journal of Explosives & Propellants. 2009, 32(6): 48-52.

Abstract: $\text{C}_3\text{N}_2\text{H}_5^+\text{C}_6\text{N}_3\text{O}_7\text{H}_2^-$ were prepared by mixing imidazole ethanol solution and picric acid (PA) ethanol solution. Single crystals suitable for X-ray measurement were cultured at room temperature. The crystal is rhombic system, space group Pbca with crystal parameters of $a=0.8950\text{nm}$, $b=1.3474(3)\text{nm}$, $c=2.0164\text{nm}$, $\alpha=\beta=\gamma=90^\circ$, $V=2.4317(3)\text{nm}^3$, $D_c=1.624\text{g/cm}^3$, $Z=8$, $F(000)=1216$. The theoretical investigation of the title compound as a structure unit was carried out by HF/6-311+G(d) and B3LYP/6-311+G(d) methods in Gaussian 03 package, and the atomic net charges and the population analysis was discussed.

13. Synthesis and Characterization of 7-Chloro-4,6-dinitro-benzofuroxans, Huo Huan, Wang Bo-zhou, Liu Qian, Luo Yi-fen, Zhang Ye-gao, [Xi'an Modern Chemistry Research Institute, Xi'an 710065,China], Chinese Journal of Explosives & Propellants. 2009, 32(4):31-33.

Abstract: Taking 4-chloro-2-nitroaniline as primary material, 7-chloro-4, 6-dinitro-benzfuroxan was synthesized by the process of oxidation, cyclization, nitration and rearrangement. Its structure was characterized by IR, NMR and elemental analysis. The effect of the nitration reaction temperature and 5-chlorobenzfuroxan/nitric acid mole ratio on the yield was studied. The best condition of nitration reaction was reaction temperature, 60°C; 5-chlorobenzfuroxan/nitric acid mole ratio, 1:10. The yield is 39%.

14. Energized Synthesis and Characterization of 1,3,5-Tris(2-hydroxyethyl)-1,3,5-triazinane-2,4,6-trione, Xu Ruo-qian, JiYue-ping, Ding Feng, Yang Wei, Liu Wei-xiao, [Xi'an Modern Chemistry Research Institute, Xi'an 710065,China], Chinese Journal of Explosives & Propellants. 2009, 32(4):38-40, 44.

Abstract: Taking 1, 3, 5-tris(2-hydroxyethyl)-1, 3, 5-triazinane-2, 4, 6-trione as primary material, 1, 3, 5-tris(2-nitroethyl)-1, 3, 5-triazinane-2, 4, 6-trione(TNEIC) and 1, 3, 5-tris(2-azidoethyl)-1, 3, 5-triazinane-2, 4, 6-trione(TAEIC) were synthesized via nitration and azidation. The optimum conditions of nitration were: HNO₃/H₂SO₄ (volume ratio), 1:1; reaction temperature, 25°C; reaction time, 0.25 h and the optimum reaction yield are 92.0%. By elemental analysis, infrared spectroscopy (IR), nuclear magnetic resonance spectroscopy (1H NMR), and identified the target product structure, analysis using DSC, the thermal properties of the compounds were determined. The results show that TAEIC has a low melting point and will be used in melt-cast explosive.

15. Preparation of Fe₂O₃/CNTs and Its Catalytic Mechanism on Thermal Decomposition of RDX, Cui Qing-zhong, Jiao Qing-jie, Zhao Wei-dong, [National Key Laboratory of Explosive Science and Technology, Beijing Institute of Technology, Beijing 100081,China], Chinese Journal of Explosives & Propellants. 2009, 32(4):42-44

Abstract: Nano Fe₂O₃/CNTs catalyzers were synthesized by the sol-gel methods. The technology parameters were optimized by an orthogonal test. The appearance of products was characterized by SEM, TEM and XRD. The catalytic properties of Fe₂O₃/CNTs on thermal decomposition of RDX were determined by using DSC method. The results show that the surface of CNTs is coated with Fe₂O₃. When mass fraction of Fe₂O₃/CNTs is about 5%, Fe₂O₃/CNTs catalyzers make the peak temperature of DSC curve for thermal decomposition of RDX decrease by 14.1°C, and the activation energy

of thermal decomposition reaction of RDX obtained by Kissinger method decrease by 38.5%.

16. New Technology for Synthesis of 1-Methyl-2,4,5-trinitroimidazoles, Wang Xiao-jun, Cao Duan-lin, Li Yong-xiang, Song Lei, Wang Jian-long, [College of Chemical Engineering and Environment, North University of China, Taiyuan 030051, China], Chinese Journal of Explosives & Propellants. 2009, 32(3):16-18.

Abstract: 1-Methyl-2, 4, 5-trinitroimidazoles (MTNI) was synthesized with 1-methylimidazole as initial material by two steps nitration reaction. Its structure was characterized by IR, ^1H NMR and elemental analysis. The effect of the drip order, ratios of volume for nitric and sulfuric acid, reaction time, temperature on the yield of 2, 4-dinitroimidazole (2, 4-MDNI) and MTNI was investigated. The results show that the conditions of good yields are: the drip order of additive of the first step, ratios of volume for nitric and sulfuric acid 1:2, the drip order of anti-additive for the second step, ratios volume for nitric and sulfuric acid 1:4, reaction time 2 h, temperature 110~115 °C.

17. Synthesis of Acrylated Span80 and Its Application in Emulsion Explosive, Qian Hua, Liu Da-bin, Ye Zhi-wen, [College of Chemical and Engineering, Nanjing University of Science and Technology, Nanjing 210094, China], Chinese Journal of Explosives & Propellants. 2009, 32(2):11-13,20.

Abstract: Esterification with acryloyl chloride was prepared by acrylation of propylene Span80. The purpose was to investigate the effect of reaction time, temperature, solvent and other factors on the iodine value of the acrylated Span80. The optimum conditions of the reaction were: triethylamine as catalyst, acrylic acid, chloride sulfoxide, Span80, triethylamine, 1.0:2.1:1.0:1.4 molar ratio, reaction time 3 h, reaction temperature 50°C and 80 mL toluene/mole of acrylic acid as solvent. The iodine value of acrylated Span80 obtained by using optimum conditions was 94.97 g I₂/100 g sample. The effect of acrylated Span80 and ordinary Span80 on properties of emulsion explosive was compared by SEM and the performance test. The results show that this acrylated Span80 has better emulsified property than ordinary Span80.

18. Green Synthesis of Glycidyl Nitrate, Wang Qing-fa, [Key Laboratory for Green Chemical Technology of State Education Ministry, School

of Chemical Engineering and Technology, Tianjin University, Tianjin 300072,China], SHI Fei, [Shandong Silk Textile Vocation College, Zibo Shandong 255300,China], ZHANG Xiang-wen, [Key Laboratory for Green Chemical Technology of State Education Ministry, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072,China], WANG Li, [Key Laboratory for Green Chemical Technology of State Education Ministry, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072,China], MI Zhen-tao, [Key Laboratory for Green Chemical Technology of State Education Ministry, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China], Chinese Journal of Explosives & Propellants. 2009, 32(2):14-16.

Abstract: A mild and high efficient method to prepare glycidyl nitrate by selective nitration of glycidol with di-nitrogen pent-oxide as the nitrating agent was developed. The influences of molar ratio of di-nitrogen pent-oxide to glycidol, reaction temperature and reaction time on the nitration of glycidol were investigated. The results indicated that the selectivity of 100% and the yield of 94% for glycidyl nitrate were obtained by carrying out the reaction at -15°C for 6 min with the molar ratio of di-nitrogen pent-oxide to glycidol at 1:1.

19. Preparation of Zirconium 3-Nitrophthalate and Its Effect on Combustion of Double-base Propellant and RDX-CMDB Propellant, Zhang Heng, Zhao Feng-qi, Zhang Xiao-hong, Pei Qing, Hao Hai-xia,[Xi'an Modern Chemistry Research Institute, Xi'an 710065,China], Chinese Journal of Explosives & Propellants. 2009, 32(1):1-4.

Abstract: Zirconium 3-nitrophthalate ($\text{Zr}(3\text{-NO}_2\text{-PHT})_2 \cdot 2\text{H}_2\text{O}$) was synthesized by using 3-nitrophthalic acid, sodium hydroxide, zirconium oxide nitrate as raw materials, and the structure was determined by elemental analysis, X-ray fluorescence diffraction and FT-IR spectra. The catalytic action of zirconium 3-nitrophthalate on double-base propellant and RDX-CMDB propellant was analyzed. The results show that the burning rates of the double-base propellant and RDX-CMDB propellant increase obviously in the low pressure range and the pressure exponents of the double-base propellant decrease obviously in the middle and high pressure range. Especially, when Zirconium 3-nitrophthalate together with copper salts is used,

the catalytic efficiency is higher.

20. Synthesis and Crystal Structure of 3,3'-Dinitro-5,5'-azo-1H-1,2,4-triazole(DNAT), Jia Si-yuan, WANG Xi-jie, Wang Bo-zhou, Xiong Cun-liang, Liu Qian, [Xi'an Modern Chemistry Research Institute, Xi'an 710065,China], Chinese Journal of Explosives & Propellants. 2009, 32(1):25-25,39.

Abstract: 3, 3'-Dinitro-5, 5'-azo-1H-1, 2, 4-triazole (DNAT) was synthesized by the oxidative coupling of 5-amino-5-nitro-1, 2, 4-triazole (ANTA) as raw material. Its structure was characterized by IR, NMR and elemental analyses. The crucial factors and mechanism in the coupling reaction were explored and the synthetically conditions were optimized. Some properties of DNAT were measured. The H₅₀ of 17.08cm (drop hammer 5kg) and friction sensitivity of 60% (pressure 3.92MPa, pendulum angle 90°) were obtained. The single crystal of DNAT·4H₂O was cultivated, and its crystal structure was determined by X-ray crystallography. The crystal of DNAT·4H₂O is monoclinic crystal system with space group P2(1)/n and D_c=1.550g·cm⁻³.

21. Synthesis and Characterization of 5-Vinyltetrazole, Liu Qing, Gan Ning, Han Tao, Zhang Zhi-gang, Li Na, Mo Hong-chang, [Xi'an Modern Chemistry Research Institute, Xi'an 710065,China], Chinese Journal of Explosives & Propellants. 2009, 32(1):29-31.

Abstract: Hydroxyethyltetrazole was synthesized by the 1, 3-polar cycloaddition of 3-hydroxypropanenitrile and NH₄N₃ that produced by the reaction of NaN₃ and NH₄Cl. The ultrasonic technology was applied in this reaction and the yield was up to 90.5%. 5-Chloroethyltetrazole was prepared by the halogenation of hydroxyethyltetrazole and SO₂Cl₂ and the yield was 77%. 5-Vinyltetrazole was obtained by the elimination of 5-chloroethyltetrazole under the condition of alkaline, and the yield was 70%. 5-Chloroethyltetrazole and 5-vinyltetrazole were characterized by IR, ¹H NMR and elemental analyses. The results show that the final product was the target product. This method has the advantages of high and stable yield and convenient preparation.

22. Synthesis and Characterization of Picrylfurazanether Compounds, Ge Zhong-xue, Qiu Shao-jun, Jiang Jun, Wang Xi-jie, [Xi'an Modern Chemistry Research Institute, Xi'an 710065,China], Chinese Journal of Explosives & Propellants. 2008,31 (6):17-20.

Abstract: In order to obtain high energy density materials with excellent synthetic performances, picryl (3-nitrofurazan-4) ether (FOP) and bis(3-nitrofurazan-4) picryl ether (DFOP) were synthesized by condensation of sodium hydroxyl nitrofurazan with picryl chloride (PcCl) and 2, 4-dichloro-1, 3, 5-trinitrobenzene (DCPc), respectively. The products were characterized by FTIR, ¹H NMR, ¹³C NMR, MS and elemental analyses. The optimal reaction conditions obtained are: FOP of the yield as 31% from PcCl, the mole ratio of PcCl to sodium nitrohydrofurazan 1.0:1.1, reaction temperature 80°C, reaction time 16h, and for DFOP of the yield as 42% from DCPc, the mole ratio of DCPc to sodium nitrohydrofurazan 1.0:2.7, reaction temperature 80°C, reaction time 2h.

23. Synthesis and Characterization of 1-Methyl-2,4,5-trinitroimidazole, Wang Wei, Yang Wei, Ji Yue-ping, Ding Feng, [Xi'an Modern Chemistry Research Institute, Xi'an 710065, China], Chinese Journal of Explosives & Propellants. 2008, 31 (6):32-34,38.

Abstract: 1-Methyl-2, 4, 5-trinitroimidazole (MTNI) was synthesized with imidazole as starting material via a 5-step sequence of reactions (nitration, thermal rearrangement, methylation, etc). The total yield is 15.6%, and its purity is more than 98%. The structure of MTNI was characterized by IR, NMR and elemental analyses. The thermal decomposition performance of MTNI was tested by DSC. The results show that the detonation performances were comparable to those of RDX, and better than TATB. MTNI is a new insensitive high explosive with its friction sensitivity similar with TNT and impact sensitivity similar with comp B. The exothermic decomposition of MTNI proceeds in three stages. The corresponding peak temperature is 177, 223 and 298°C, and decomposition heat 327.67, 11.2 and 54.84kJ/mol, respectively.

24. Synthesis and Characterization of Energetic Intermediate 5-Hydrazinotetrazole, Zhu Ya-hong, Sheng Di-lun, Chen Li-kui, Ma Feng-e, [Shaanxi Applied Physicochemical Research Institute, Xi'an 710061, China], Chinese Journal of Explosives & Propellants. 2008, 31(6):39-41.

Abstract: 5-Hydrazinotetrazole was synthesized with 5, 5'-azotetrazolate as starting material by the acidizing of hydrochloric acid and re-crystallizing of sodium acetate processes. Its structure was characterized by Fourier transform infrared, melting point and elemental analyses. The key factors affecting acidizing and

re-crystallizing of synthesis were discussed. The results show that the mass fraction of material used during acidizing is 10% for 5, 5'-azotetrazolate solution and 10%-15% for hydrochloric acid solution. The yield of 5- hydrazinotetrazole is 55% - 60%, and melting point is 196-198.9°C.

25. Synthesis and Characterization of 4,4'-Dinitrodifurazalyl Ether, WANG Xi-jie, Ge Zhong-xue, Jiang Jun, Wang Bo-zhou, Zhang Ye-gao, [Xi'an Modern Chemistry Research Institute, Xi'an 710065,China], Chinese Journal of Explosives & Propellants. 2008, 31(6):12-14,27.

Abstract: 4, 4'-Dinitrodifurazalyl ether (FOF-1) was synthesized from 3, 4-diamino-furazan (DAF) after Caro-acid oxidation and etherification of nitro-group. Its structure was characterized by IR, MS, NMR and elemental analysis. The reaction mechanism of intermolecular etherification of nitro-group was preliminarily discussed. In addition, the synthetic procedures were optimized, and the optimal conditions of oxidization and intermolecular etherification reaction were determined. The best condition was obtained as follows: the oxidation reaction time is 3.5h, initial content of H₂SO₄ is 51.7%, the etherification reaction time is 2.5h, content of water is less than 0.03%, the overall yields is 42% and the purity is 99.6%.

26. Synthesis and Properties of Energetic Binder PNIMMO, Mo Hong-chang, Gan Xiao-xian, Xing Ying, Li Na,[Xi'an Modern Chemistry Research Institute, Xi'an 710065,China], Chinese Journal of Explosives & Propellants. 2008, 31(5):24-27.

Abstract: Using 1, 4-butanediol as initiator, boron trifluoride etherate as catalyst and CH₂Cl₂ as solvent, poly (3-nitratomethyl-3-methyl oxetane) (PNIMMO) was prepared by 3-nitratomethyl-3-methyloxetane via cationic ring-opening polymerization. The effect of molar ratio for catalyst and initiator, reaction temperature and the dropping rate of monomer on polymerization were discussed. The optimum conditions were determined as: molar ratio for catalyst and initiator was 0.50 - 0.75; reaction temperature was around 10°C and dropping monomer slowly. The polymer was characterized by IR and ¹³C NMR. The results show that the glass transition temperature, the enthalpy of decomposition and the decomposition peak temperature of the polymer are -24.52°C, +1212J/g and 221.78°C, respectively. The mechanical properties of polyurethane film cured by N-100 are

3.5 - 3.7MPa for δ and 260%-280% for ϵ at room temperature.

27. Research Progress on Poly-nitro-imidazoles and Their Derivatives, Yang Wei, Ji Yue-ping, [Xi'an Modern Chemistry Research Institute, Xi'an 710065,China], Chinese Journal of Explosives & Propellants. 2008, 31(5):46-50.

Abstract: Synthesis and properties of poly-nitro-imidazoles, such as di-nitro-imidazole, tri-nitro-imidazole and their derivatives and their application in energetic materials and medicines were summarized with 26 references. Nitro-imidazole was synthesized by nitration, thermal rearrangement and methylation with the imidazole or iodoimidazole as primary substance. Considering that tri-nitro-imidazole is a new insensitive high explosive with high formation enthalpy, fine thermal stability and relatively good safety characteristics.

28. Synthesis and Characterization of 3-Propargyl-5,5-dimethylhydantoin, Zhang Li-na, Yang Rong-jie, [School of Materials Science and Engineering, Beijing Institute of Technology, Beijing 100081,China], Chinese Journal of Explosives & Propellants. 2008, 31(5):18-21.

Abstract: In order to improve the mechanical properties of solid propellant, a new bonding agent, 3-propargyl-5, 5-dimethylhydantoin (PDMH) was synthesized by the Gabriel method. The condition of the reaction was: n(DMH): n(propargylbromine):n(methyl alcohol solvent of KOH)=1:1:1, water as solvent, reaction temperature 65°C, reaction time 3h. The yield of PDMH was 50%. Chemical structure of PDMH was identified by FT-IR, NMR, MS and TGA-DTA. Melting point of PDMH is 170 - 171°C and its decomposition temperature 185.5°C, it is expected to be used in composite solid propellant.

29. Synthesis and Characterization of 1,5-Diazido-3-nitrazapentane (DIANP), Ji Yue-ping, Lan Ying, Li Pu-rui, Wang Wei, Ding Feng, Liu Ya-jing, [Xi'an Modern Chemistry Research Institute, Xi'an 710065,China], Chinese Journal of Explosives & Propellants. 2008, 31(3): 44-46.

Abstract: 1, 5-Diazido-3-nitrazapropant (DIANP) was synthesized from DINA and sodium azide, via azidation, extraction, washing, discolors filtration and vacuum distillation. Its structure was

characterized by IR, NMR and elemental analyses. Relative properties were analyzed. The parameters affecting the yield, such as ratio, solvent, temperature and reaction time, were discussed. The results show that the optimum reaction condition of synthesizing DIANP is: the mass ratio of DINA to sodium azide, about 1:0.59; solvent, DMSO; reaction temperature, 80 - 85°C and reaction time, 7-8h. The yield of DIANP is about 80% and purity 98%.

30. Synthesis of 1,3,5-Tri-Substituted Perhydro-s-triazines, Yu Qin-wei, Yang Jian-ming, Zhao Feng-wei, Lü Jian, [Xi'an Modern Chemistry Research Institute, Xi'an 710065, China], Chinese Journal of Explosives & Propellants. 2008,31(3):50-52.

Abstract: 1, 3, 5-Tri-substituted perhydro-s-triazines were synthesized from nitriles (acetonitrile, propionitrile, butyronitrile and benzonitrile), and 1, 3, 5-trioxane. The products were characterized by ¹H NMR, IR, MS and elemental analysis. The effects of ratios of raw materials, reaction temperature and reaction time on the yield were investigated by orthogonal experiment. Results show that on the optimal reaction conditions, the yields of the corresponding 1, 3, 5-tri-substituted perhydro-s-triazines synthesized from acetonitrile, propionitrile, butyronitrile, benzonitrile and 1, 3, 5-trioxane were 95.7%, 96.1%, 84.2% and 98.1%, respectively.

31. Synthesis and Properties of ETPE Based on BAMO/AMMO, Gan Xiao-xian, Li Na, Lu Xian-ming, Han Tao, Xing Ying, Liu Qing, [Xi'an Modern Chemistry Research Institute, Xi'an 710065, China], Chinese Journal of Explosives & Propellants. 2008,31(2):81-85.

Abstract: Bromopolyether was prepared from 3-bromomethyl-3-methyl oxetane (BrMMO) by cation ring-opening polymerization. Azide polyether PAMMO was synthesized by the azido reaction of bromopolyether. Azide polyether PBAMO was prepared from 3, 3-bisbromomethyl oxetane (BAMO) by directly ring-opening polymerization. Using tetrahydrofuran as solvent, PBAMO as hard block, PAMMO as soft block, 2, 4-toluene diisocyanate (TDI) as diisocyanate monomer, butane-1, 4-diol urethane oligomer as linking compound, an energetic thermoplastic elastomer (ETPE) of number average molecular weight about 25,000 was prepared by one-step solution polymerization. ETPE that prepared was meltable and soluble. Its tensile strength and elongation at room temperature were about 5MPa and 400%, respectively.

32. Synthesis and Characterization of Bis(1,3-diazido-2-propyl) formal(BDPF), Ji Yue-ping,Wang Wei,Ding Feng,Chen Bin,Yu Tao,Liu Wei-xiao, [Xi'an Modern Chemistry Research Institute, Xi'an 710065,China], Chinese Journal of Explosives & Propellants. 2008, 31(2):86-88.

Abstract: The intermediate bis(1, 3-dichloro-2-propyl) formal (BCPF) was prepared by condensation reaction in the presence of a catalyst with 1, 3-dichloro-2-propanol and polyformaldehyde as primary materials. The title compounds bis(1, 3-diazide-2-propyl) formal (BDPF) was obtained by BCDF reacted with a metal azide in a solvent with the yield of 98% and purity of 98%. Their structures were characterized by IR, NMR and elemental analysis. The effect of catalyst, solvent and reaction temperature on above mentioned reactions was studied. The optimum reaction conditions are: for condensation reaction, reaction temperature 0-5°C, 4mL sulfuric acid as catalyst, ethylene dichloride as dissolvent; for hydrazoate reaction, reaction temperature 95 - 99°C, dimethyl sulfoxide as dissolvent, reaction time 4h.

33. Synthesis and Characterization of 3-Bromomethyl-3-Methyloxetane Homopolymer, Dong Jun, Gan Xiao-xian, [Xi'an Modern Chemistry Research Institute, Xi'an 710065,China], Chinese Journal of Explosives & Propellants. 2008, 31(2):89-92.

Abstract: Using 1, 4-butanediol (BDO) as initiator, boron-trifluoride etherate as catalyst, 3-bromomethyl-3-methyloxetane (BrMMO) as monomer, CH₂Cl₂ as solvent, an organic binder, 3-bromomethyl-3-methyloxetane homopolymer (PBrMMO), was synthesized by cationic ring-opening polymerization mechanism. The monomer conversion rate changes with time under low-temperature conditions were studied, and the BrMMO conversion rate-time curve was obtained. The effect of catalyst concentration and temperature of reaction system on polymerization were studied. The results show that the optimum conditions of the controlled polymerization are: n(BF₃·Et₂O):n(BDO)=0.5:1.0, add the BrMMO in reaction system at 0°C and keep reacting for three days. The structure and characterization of the final product were characterized by IR, ¹H NMR, DSC and TGA.

34. Study Progress of Several High Energy Density Materials(HEDM), Zhang Zhi-zhong, Wang Bo-zhou, Ji Yue-ping, Zhou Yan-shui, Zhou Cheng, Liu Qian, Zhu Chun-hua, [Xi'an Modern Chemistry Research

Institute, Xi'an 710065,China], Chinese Journal of Explosives & Propellants. 2008, 31(2):93-97,101.

Abstract: The current situation of investigating five HEDMs (DNTF, ADN, TNAZ, FOX-12 and FOX-7) in China was summarized. Their synthesis methods, physicochemical and explosive properties, compatibility and applications in the formulation of explosive and propellant were introduced. DNTF shows an outstanding performance in composite explosives and explode network and is used as oxidant in propellant. ADN can be used as high energetic oxidant of the low specific signal propellant. TNAZ can be used in casting explosive and gun propellant. FOX-12 and FOX-7 are potential compositions of insensitive explosives, with 24 references.

35. Synthesis and Characterization of 1H,4H-3,6-Dinitropyrazolo [4,3-c]pyrazole Amine Salts, Luo Yi-fen, Ge Zhong-xue, Wang Bo-zhou, Zhang Hai-hao, Xiong Cun-liang, [Xi'an Modern Chemistry Research Institute, Xi'an 710065,China], Chinese Journal of Explosives & Propellants. 2008, 31(2):98-101.

Abstract: Taking 1H, 4H-6-nitropyrazolo [4, 3-c] pyrazole-3-carboxy as primary material, 1H, 4H-3, 6-dinitropyrazolo [4, 3-c] pyrazole (DNPP) was synthesized by one step reaction of decarboxylation and nitration. By using DNPP as primary material, two DNPP amine salts, TAG-DNPP and GUDNPP, were synthesized with solid triaminoguanidinium (TAG) nitrate and solid guanidylurea (GU) hydrochloride, respectively. Their structures were confirmed by IR, ¹H NMR, ¹³C NMR and elemental analysis. The reaction mechanism of decarboxylation and nitration was investigated. Some reasons was analyzed for triaminoguanidinium 3, 6-dinitropyrazolo [4, 3-c] pyrazole as the gun propellant additive. The results show that the pyrolysis residue of TAG-DNPP can form new melon compounds. These novel compounds make flame temperature suppress and burning rate of the gun propellants improve.

36. Synthesis and Characterization of 3-Nitropyrazole and its Salts, Li Hong-li, Xiong Bin, Jiang Jun, Zheng Xiao-dong, Li Zhi-peng, Ma Yu-xia, [Xi'an Modern Chemistry Research Institute, Xi'an 710065,China], Chinese Journal of Explosives & Propellants. 2008, 31(2):102-104,108.

Abstract: In order to synthesize the salts of 3-nitropyrazole, N-nitropyrazole was synthesized with pyrazole as raw material, and

HNO₃-Ac₂O-HAc system as nitration agent. N-nitropyrazole at high temperature was rearranged as 3-nitropyrazole. Its organic copper and lead salts were synthesized by the reaction of 3-nitropyrazole with some inorganic copper and lead salts. The structure of products was characterized by melting point, IR, NMR and elemental analysis, showing that the products were target products. The optimum reaction yield was 85.5% for nitration, 92.8% for rearrangement reaction and 79.3% for total yield.

37. Synthesis and Properties of Azido Terminated Glycidyl Azide Polymer, Li Na, Gan Xiao-xian, Xing Ying, Mo Hong-chang, Zhang Zhi-gang, Han Tao, [Xi'an Modern Chemistry Research Institute, Xi'an 710065, China], Chinese Journal of Explosives & Propellants. 2008, 31(1):20-22.

Abstract: Using 1, 4-butanediol as initiator, boron-trifluoride etherate as catalyst, polyepichlorohydrin (PECH) was synthesized by the opening-ring polymerization of epichlorohydrin. Using the method of tosylation, tosylate terminated epichlorohydrin polymer as intermediate was synthesized by PECH and 4-toluenesulfonylchloride in pyridine, azido terminated glycidyl azide polymer (ATGAP) was obtained by the reaction of intermediate and sodium azide. The structure of ATGAP was characterized by IR, ¹H NMR and ¹³C NMR, showing that the final product was target product. The glass transition temperature of ATGAP was -73°C. Its thermal decomposition temperature was 252.7°C. ATGAP has small viscosity and can be used as an energetic plasticizer.

38. Synthesis of Poly(ether glycol)s Containing Isocyanurate Segments, Chang Hai, Fan Xiao-dong, Wang Sheng-jie, [Department of Applied Chemistry, School of Science, Northwestern Polytechnical University, Xi'an 710072, China], Chinese Journal of Explosives & Propellants. 2007, 30(6):13-16.

Abstract: The cationic ring-opening polymerizations of epoxide based monomers were studied using tris(2-hydroxyethyl) isocyanurate (THEIC) as initiator and tri-fluoro-boron plus ether complex system as catalyst. It was found that the ring opening polymerizations of epoxide based monomers with THEIC can be carried out in a heterogeneous medium smoothly. However, using THEIC initiator, the reaction rate for epichlorohydrin is faster than that of propylene oxide and 2-butoxyxirane, respectively. By simply adjusting the monomer feeding sequence, the block poly(ether glycol)

copolymers containing isocyanurate segments can be prepared successfully.

39. Synthesis of LLM-116 by VNS Reaction, Wang Ying-lei, Zhang Zhi-zhong, Wang Bo-zhou, Luo Yi-fen, [Xi'an Modern Chemistry Research Institute, Xi'an 710065, China], Chinese Journal of Explosives & Propellants. 2007, 30(6):20-23.

Abstract: 3,5-Dinitropyrazole ammonium salt was synthesized by rearranging 1, 3-dinitropyrazole as initial material and bubbling ammonia, and acidified to 3, 5-dinitropyrazole. 1, 1, 1-Trimethylhydrazinium iodide (TMHI) as a VNS agent was reacted with 3, 5-dinitropyrazole in the presence of t-BuOK as catalyst to get 4-amino-3, 5-dinitropyrazole (LLM-116) through the VNS reaction. Their structures were confirmed by IR, NMR, MS and elemental analyses. The VNS reaction mechanism and factors of influencing the reaction were discussed. The results show that under optimal condition of TMHI as VNS reaction reagent and the reaction at 25°C for 4 h, the yield of LLM-116 was 60%.

40. Preparation and Crystal Structure of $[\text{Cu}(\text{DNI})_2(\text{H}_2\text{O})_2]\cdot 3\text{H}_2\text{O}$, Cui Rong, [Xi'an Modern Chemistry Research Institute, Xi'an 710065, China], Zheng Xiao-dong, [Xi'an Modern Chemistry Research Institute, Xi'an 710065, China], Mao Zhi-hua, [Analytical and Testing Centre of Sichuan University, Chengdu 610041, China], Zhang Zhi-zhong, [Xi'an Modern Chemistry Research Institute, Xi'an 710065, China], Feng Li-min, [Xi'an Modern Chemistry Research Institute, Xi'an 710065, China], Yao Yi-lun, [Xi'an Modern Chemistry Research Institute, Xi'an 710065, China], Li Hong-li, [Xi'an Modern Chemistry Research Institute, Xi'an 710065, China], Jiang Jun, [Xi'an Modern Chemistry Research Institute, Xi'an 710065, China], Chinese Journal of Explosives & Propellants. 2007, 30(6):27-30.

Abstract: $[\text{Cu}(\text{DNI})_2(\text{H}_2\text{O})_2]\cdot 3\text{H}_2\text{O}$ was prepared by the reaction of the aqueous solution of sodium 2, 4-dinitroimidazolate and copper sulfate. The single crystal of $[\text{Cu}(\text{DNI})_2(\text{H}_2\text{O})_2]\cdot 3\text{H}_2\text{O}$ suitable for X-ray determination was obtained by slow evaporation method. The single crystal structure of $[\text{Cu}(\text{DNI})_2(\text{H}_2\text{O})_2]\cdot 3\text{H}_2\text{O}$ has been determined by single crystal X-ray diffraction analysis. The crystal is triclinic, space group P-1 with crystal parameters of $a=7.2560(10)\times 10^{-1}$ nm, $b=7.762(2)\times 10^{-1}$ nm, $c=16.685(3)\times 10^{-1}$ nm, $\alpha=87.13(3)^\circ$, $\beta=83.81(3)^\circ$, $\gamma=62.25(3)^\circ$, $V=826.8(3)\times 10^{-3}$ nm³, $Z=2$,

$D_c=1.871 \text{ g}\cdot\text{cm}^3$, $\mu=1.411 \text{ mm}^{-1}$, $F(000)=470$. The final deviation factor R is 0.0388. According to the analytical results of IR, the elemental analyses and X-ray diffraction, the chemical component of the 2, 4-DNI copper complex is $\text{C}_6\text{H}_{10}\text{CuN}_8\text{O}_{13}$ and its formula is $[\text{Cu}(\text{DNI})_2(\text{H}_2\text{O})_2]\cdot 3\text{H}_2\text{O}$.

41. Synthesis of 3-Bromomethyl-3-Methyloxetane, Dong Jun, Gan Xiao-xian, [Xi'an Modern Chemistry Research Institute, Xi'an 710065, China], Chinese Journal of Explosives & Propellants. 2008, 31(2):89-92.

Abstract: The 3-bromomethyl-3-methyloxetane (BrMMO) was synthesized by the closed-ring reaction between 2, 2-dibromomethyl propanol (BBMP) as primary substance and alkali. The effect of kinds of alkali and its amount on the closed-ring yield of BBMP was discussed. The effect of the base concentration, reaction temperature and the reaction time on the yield of BrMMO in the closed-ring reaction was discussed. Under the reaction conditions of $n(\text{BBMP}):n(\text{NaOH})=1.0:1.1$, NaOH mass fraction 12%, reaction temperature 78°C , reaction time 4h, the yield of BrMMO was 65%. The structure of BrMMO was identified by elemental analysis, IR and ^1H NMR. The results showed that it was the target compound BrMMO. This experiment process was easy to do, raw material was liable to attain, and the solvent can be retrieved, so the pollution was small.

42. Synthesis of 2-Nitroimino-5-nitrohexahydro-1,3,5-triazine(NNHT), Zhang Hai-hao, Wang Bo-zhou, Liu Qian, Xiong Cun-liang, Jia Si-yuan, [Xi'an Modern Chemistry Research Institute, Xi'an 710065, China], Chinese Journal of Explosives & Propellants. 2007, 30(6):48-50.

Abstract: Taking formaldehyde, tert-butyl amine and nitroguanidine as primary materials, 2-nitroimino-5-nitrohexahydro-1, 3, 5-triazine (NNHT) was obtained by the process of nitration and Mannich reaction. Its structure was identified by NMR, IR and elemental analysis. The effect of temperature on Mannich reaction was investigated, the yield reached 89% while the temperature was 80°C . The conditions of nitration were further optimized, the yield rose to 94% while the reaction was controlled under the room temperature. Instead of 100% nitric acid, industrial nitric acid was used in the nitration under the room temperature, and the yield was 88%.

43. Synthesis of BBMO and BAMO by Phase Transfer Catalysis Method, Zhang Zhi-gang, Lu Xian-ming, Gan Xiao-xian, Han Tao, Xing Ying, [Xi'an Modern Chemistry Research Institute, Xi'an 710065, China], Chinese Journal of Explosives & Propellants. 2007, 30(5):32-35.

Abstract: Using water and toluene as solvent, quaternary ammonium salt as phase transfer catalyst, under the effect of NaOH, 3, 3-dibromomethyl oxetane (BBMO) was synthesized by the cyclization of 1, 1, 1-tribromomethyl-1-hydroxymethyl methane. Using water as solvent, quaternary ammonium salt as phase transfer catalyst, 3, 3-diazidomethyl oxetane (BAMO) was obtained by the substitution of BBMO with NaN_3 . The structure of BBMO and BAMO was identified by HNMR and FTIR. The yield and purity are 81% and 97.2% for BBMO, and 80.9% and 98.37% for BAMO. The results show that the synthesis of BBMO and BAMO by phase transfer catalysis possesses advantages of safety, high yield and high purity.

44. Synthesis and Application of the Heat-resistant Explosive PCS, Deng Ming-zhe, Ye Zhi-hu, Zhao Sheng-xiang, Tian Zhan-huai, [Xi'an Modern Chemistry Research Institute, Xi'an 710065, China], Chinese Journal of Explosives & Propellants. 2007, 30(5):42-44.

Abstract: The heat-resistant explosive 2, 2', 4, 4', 6, 6'-hexanitrodiphenyl sulfone (PCS) was synthesized by oxidation with CrO_3 as oxidant in HNO_3 medium of a intermediate, 2, 2', 4, 4', 6, 6'-hexanitro-diphenyl sulfide (DPS), which was prepared by condensation reaction using 2, 4, 6-trinitrochlorobenzene and sodium thiosulfate as starting materials. The total yield was over 85%. The DSC exothermic peak temperature of the product was 360.1°C , and its purity was 98.3%. In heat-resistant test under the condition of 200°C and 48 h, the mass loss of PCS was only 0.62%. The vacuum stability test result under the condition of 120°C and 48 h was 0.35ml/5g. The impact and friction sensitivity were 100% and 94%, respectively. The charge density of the mixed heat-resistant explosive JF1 that mainly based on PCS was prepared. The application test results show that JF1 can completely replace ordinary explosive to use in oil explosive materials.

45. Development of Hexanitrohexaazaisowurtaitane at abroad, Wang Xin, Peng Cui-zhi, [CNGC North Institute for Scientific and Technical Information, Beijing 100089, China], Chinese Journal of Explosives & Propellants. 2007, 30(5):45-48.

Abstract: The current situation about the synthesis method and industrialization production ability of CL-20 at abroad are overviewed, and the application of CL-20 in propellant and explosive formulations, including CL-20 based explosive formulations LX-19, PAX-12, PAX-11, PAX-29, DLEC038 and PBXW-16, is introduced with 21 references.

46. Synthesis of Polyurethane Thermoplastic Elastomer for Gun Propellants, Li Yu, Jian Xiao-xia, Zhou Wei-liang, Xu Fu-ming, [Department of Chemical Engineering, Nanjing University of Science and Technology, Nanjing 210094], Chinese Journal of Explosives & Propellants. 2007, 30(4):58-61.

Abstract: A thermoplastic polyurethane elastomer is synthesized for the need of the binder in a novel gun propellant with polyethylene glycol (PEG) as soft segments, which has good miscibility with nitrate ester, 4' 4-methylenetis (phenyl isocyanate) and ethylene glycol as hard segments. The principle of molecular designation of the elastomers is analyzed and discussed. DSC, FTIR and DMA are applied to characterize the elastomers. Results show that the elastomers have structure characteristic of polyurethane structure and good microphase segregation in accordance with the molecular designation. Soft segment's T_g show that the elastomers have good low temperature mechanical properties.

47. Synthesis and Theoretical Analysis of 2-(3-nitrophenyl) Fulleropyrrolidine, Peng Ru-fang, [China Academy of Engineering Physics, Mianyang Sichuan 621900, China], JIN Bo, [College of Material Science and Engineering, Southwest University of Science and Technology, Mianyang Sichuan 621010, China], TAN Bi-sheng, [College of Material Science and Engineering, Southwest University of Science and Technology, Mianyang Sichuan 621010, China], CHU Shi-jin, [College of Material Science and Engineering, Southwest University of Science and Technology, Mianyang Sichuan 621010, China], Chinese Journal of Explosives & Propellants. 2007, 30(3):22-25.

Abstract: A new fullerene derivative 2-(3-nitrophenyl) fulleropyrrolidine (mNPF) containing energy-producing groups was prepared with glycine, m-nitrobenzaldehyde and fullerene as primary materials, and the reaction conditions were investigated by orthogonal test. The optimum reaction conditions with 82.1% yield (based on consumed C₆₀) are: molar ratio of C₆₀, m-nitro-

benzaldehyde and glycine 1:4:6, reaction temperature 100°C, reaction time 24h, volume of toluene solvent 80mL. The structure of mNPF was characterized by UV-vis, FT-IR, ¹H NMR, ¹³C NMR and MS. The feasibility of reaction was studied by semiempirical calculations PM3 method. The thermal stability of mNPF was studied by DTA, showing that mNPF has good thermal stability.

48. Synthesis of 2-(2-Nitrophenyl)fullerenopyrrolidine, PENG Ru-fang, [Graduate School, CAEP, Mianyang Sichuan 621900, China], JIN Bo, [College of Material Science and Engineering, Southwest University of Science and Technology, Mianyang Sichuan 621010, China], MA Dong-mei, [College of Material Science and Engineering, Southwest University of Science and Technology, Mianyang Sichuan 621010, China], CHU Shi-jin, [College of Material Science and Engineering, Southwest University of Science and Technology, Mianyang Sichuan 621010, China], Chinese Journal of Explosives & Propellants. 2007, 30(2):29-32.

Abstract: A new nitrofullerenopyrrolidine derivative 2-(2-nitrophenyl)fullerenopyrrolidine (NPF) was synthesized with fullerene, glycine and o-1-nitrobenzaldehyde as primary materials by 1, 3-dipolar cycloaddition reaction. Its structure was characterized by UV-Vis, FT-IR, ¹H NMR, ¹³C NMR and MS. Effects of the ratios of raw materials, temperature, reaction time and the volume of toluene on the reaction were investigated by orthogonal method. The results show that the reaction conditions of synthesizing NPF with the yield of 81.2% (based on consumed C₆₀) are: molar ratio of C₆₀, o-nitrobenzaldehyde and glycine 1:4:6, reaction temperature 80°C, reaction time 48h, volume of toluene solvent 70 mL.

49. Synthesis and Application of Geminal Dinitro Energetic Plasticizers, Chen Bin, Zhang Zhi-zhong, Ji Yue-ping, [Xi'an Modern Chemistry Research Institute, Xi'an 710065, China], Chinese Journal of Explosives & Propellants. 2007, 30(2):67-70,74.

Abstract: According to the structure and synthesis character of the geminal dinitro energetic plasticizers, the current situation about the synthesis, the property and application of geminal di-nitro aldehyde acetals, esters and ether energetic plasticizers is summarized with 21 references. The preparation technique of aldehyde acetals energetic plasticizers BDNPF and BDNPA is introduced. Their physico-chemical properties, energy characteristics, thermal performance and application in the formulations of explosives and propellants are

reviewed, considering that synthesis and application of geminal dinitro energetic plasticizers are the key point in energetic plasticizer study.

50. The Green Synthesis of 1,2-Propylene Glycol Dinitrate, Shi Fei, Wang Qing-fa, Zhang Xiang-wen, Wang Li, Mi Zhen-tao, [Key Laboratory for Green Chemical Technology of State Education Ministry, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072,China], Chinese Journal of Explosives & Propellants. 2007, 30(2):75-77.

Abstract: In order to solve the environmental pollution of synthesizing 1, 2-propylene glycol di-nitrate (PGDN) with propylene oxide (PO) as raw material and the mixture of nitric acid and sulfuric acid as nitrating agent, a new method for preparation of PGDN by nitrating PO with di-nitrogen pent-oxide (N_2O_5) as a clean nitrating agent was presented. This reaction is environmental friendly with high atomic economy. Effects of the drip order, molar ratio of N_2O_5 to PO, reaction temperature and solvents on the yield and selectivity of PGDN were studied. The results show that the optimum reaction conditions are: dropping the PO into the solution of N_2O_5 /organic solvent, the molar ratio of N_2O_5 to PO above 1.1:1.0, the reaction temperature $15^\circ C$ and dichloromethane as solvent. Under the above optimum conditions, the yield of PGDN is about 96.3%, and the selectivity is nearly 100%.

51. Synthesis and Properties of 3,4-Bis(4'-aminofurazano-3')furoxan, ZHOU Yan-shui, LI Jian-kang, HUANG Xin-Ping, ZHOU Cheng, ZHENG Wei, ZHANG Zhi-zhong, [Xi'an Modern Chemistry Research Institute, Xi'an 710065,China], Chinese Journal of Explosives & Propellants. 2007, 30(1):54-56.

Abstract: 3, 4-bis(4'-aminofurazano-3') furoxan was synthesized using dicyanopropane as starting material by , diazotization and condensation steps in turn, with overall yield 50%.Some physical and detonation properties were also measured, with density $1.795g/cm^3$, melt point $170 - 171^\circ C$, detonation velocity $7177m/s$ ($1.530g/cm^3$), temperature of decomposition $260^\circ C$, friction sensitivity 8% (90°), impact sensitivity 60% (10kg, 25cm), and vacuum stability test 0.4 - 0.7mL (5g, $100^\circ C$, 48h). The thermal stability and compatibility of DATF were investigated by DSC. The results show that DATF has better thermal stability, lower sensitivity and good compatibility with energetic materials of RDX, HMX, NC

and NC/NG system.

52. A Review on 3-Nitro-1,2,4-Triazol-5-One and its Salts, Ma Hai-xia, [School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing 210094,China], Song Ji-rong, [College of Chemical Engineering/Shaanxi Key Laboratory of Physico-Inorganic Chemistry, Northwest University, Xi'an 710069,China], Hu Rong-zu, [College of Chemical Engineering/Shaanxi Key Laboratory of Physico-Inorganic Chemistry, Northwest University, Xi'an 710069, China], Chinese Journal of Explosives & Propellants. 2006, 29(6):9-15.

Abstract: The synthesis and properties of a new energetic material 3-nitro-1, 2, 4-triazol-5-one (NTO),including synthesis methods, crystal structure, quantum chemistry, thermal behaviors and toxicity were reviewed in details. The molecule structure and thermodynamic properties of twenty-one kinds of NTO complexes of alkali, alkaline earth, transition metals and rare earth metals were introduced emphatically and the thermal decomposition products of NTO alkali complexes were concluded as carbonate with Li, Na and K, and those of Rb and Cs complexes of NTO were carbonate, metal oxide and polymers. The relationship between the enthalpy of activation (ΔH_{\neq}) and the value ($T_{(pdo)}$) of the peak temperature among NTO alkali metal complexes was obtained with 73 references.

53. Amination of Nitrotoluenes via Vicarious Nucleophilic Substitution(VNS) of Hydrogen, Li Jia-rong, [School of Chemical Engineering and Environment, Beijing Institute of Technology, Beijing 100081,China], ZHAO Jian-min, [School of Chemical Engineering and Environment, Beijing Institute of Technology, Beijing 100081,China], WEI Xiao-jie, [School of Chemical Engineering and Environment, Beijing Institute of Technology, Beijing 100081,China], ZHAO Xiao-fan, [School of Chemical Engineering and Environment, Beijing Institute of Technology, Beijing 100081,China], DONG Hai-shan, [Institute of Chemical Engineering and Material, CAEP, Mianyang Sichuan 621900,China], Chinese Journal of Explosives & Propellants.2006, 29(6):30-32.

Abstract: The VNS amination reaction of nitrotoluene with ATA in DMSO in the presence of MeONa via vicarious nucleophilic substitution (VNS) of hydrogen was studied. The results indicated that 3-amino-2, 4-dinitrotoluene was obtained by VNS amination of DNT in the yield of 10.5%, and 3, 5-diamino-2, 4, 6-trinitrotoluene

was obtained via VNS amination of 2, 4, 6-trinitrotoluene in the yield of 27.6%. The yields were lower under microwave radiation than that at room temperature. The amination of TNT in hydroxylamine gave DATNT in poor yield. The products were characterized by IR, nuclear magnetic resonance, elemental analyses and MS.

54. Preparation and Performance of Double Base Propellant Modified by NGEC, Wang Fei-jun, [School of Materials Science and Engineering, Beijing Institute of Technology, Beijing 100081,China],Yang Fei-fei,[School of Materials Science and Engineering, Beijing Institute of Technology, Beijing 100081,China], Wang Jiang-ning, [Xi'an Modern Chemistry Research Institute, Xi'an 710065,China], Shao Zi-qiang, [School of Materials Science and Engineering, Beijing Institute of Technology, Beijing 100081,China]. Chinese Journal of Explosives & Propellants.2006, 29(6):51-53.

Abstract: In order to enhance the mechanical performance of double-base propellant at low temperature, the cellulose was converted to cellulose glycidyl via basification and etherization reactions. A novel energetic binder named nitric acid ester of cellulose glycidyl ether (NGEC) with different esterification and etherification degree was synthesized by nitrating cellulose glycidyl. The mechanical performance and the section appearance of the two double base propellants based on NGEC and NC were surveyed and analyzed. The detonation heat and specific volume of the two propellants were tested and contrasted. The results show that the double-base propellant based on NGEC has better mechanical performance, detonation heat and specific volume level over aging those of double base propellant based on NC and its inner-structure turns more uniform. Its compressive strength σ_m (+50°C), elongation ε_m (25°C) and specific impulse are no less than 11.0MPa and 40% and 2218N·s·kg⁻¹, respectively.

55. HZSM-5 Assisted Clean Nitration of Toluene with Dinitrogen Pentoxide, Qian Hua, Ye Zhi-wen, Lü Chun-xu,[School of Chemical and Engineering, Nanjing University of Science and Technology, Nanjing 210094,China], Chinese Journal of Explosives & Propellants.2006, 29(5):9-13.

Abstract: In order to solve the problem of synthesizing p-mono-nitrotoluene involving the concentrated mineral acids as the catalysts produces huge amounts of wastes along with a large amount of

undesired o-MNT due to the nonselective nitration of toluene, the nitration of toluene by N_2O_5 has been investigated with solid acids catalysts HZSM-5. By the use of new nitrating agent, the reaction eliminated the use of concentrated sulfuric acid and was environmental friendly with high atom economy. The excellent selectivity of HZSM-5 makes the ratio of p-mononitrotoluene increase greatly. Effects of reaction temperature, reaction time, amount of catalyst and the ratio of Si/Al on the nitration were investigated, showing that under optimum conditions, the yield of nitration of toluene was 42%, and para-selectivity was 78.9%.

56. Research on Coating HNIW with Water-borne Branched Polyurethane, Liao Su-ran, [Textile and Chemical Engineering Department, Henan Textile College, Zhengzhou 450007, China], Luo Yun-jun, [School of Material Science and Engineering, Beijing Institute of Technology, Beijing 100081, China], Yang Yin, [School of Material Science and Engineering, Beijing Institute of Technology, Beijing 100081, China], Sun Jie, [Institute of Chemical Materials, CAEP, Mianyang Sichuan 621900, China], Tan Hui-min, [School of Material Science and Engineering, Beijing Institute of Technology, Beijing 100081, China], Chinese Journal of Explosives & Propellants. 2006, 29(5):22-24, 28.

Abstract: The waterborne branched polyurethane (WBPU) was synthesized from toluene diisocyanates (TDI), TDB-2000, TMN-450, dimethylolpropionic acid (DMPA) and 1, 4-butanediol (BDO) as raw materials under acetone reflux. The cast films obtained were characterized by FT-IR, 1H NMR and DSC. The DSC curve presented an endothermic decomposition bimodal profile, showing that water-borne branched polyurethane resin degraded obviously at about 299°C and 380°C. The SEM photographs and FT-Raman spectra revealed that hexanitro-hexaazaisowurtzitane (HNIW) was coated with water-borne branched polyurethane by means of latex deposition. The impact sensitivity results show that the characteristic height $H(50)$ of HNIW coated by water-borne branched polyurethane increases from 25.1cm to 31.6cm, indicating that the water-borne branched polyurethane can decrease the impact sensitivity of HNIW.

57. Synthesis and Properties of a Novel Azido Energetic Curing Agent, Zheng Xiao-dong, Li Hong-li, Jiang Jun, Gan Xiao-xian, [Xi'an Modern Chemistry Research Institute, Xi'an 710065, China], Ma Xiao-dong, [Military Office, Xi'an North Huian Chemical Industrial Co. Ltd, Xi'an 710302, China], Qiu Shao-jun, [School of Materials

Science and Engineering, Northwestern Polytechnic University, Xi'an 710072, China], "Chinese Journal of Explosives and Propellants", 2006, 29 (5):63-66.

Abstract: To improve the mechanical properties of the binder system, a novel azido poly-isocyanate energetic curing agent (EC) was synthesized via additional reaction of azido polyether polyol and hexamethylene diisocyanate (HDI). The material ratio, reaction temperature and post processing steps on the reaction were studied. The DSC results show that for EC, there was an exothermic peak at 252.89°C and the glass transition temperature (T_g) was found at -47.13°C; for the EC/GAP system, thermal decomposition peak was at 254.56°C and the glass transition temperature (T_g) was found at -45.78°C. And the EC/GAP/50% TEGDN system has good physical and chemical compatibility, there were two peaks at 213.05°C and 250.89°C, and the glass transition temperature (T_g) was found at -69.08°C. The tensile strength and break elongation value of GAP/EC system is 0.67MPa and 129%, respectively, which is better than that of 0.5MPa and 56.5% of GAP/N100 system at 20°C.

58. Synthesis and Properties of 3-Azidomethyl-3-Ethyloxetane and its Homopolymer, Han Tao, Gan Xiao-xian, Xing Ying, Li Na, Lu Xian-ming, Zhang Zhi-gang, Mo Hong-chang, [Xi'an Modern Chemistry Research Institute, Xi'an 710065, China], Chinese Journal of Explosives & Propellants. 2006, 29(5):72-75.

Abstract: To develop new energetic binder, a new azide oxetane monomer, 3-azidomethyl-3-ethyloxetane (AMEO) was synthesized by 1, 1, 1-tri(hydroxymethyl) propane, diethylcarbonate, 4-toluene-sulfonyl chloride and sodium azide as raw materials. Its structure and properties were identified by ¹H NMR, FTIR, elemental analyses and DSC. At the present of catalyst boron-trifluoride etherate, a solid energetic polymer, homopolymer of 3-azidomethyl-3-ethyloxetane PAMEO was prepared by the cationic polymerization of monomer AMEO with (1, 4)-butanediol as initiator and dichlorometane as solvent. The structure of the polymer was identified by IR, (¹H NMR) and elemental analyses. The properties of the polymer were characterized by TGA, DSC, and hydroxyl equivalent and number-average molecular weight.

59. Synthesis and Characterization of Ultrafine Cupric 2,4-Dihydroxybenzoate(β -Cu), Li Yu, Guo Yu, Liu You-zhi, Shi Guo-liang, XIE Wu-xi, [Research Center of Shanxi Province for High Gravity

Chemical Engineering and Technology, Taiyuan 030051,China], Chinese Journal of Explosives & Propellants.2006, 29(3):32-35.

Abstract: Using impinging steam-rotating packed bed (IS-RPB), ultrafine β -Cu powder was synthesized from $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and β -H as primary substances by high gravity reactive precipitation method. The TEM, laser size analysis (LSA), BET and TG-DTG techniques were used to characterize the product. Effects of the operation conditions of rotational speed, impact velocity and post-treatment conditions on the average particle size of β -Cu were also studied systematically. The results show that the operation conditions are optimized as: rotational speed, 1000r/min, impact velocity, 28m/s and vacuum desiccation temperature, 100°C. Under the above-mentioned conditions the sheet β -Cu particles with size of 0.12 μm to 0.363 μm , an average particle size of 610nm and a specific surface area of 11.6265 m^2/g are obtained.

60. Researches and Applications of Borate Surfactants, Wang Hai-ying, Li Bin-dong, Lü Chun-xu, Zou Qi, [School of Chemical Engineering, Nanjing University of Science & Technology, Nanjing 210094, China], Chinese Journal of Explosives & Propellants.2006, 29(3):36-38,42.

Abstract: The structures of the borate surfactant and its improved methods of properties are briefly introduced. The progress in synthesis of borate surfactant and their applications in the fields of antistatic, anti-wear, and flame retardancy were introduced. The antistatic researches of polymeric borate surfactant are described, and their application prospect in the industrial area such as the energetic material area is reviewed with 27 references.

61. Synthesis of CL-20 by Clean Nitration, Qian hua, Lü Chun-xu, Ye Zhi-wen, [Chemical Engineering School, Nanjing University of Science and Technology, Nanjing 210094,China], Chinese Journal of Explosives & Propellants.2006, 29(3):52-53,64.

Abstract: CL-20 is a high energy material. Usually It Is prepared via nitration with nitric and sulfuric acid Concentrated, this technique aims pollutes the environment. In this section, CL-20 was synthesized with 2, 6, 8, 12-tetraacetylhexaazatetracyclo [5, 5, 0, 0^{3,11},0^{5,9}] dodecane (TAIW) and dinitrogen pentoxide clean nitrating agent. By the use of new nitrating agent the reaction eliminated the use of concentrated sulfuric acid and environmental friendly with

high was atom economy. The structure of the compound was characterized by elemental analysis, IR, ¹H NMR and MS. Meanwhile, The effects of reaction temperature and reaction time on the yield were also investigated, showing that under the conditions of reaction temperature, 0°C and reaction time, 1h, the optimum yield of CL-20 was up to 62%.

62. Synthesis Mechanism of Tetranitrodiazidopropionylhexaazaisowurtzitanene, Meng Zheng, Ou Yu-xiang, Liu Jin-quan, Wang Yan-fei, [College of Materials Science and Engineering, Beijing Institute of Technology, Beijing 100081,China], Chinese Journal of Explosives & Propellants.2006, 29(3): 63-67.

Abstract: TAIW was formed from hydrogenolysis debenzoylation of TADBIW using Pt as catalyst. TADCPIW was synthesized by α -chloropropionylation of TAIW. A mixture contained TNDCPIW was obtained by nitration of TADCPIW, and then azido groups were introduced into product. Tetranitrodiazidopropionylhexaazaisowurtzitanene (TNDAPIW) with high nitrogen content and high enthalpy of formation can be obtained by the product separation using column chromatography. The structures of TNDAPIW and the intermediate compounds were identified by IR, ¹H NMR and elemental analysis. The related conditions and mechanisms of reactions such as hydrogenolysis, α -chloropropionylation, nitration and azidation were discussed. The results show that because of the caged structure of TAIW and the electrophilic effect in the-acyl radical, it is necessary for the actively reacting composite such as α -chloropropionyl chloride used in the chloropropionylation reaction; the nitration reagent should be appropriately used in the nitration, if not TADCPIW will be nitrated into HNIW; as the diazo-reaction is S_N2 reaction, it is advantageous for the reaction to choose the dipolar protophilic solvent like DMF or DMSO.

63. Synthesis of Trinitropyridine and its N-Oxide, Zhao Jian-min, [School of Chemical Engineering and Environment, Beijing Institute of Technology, Beijing 100081,China], Li Jia-rong, [School of Chemical Engineering and Environment, Beijing Institute of Technology, Beijing 100081,China], Wei Xiao-jie, [School of Chemical Engineering and Environment, Beijing Institute of Technology, Beijing 100081,China], Li Wen-ting, [School of Chemical Engineering and Environment, Beijing Institute of Technology, Beijing 100081,China], Dong Hai-shan, [Institute of Chemical Engineering and Material, China Academy of Engineering

Physics, Mianyang 621900,China], Chinese Journal of Explosives & Propellants.2006, 29(3):73-76.

Abstract: 2, 2-Dinitropropane-1, 3-diol was synthesized from nitromethane in low temperature by oxidative nitration method. Silver was successfully recycled with a yield upon 93% and reused in the synthesis of 2, 2-dinitropropane-1, 3-diol. Potassium 2, 2-dinitroethanol, the key intermediate compound for synthesis of trinitropyridine (TNPy), was prepared through one-pot method with a yield upon 62%, which is 10% higher than conventional method. Controlling the pH value in the range of 1 - 2, trinitropyridine N-oxide (TNPyO) was synthesized by the cyclization of potassium 2, 2-dinitroethanol in 68% nitric acid at 50 - 60°C. Maintaining the temperature between 80-90°C, TNPyO can be further reduced to produce TNPy by refluxing for 1 h; the yields of TNPyO and TNPy are 50% and 15%, respectively. TNPyO can also be prepared from potassium 2, 2-dinitroethanol under phosphoric acid and sulfuric acid. The products were characterized by IR, nuclear magnetic resonance, elemental analysis and EI-MS.

64. Synthesis of Rich-Nitrogen Compound of 3,3'-Azobis(6-Amino-1,2,4,5-Tetrazine), Wang Bo-zhou, Lian Peng, Liu Qian, Wang Xi-jie, Zhang Zhi-zhong, Huang Xin-ping, [Xi'an Modern Chemistry Research Institute, Xi'an 710065,China], Chinese Journal of Explosives & Propellants.2006, 29 (2):15-18.

Abstract: 3, 3'-azobis (6-amino-1, 2, 4, 5-tetrazine) (DAAT) was synthesized with triaminoguanidine nitrate and 2, 4-pentanedione as primary substances by condensation, oxidation, hydrazinolysis, oxidation-bromation, aminolysis and hydrolysis in turn. DAAT is a new rich-nitrogen energy material with remarkable thermal stability and insensitivity against friction and impact. DAAT decomposes at relatively high temperatures (250°C) measured by DSC. The details of each reaction process and yields were described; the results are according with the references. The overall yield of DAAT is 19%. Its structure was confirmed by IR, HNM and DSC. The mechanisms of the condensation and oxidation-bromation reactions were presented.

65. Study on the Synthesis of TEX, Xu Rong, Zhou Xiao-qing, Zeng Gui-yu, Liu Chun, [The Institute of Chemical Materials, CAEP, Mianyang Sichuan 621900,China], Chinese Journal of Explosives & Propellants.2006, 29(2):26-28.

Abstract: 1, 4-Diformyl-2, 3, 5, 6-tetrahydroxypiperazine (THDFP) was synthesized with glyoxal and amides as primary substance. The cage explosive 4,10-dinitro-2, 6, 8-12-tetraoxa-4,10-diazatetracyclo-[5.5.0.0^(5,9)0^(3,11)]-dodecane (TEX) was prepared using the method that taking THDFP into 98% H₂SO₄ and fuming HNO₃ at lower temperature, producing enough the cage compound, then carrying out nitration in higher temperature. The purity and overall yield of TEX are 99.5% and 34.8%, respectively. The effect of THDFP dry time, the temperature of adding material and reaction temperature on the synthesis of TEX were studied. Results show that THDFP of full dried for synthesis is favored, should control the temperature of adding material in the range 45~50°C and the reaction temperature in the range of 75~80°C.

66. Experimental Studies on the 2,4,6-Trinitro-m-Xylene Crystal, Guo Jin-Yu, Zhang Tong-Lai, Zhang Jian-Guo, LIU Yan-Hong, [State Key Laboratory of Explosion Science and Technology, Beijing Institute of Technology, Beijing 100081,China], Chinese Journal of Explosives & Propellants.2006, 29(2):58-62,65.

Abstract: The crystal of 2, 4, 6-trinitro-m-xylene (TNMX) has been synthesized, cultured and characterized by X-ray single crystal diffraction, ¹H NMR, MS and FT-IR techniques. TNMX is crystallized into orthorhombic, PbCn space group, $a=(5.749(2))\times 10^{-10}\text{m}$, $b=15.043(3)\times 10^{-10}\text{m}$, $c=11.415(2)\times 10^{-10}\text{m}$, $\alpha=\beta=\gamma=90.00^\circ$, $V=987.2(3)\times 10^{-30}\text{m}^3$, $Z=4$, $D_c=1.623\text{g}/\text{cm}^3$ (calculated density), final R indices [I2 σ (I)], $R_1=0.0359$, $wR_2=0.1006$, R indices for all data, $R_1=0.0459$, $wR_2=0.1045$. By means of weak interactions among the nitro O atoms from different TNMX molecules, two-dimensional frameworks come into being in this complex. The DSC and TG-DTG thermal analyses have also carried to predict its thermal decomposition mechanism. Based on thermal analyses, the crystal was predicted to decompose completely in one step.

67. Optimization of the Synthetical Craft of 2,6-Diamino-3,5-Dinitropyrazine-1-Oxide, Guo Feng-bo, Liu Yu-cun, Liu Deng cheng, Yu Yan-wu, [Department of Environmental and Safety Engineering, North University of China, Taiyuan 030051,China], Chinese Journal of Explosives & Propellants.2006, 29(1):17-19,22.

Abstract: LLM-105 was synthesized with 2, 6-dichloropyrazine as primary substance by substitution, nitration, and ammoniating and

oxidation steps in turn and the overall yield of LLM-105 is greater than 36%. The purity of LLM-105 is more than 98%. Its structure was characterized by elemental analysis, IR, MS and NMR. Effects of the consumption of CH_3ONa , the volume proportion of HNO_3 and H_2SO_4 , the consumption of $\text{NH}_3\cdot\text{H}_2\text{O}$ and the volume proportion of trifluoroacetic acid and H_2O_2 on the overall yield of LLM-105 were investigated. The optimal conditions of synthesizing LLM105 were ascertained as: for the substitution reaction, under the conditions of reflux, reaction time, 2h; the consumption of CH_3ONa is 120% for the nitration reaction, reaction time 4h; reaction temperature $60\sim 70^\circ\text{C}$, the volume proportion of HNO_3 and H_2SO_4 , .83; or the ammoniating reaction, under the conditions of 2h and 60°C , the consumption of $\text{NH}_3\cdot\text{H}_2\text{O}$, 200%; for the oxidation reaction, under the conditions of 24h and room temperature, the volume proportion of trifluoroacetic acid and H_2O_2 :.10.

68. Progress in the Synthesis of TATB Free from Chloride, Zhou Xin-li, [School of Chemical Engineering, Nanjing University of Science & Technology, Nanjing 210094, China], Chinese Journal of Explosives & Propellants.2006, 29(1):26-28.

Abstract: Based on references, synthesis methods of insensitive explosive TATB are summarized. Modified synthesis methods of TATB containing chloride compounds are simply introduced. The progresses in the synthesis of TATB free from chloride by different raw materials and synthesis process are mainly introduced, especially using direct amine hydrogen synthesis principle and process of TATB according to vicarious nucleophilic substitution of hydrogen (VNS) are emphasized, including influences of raw materials, mole specific, amine agent and its addition methods, methods of quenching reaction on yield, particle size, purity and physical appearance. It is shown that VNS is a new method for preparation of energetic materials containing multi nitro and amino aromatic compounds.

69. Synthesis and Properties of N-guanylurea Dinitramide, Liu Qian, Wang Bo-zhou, Zhang Zhi-zhong, Zhu Chun-hua, Lian Peng, [Xi'an Modern Chemistry Research Institute,Xi'an 710065,China], Chinese Journal of Explosives and Propellants. 2006, 29 (1): 29 – 31.

Abstract: N-guanylurea dinitramide (GUDN) was synthesized with N-guanylurea hydrochloride as primary substance by hydrolysis and double decomposition reaction in turn and the overall yield of GUDN is 79%. The structure of GUDN was identified by elemental

analysis, IR and UV. Some properties of GUDN were determined as: density, 1.755g/cm^3 , friction sensitivity, (2.45MPa, 20mg, 66°); H_{50} 197cm (2kg) etc. And its properties were compared with properties of ADN. GUDN has low sensitivity, good thermal stability and unhygroscopicity. The results obtained by DSC show that GUDN is compatible with common energetic materials such as HMX and RDX. Application tests indicate that GUDN can be used in double base propellant.

70. A Review of Recent Advances of Energetic Plasticizers, Ji Yue-Ping, Li Pu-rui, Wang Wei, Lan Ying, Ding Feng, [Xi'an Modern Chemistry Research Institute, Xi'an 710065, China], Chinese Journal of Explosives & Propellants. 2006, 29(1):29-31.

Abstract: The current situation about the synthesis and application of energetic plasticisers based on the kinds of energetic group is summarized. The primary role of energetic plasticisers in energetic material formulation is considered to modify the mechanical properties of charge to improve safety characteristics. The nitrate ester plasticizers' is a sensitive explosive easily initiated by friction and impact. The value of HD for most of the energetic nitrate esters is 1.1. The novel energetic compounds or oligomeric containing azido geminal dinitro and nitramine group with excellent properties are considered as primary research subject of energetic plasticisers. The shortcoming in the synthesis technology, variety and application of energetic plasticizer in domestics is analysed. The suggestions in the synthesis and application of novel energetic plasticizers are presented.

71. Synthesis of Polyurethane Elastomer Used in the Coating of Some Propellant and its Application, Zhu Kai-jin, Xiao Zhong-liang, [Department of Chemical Engineering, North University of China, Taiyuan 030051, China], Chinese Journal of Explosives & Propellants. 2005, 28(4):55-57.

Abstract: By utilizing toluene diisocyanate (TDI) and liquefied diphenylmethane diisocyanate (MDI) to synthesize polyisocyanate, and then to synthesize the adhesive of polyurethane as main component of certain propellant coating, a coating with good mechanical property and low smoke fog property is obtained. The results show that it is fit to choose the ratio 7:3 of TDI to MDI, the reaction temperature 80°C , the reaction time (30min) and the solidified time 4~5d. The originality of the study rests on that TDI

and liquefied MDI are simultaneously used as the synthetic material of polyisocyanate to make the coating of some propellant.

72. Progress of the High Density Hydrocarbon Fuel of Exo-tetrahydrodicyclopentadiene, Du Yong-mei, Li Chun-ying, Lü Jian, [Xi'an Modern Chemistry Research Institute, Xi'an 710065, China], Chinese Journal of Explosives & Propellants. 2005, 28(4):58-60.

Abstract: The current situation of synthetic methods of exo-tetrahydrodicyclopentadiene including hydrogenation of dicyclopentadiene and isomerization from endo-tetrahydrodicyclopentadiene to exo-tetrahydrodicyclopentadiene is summarized. Different hydrogenation catalysts and process are generalized and several hydrogenation catalysts are compared. Continuous and intermittent process is recapitulated. Isomerization catalysts and mechanism of isomerization with Lewis acid catalysts are introduced. Development direction of hydrogenation catalysts and isomerization catalysts is presented. New synthetic methods of exo-tetrahydrodicyclopentadiene are suggested.

73. Nitration of Halobenzenes with Fluorous Biphasic System, Yi Wen-bin, Cai Chun, [Chemical Engineering College, Nanjing University of Science & Technology, Nanjing 210094, China], Chinese Journal of Explosives & Propellants. 2005, 28(3):45-48.

Abstract: Halobenzenes can be nitrated effectively in fluoruous phase in the presence of ytterbium (III) perfluorooctanesulfonate ($\text{Yb}(\text{OS O}_2\text{C}_8\text{F}_{17})_3$) catalyst. Perfluorodecalin ($\text{C}_{10}\text{F}_{18}$) was used as a fluoruous solvent for this reaction. The fluoruous phase after separating catalyst can be reused many times, and P/O ratio of p-isomer to o-isomer in the products of mononitration of fluobenzene, chlorobenzene and iodobenzene can be increased to 7.20, 2.45, 4.01 and 0.91 respectively. Partition coefficients involving organic and fluoruous phase under different temperatures have been measured. Effects of reaction temperature, the ratio of fluoruous phase/organic phase and the water content in the reaction system on the nitration were investigated. It was observed that the optimum temperature for fluoruous biphasic nitrations of fluobenzene, chlorobenzene, bromobenzene and iodobenzene were 60°C, 60°C, 80°C and 80°C respectively. Reducing the ratio of fluoruous phase/organic phase and the water content in the reaction system can increase P/O ratio.

74. Synthesis of Ammonium Dinitramide from Ethyl Carbamate, Wang Bo-zhou, Liu Qian, Zhang Zhi-zhong, Lian Peng, Zhu Chun-hua, [Xi'an Modern Chemistry Research Institute, Xi'an 710065, China], Chinese Journal of Explosives & Propellants. 2005, 28(3):49-51.

Abstract: In $\text{HNO}_3\text{-H}_2\text{SO}_4$, ammonium N-nitro carbamate ethyl ester was synthesized from ethyl carbamate, then taking N_2O_5 as nitrating agent; ammonium dinitramide (ADN) was prepared. its yield reached to 70%. It was re-crystallized to yield a white hygroscopic powder with a melting point of $90\sim 92^\circ\text{C}$. Its structure was identified by elemental analysis, infrared spectrum and ultraviolet spectroscopy. The main factors such as reaction medium, stuff ratio, reaction temperature were also briefly discussed; its optimum condition was obtained.

75. Synthesis and Characterization of High-Nitrogen Energetic Compounds Derived from Azotetrazolate, Xu Song-Lin, Yang Shi-qing, Yue Shou-ti, [College of Aerospace and Material Engineering, National University of Defense Technology, Changsha 410073, China], Chinese Journal of Explosives & Propellants. 2005, 28(3):52-54.

Abstract: Three new high-nitrogen energetic compounds bis-(ammonium)-5, 5'-Azotetrazolate, bis-(guan-idinium)-5, 5'-Azotetrazolate and bis-(triaminoguanidinium)-5, 5'-Azotetrazolate have been synthesized from 5-aminotetrazole as a starting materials. Their structures were identified by IR, NMR, DSC, melting point test and elemental analysis. Their explosive performances were also introduced. It shows that these azotetrazolate compounds are possessed of positive enthalpy of formation, high gas generating ability with little or no smoke or residue produced nonhygroscopic and excellent explosive performances. They are the important ingredients of gas generating, low signature propellants, pyrotechnics and high performance explosives.

76. Synthesis and Characterization of Diacetyltetrabenzylhexaazaisowurtzitane, Chen Fei, [School of Material Science & Technology, Beijing Institute of Technology, Beijing 100081, China], Pang Si-ping, [School of Life Science & Technology, Beijing Institute of Technology, Beijing 100081, China], Yu Yong-zhong, [School of Material Science & Technology, Beijing Institute of Technology, Beijing 100081, China], ZHAO Xin-qi, [School of Material Science & Technology, Beijing Institute of Technology, Beijing

100081, China], Chinese Journal of Explosives & Propellants. 2005,28(3):55-56,69.

Abstract: The oxidation of hexabenzylhexaazaisowurtzitane (HBIW) by cerium (IV) ammonium nitrate has been studied. Diacetyl tetrabenzylhexaazaisowurtzitane (DATBIW) was obtained and its structure was characterized by FT-IR, MS and ¹H NMR. The mechanism of the oxidation-debenzylation process of HBIW was deduced.

77. Synthesis of 3-Azidomethyl-3-Methyloxetane, Li Na, Gan Xiao-xian, [Xi'an Modern Chemistry Research Institute, Xi'an 710065, China], Chinese Journal of Explosives & Propellants. 2005,28(3):57-59

Abstract: 3-Hydroxymethyl-3-methyl oxetane (HMMO) was prepared by the cyclization of raw materials 1, 1, 1-tri-(hydroxymethyl) ethane and diethyl carbonate. Under lower temperature, 3-methoxytosyl-3-methyl oxetane (MTMO) was synthesized by the reaction of HMMO with 4-toluenesulfonyl-chloride. 3-Azidomethyl-3-methyl oxetane was synthesized by the reaction of MTMO and sodium azide. The yields of the three steps were 76%, 96%, 85%, respectively. The structure and properties of AMMO were identified by ¹H NMR, FTIR, elemental analysis and DSC. The results show that final product was target compound. AMMO was an important energetic oxetane monomer. It can conduct steady cationic polymerization.

78. Synthesis and Thermal Decomposition of 1,4-Dinitromidazole, Cao Duan-lin, [Department of Chemical and Engineering, North University of China, Taiyuan 030051, China], Liu Hui-jun, [Department of Chemistry, Education University of Yanbei, Datong 037009, China], Li Yong-xiang, [Department of Chemical and Engineering, North University of China, Taiyuan 030051, China], Chinese Journal of Explosives & Propellants. 2005,28(3):60-62.

Abstract: 1, 4-Dinitroimidazole (1, 4-DNI) is synthesized by following the reactions: 4-dinitroimidazole was N₃-acetylated by acetic anhydride in acidic solution to obtain acylate and acylate thus obtained was nitrated by the mixture of concentrated sulfuric acid, acetic anhydride and sodium nitrate to obtain 1, 4-DNI. The synthetic condition is optimized by the orthogonal experiment. The optimum parameters are as follows: n (4-nitr-oimidazole) / n (sulfuric acid) / n (sodium nitrate) / n (acetic anhydride) = 2/3/8/15, reaction

temperature 30~40°C and reaction time 3h. Thermal decomposition of 1, 4-DNI is studied by DSC.

79. Homogeneous Synthesis of Azidodeoxycellulose, Shao Zi-qiang, [School of Materials Science and Engineering, Beijing Institute of Technology, Beijing 100081, China], Wang Fei-jun, [School of Materials Science and Engineering, Beijing Institute of Technology, Beijing 100081, China], Wang Wen-jun, [School of Materials Science and Engineering, Beijing Institute of Technology, Beijing 100081, China], Liao Bing, [GuangZhou Institute of Chemistry. Academia Sinca, Guangzhou 510650, China], Chinese Journal of Explosives & Propellants.2005,28(2):47-49.

Abstract: A new high energetic bonder intermediate azidodeoxy-cellulose for solid propellant was synthesized from the raw material cotton linters under homogeneous conditions. The process of preparing azidodeoxycellulose includes two steps. The first is the tosylation of cellulose with tosylchloride using triethylamine as catalyst and the dimethylacetamide/LiCl system as solvent to obtain cellulose tosylate with certain ester number. The second is nucleophilic substitution reaction of the cellulose tosylate with NaN_3 in DMSO to obtain azidodeoxycellulose with the degree of substitution (DS) of 0.6 ~ 1.0. The effects of cellulose tosylate/DMSO ratio, reaction temperature and reaction time on the value of DS of azidodeoxycellulose were discussed. The samples were characterized by elemental analysis, FT-IR and X-ray diffraction.

80. Nitrolysis with Nitrogen Peroxide for Synthesis of 1,4,5,8-Tetranitro-1,4,5,8- tetraazabicyclo[4.4.0] decalin, Cai Chun, Lü Chun-xu, [Chemical Engineering School, Nanjing University of Science & Technology, Nanjing 210094,China], Chinese Journal of Explosives & Propellants.2005,28(2):50-51.

Abstract: 1, 4, 5, 8-Tetranitro-1, 4, 5, 8-tetraazabicyclo [4.4.0] decalin (TNAD) is used as an explosive and has several superior physical properties, such as heat-resistance and insensitivity to impact. This compound could be prepared from the raw material 1, 4, 5, 8-tetraazabicyclo [4.4.0] decalin via nitrosation with sodium nitrite in hydrochloric acid, and followed nitrolysis with N_2O_5 in mixed acid. In nitrolysis step, the effect of reaction medium and the reaction temperature on the yield have been investigated. The structure of

compound was characterized by IR and elemental analysis. The total yield could reach as high as 85%.

81. Synthesis and Properties of 1,1-Diamino-2,2-Dinitroethylene, Zhou Cheng, Zhou Yan-shui, Huang Xin-ping, Wang Xi-jie, [Xi'an Modern Chemistry Research Institute, Xi'an 710065, China], Chinese Journal of Explosives & Propellants.2005,28(2):65-67.

Abstract: 1, 1-Diamino-2, 2-dinitroethylene (DADE) was synthesized with 2-methylimidazole as primary substance by nitration and hydrolysis steps in turn and the yield of DADE is 13.4%. Its structure was characterized by elemental analysis, IR, MS and NMR. The effects of concentration of sulfuric acid, reaction temperature, reaction time on the yield were investigated. Some important properties of DADE were determined as: density, 1.885g/cm³, detonation velocity, 8047m/s ($\rho=1.696\text{g/cm}^3$); friction sensitivity, 10% (3.92MPa, 90°); impact sensitivity, 6% (10kg, 25cm); H₅₀, 89.1cm (5kg); vacuum stability test, 0.14ml/5g (100°C, 48h), explosion temperature, 285°C (5s delay).

82. Synthesis and Characterization of 1,1,1-Trimethylolpropane Trinitrate, Cui Jian-lan, [Department of Chemical Engineering, North University of China, Taiyuan030051, China], Guo Wen-long, [The College of Pharmaceuticals and Biotechnology of Tianjin University, Tianjin 300072, China], Cao Duan-lin, [The College of Pharmaceuticals and Biotechnology of Tianjin University, Tianjin 300072, China], Xu Chun-yan, [The College of Pharmaceuticals and Biotechnology of Tianjin University, Tianjin 300072, China], Chinese Journal of Explosives & Propellants.2005,28(2):78-79.

Abstract: 1, 1, 1-Trimethylolpropane trinitrate was synthesized from the raw material trimethylolpropane via nitration reaction. The effect of nitrating agent on the yield of nitration reaction was studied and the proper additive and nitrating agent was found. The experimental results showed under the following reaction conditions: 98% nitric acid as nitrating reagent, the molar ratio of trimethylolpropane to nitric acid, 10:1; reaction time, 2h; reaction temperature, 0~20°C, the yield of the title compound was up to 99.7%, providing a new highest yield method of synthesizing 1, 1, 1-Trimethylolpropane trinitrate. The product was characterized by IR, nuclear magnetic resonance and elemental analysis.

83. Kinetics of Synthesis of TADF by Hydrogenolysis Debenzylation of TADB, Ma Ai-ling, Sun Cheng-hui, Fang Tao, Zhao Xin-qi, [Beijing Institute of Technology, Beijing 100081, China], Chinese Journal of Explosives & Propellants. 2005, 28(2): 43-45.

Abstract: The reaction kinetics of synthesis of tetraacetyldiformylhexaazaisowurtzitane (TADF) by hydrogenolysis debenzylation of tetraacetyldibenzylhexaazaisowurtzitane (TADB) has been studied over $\text{Pd}(\text{OH})_2/\text{C}$ catalyst in formic acid. The experiment was investigated in an atmosphere of hydrogen. The effects of both internal and external diffusions were eliminated by stirring adequately. The effects of catalyst and solvent were eliminated by the experiments without adding substrate. The changes of the absorption amount of hydrogen with reaction time were measured. The absorption amount of hydrogen was used to stand for the reaction extent. Kinetics calculations of the experimental data at various temperatures were carried out, according to the integrate reaction rate equation. Experimental results indicate that the reaction is the first-order with respect to TADB under the experimental conditions. The apparent activation energy (E_a) of the reaction is 50.41 kJ/mol and preexponential factor (A) ($4.5326 \times 10^6 \text{ min}^{-1}$). It showed that the reaction of hydrogenolysis debenzylation of tetraacetyldibenzylhexaazaisowurtzitane in formic acid can undergo easily.

84. A New Technique for Preparation of Pentaerythritol Diazido Dinitrate, Su Tian-duo, Zhang Li-jie, Liu Heng, Zhang Hong-yu, Cui Rong, [Xi'an Modern Chemistry Research Institute, Xi'an 710065, China], Chinese Journal of Explosives & Propellants. 2005, 28(1): 52-53, 60.

Abstract: A new technique of preparing pentaerythritol diazido dinitrate (PDADN) via bromization reaction of pentaerythritol as starting material, azidation reaction of 2, 2-bromomethyl-1, 3-propanediol and nitration reaction of 2, 2-azido-1, 3-propanediol was presented. The structure of PDADN was characterized by IR, ^1H NMR and elemental analysis.

85. An Improved Synthetic Method of DADE with High Yield, Wang Xi-jie, Zhou Cheng, Wang Bo-zhou, Zhang Zhi-zhong, Fu Xia-yun, [Xi'an Modern Chemistry Research Institute, Xi'an 710065, China], Chinese Journal of Explosives & Propellants. 2005, 28(1): 61-62, 66

Abstract: An improved synthetic route for DADE was investigated by the nitration of 2-methyl-4, 6-pyrimidindione in nitric acid/sulphuric acid and hydrolysis of the intermediate 2-dinitromethylene-5, 5-dinitro-dihydro-pyrimidine-4,6-dione based on the perfect detonation properties of DADE and a comparison of its reported preparation methods. Its total yield is over 83%. The structure of DADE was characterized by IR, MS, NMR and elemental analysis.

86. Synthesis and Properties of 3-azidomethyl-3-cyanoethoxyl-methyloxetane Polymer, Gan Xiao-xian, Xing Ying, Li Na, Zhang Zhi-Gang, Lu Xian-Ming, [Xi'an Modern Chemistry Research Institute, Xi'an 710065, China], Chinese Journal of Explosives & Propellants.2004,27(4):10-13.

Abstract: With indirect method, a new liquid hydroxyl-terminated azider polyether binder, 3-azidomethyl-3-cyanoethoxyl-methyloxetane homopolymer (PAMCMO) was synthesized by 3-bromomethyl-3-cyanoethoxylme-thyloxetane homopolymer (PB MCMO) and sodium azide in DMF. PAMCMO had the following properties: number average molecular weights 2,500; glass transition temperature -38.75°C , decomposition temperature of azido group 257.35°C . PAMCMO had good compatibility with nitrate ester plasticizers, because the introduction of cyanoethoxyl group could increase its solubility parameter to $23.45(\text{J}/\text{cm}^3)^{0.5}$.

87. Synthesis and Characterization of C/N Heterocyclic Vinyl Ester Resin, Yang Shi-shan, Wang Ji-gui, Li Dong-lin, Gan Xiao-xian, [Xi'an Modern Chemistry Research Institute, Xi'an710065, China], Chinese Journal of Explosives & Propellants.2004,27(4):59-62.

Abstract: C/N heterocyclic vinyl ester resin (CNVER) was synthesized by the reaction of ISEP and methacrylic acid. The technological conditions of synthesizing CNVER were optimized. Influence of the molar ratio of epoxy group and carboxy group, the amount of catalyzer and the reaction temperature on the reaction was discussed. The structure of CNVER was confirmed by IR spectrum. Styrene was chosen as a cross-linking agent of CNVER. The properties of CNVER were studied. Its elongation is 7.2% and tensile strength 74.7 MPa, indicating that the mechanical properties of CNVER are good.

88. Preparation of Polyurethane-acrylate Core-shell Latex and its Coating of RDX, Lu Ming, [School of Material Science and Engineering, Beijing Institute of Technology, Beijing100081, China], Sun Jie,[Institute of Chemical Materials, CAEP, Mianyang 621900, China], Chen Yu, [School of Material Science and Engineering, Beijing Institute of Technology, Beijing100081, China], Luo Yun-jun, [School of Material Science and Engineering, Beijing Institute of Technology, Beijing100081, China], Tan Hui-min, [School of Material Science and Engineering, Beijing Institute of Technology, Beijing100081, China], Chinese Journal of Explosives & Propellants.2004,27(3):17-20.

Abstract: Waterborne polyurethane (WPU) was prepared with TDI, DL-400 ($M_n=340$), DMPA and BDO as main materials, whose structure was characterized by FTIR. Polyurethane-acrylate (PUA) latex was synthesized through the method of the seed-latex polymerization with WPU, water and butyl acrylate as starting materials, two kinds of initiator, AIBN and $(NH_4)_2S_2O_8-NaHSO_3$. Latex particles shape of PUA were determined through TEM, and the results indicated that PUA latex with core-shell structure was synthesized with AIBN as initiator, whose shell were black polyurethane particles and core white polyacrylate ones. PUA latex initiated by $(NH_4)_2S_2O_8-NaHSO_3$ has no core-shell structure. The method was used for the first time to deposit core-shell latex to coat RDX with 10% $KAl(SO_4)_2 \cdot 12H_2O$ solution, distilled water, 40°C. Through SEM, the surface of RDX was observed to have been covered with a layer of even film after being coated with PUA and the particles among RDX were perfectly dispersed.

89. Synthesis and Properties of 3,3-diazidomethyloxetane and its Polymer, Lu Xian-ming, Gan Xiao-xian, [Xi'an Modern Chemistry Research Institute, Xi'an 710065, China], Chinese Journal of Explosives & Propellants.2004,27(3):49-52.

Abstract: Using absolute alcohol as solvent, under the effect of NaOH, the 3, 3-dibromomethyl oxetane (BBMO) was synthesized by the cyclization of 1, 1, 1-tribromomethyl-1-hydroxymethyl methane. 3, 3-Diazidomethyloxetane (BAMO) was obtained by the substitution of BBMO with NaN_3 using 1, 4-butylene-glycol as initiator and CH_2Cl_2 as solvent, a solid energetic binder (PBAMO) was synthesized by the cationic polymerization of the monomer BAMO. The structure of the polymer was identified by H NMR,

FTIR, DSC and GPC. The physical chemistry properties of PBAMO are determined. The results show that PBAMO is an energetic binder with lower sensitivity; suitable melting point and lower melt viscosity and can be used as the composition of energetic thermoplastic elastomer.

90. Macro-kinetics Study of Ozone-mediated Nitration Reaction of Aromatic Compounds with Nitrogen Tetroxides, Lü Zao-sheng, [Wuhan University of Science and Technology, Hubei430081, China], Wang Xiao-yan, [Wuhan University of Science and Technology, Hubei430081, China], Lü Chun-xu, [Nanjing University of Science & Technology, Nanjing210094, China], Chinese Journal of Explosives & Propellants.2004,27(3):66-69.

Abstract: The kinetics character in ozone-mediated nitration aromatic compound reaction with nitrogen tetroxide has been studied. Kinetics model has been constructed with the aid of stable state treatment method. Raman spectrum shows no nitronium ion in N_2O_4/O_3 , which demonstrates N_2O_4/O_3 nitration aromatics, is not an affinitive electronic substitution process. Experiment results show that the reaction rate of N_2O_4/O_3 nitration benzene and toluene is zero order in benzene and toluene, half order in N_2O_4 , the reaction rate of N_2O_4/O_3 nitration fluorobenzene is first order in fluorobenzene, zero order in N_2O_4 . By competing reaction, Hamett's equation of $N_2O_4-O_3$ nitrating substituted aromatics is obtained with $\log f \sim \rho H = -7.26\sigma + p - 0.125$. The reaction constant ($\rho = -7.26$) is approaching to the result of mixture acid nitrating substituted aromatics, which shows the transition state that decides isomer distribution during two kinds of nitrating reaction has similar structure.

91. Hydrogenolysis Debenzylation of TADBIW in Propionic Acid and n-Butyric Acid, Liu Jin-quan, Ou Yu-xiang, Han Wei-rong, Chen Bo-ren, [School of Science of Materials and Engineering, Beijing Institute of Technology, Beijing100081, China], Chinese Journal of Explosives & Propellants. 2004, 27(2):10-12.

Abstract: Tetraacetyldibenzylhexaazaisowurtzitane (TADBIW) is a product of hydrogenolysis debenzylation of hexabenzylhexaazaisowurtzitane (HBIW). Various products can be formed from hydrogenolysis debenzylation of TADBIW in different media using Pd catalyst prepared at the lab. Tetraacetylhexaazaisowurtzitane (TAIW) is obtained by hydrogenolysis of TADBIW in propionic acid and n-butyric acid. The related reaction mechanism is also discussed.

92. Development of High Strained Caged Hydrocarbons Used as High Density Fuels, Xing En-hui, Mi Zhen-tao, Zhang Xiang-wen, [Technology, Tianjin University, Tianjin300072, China], Chinese Journal of Explosives & Propellants.2004,27(2):13-16.

Abstract: This paper introduces the recent development of a new class of high energy hydrocarbon fuels. These caged hydrocarbons with high energy and high density have been synthesized to be used as high energy fuels or fuel additives, with the expectation that their inclusion in the fuel mixture will result in a net increase in volumetric combustion value of the current generation of power-plants. These caged hydrocarbons exhibit high density and contain a moderate amount of strain energy, which contributes to the energy output during combustion. Research and development direction of caged hydrocarbon fuels are presented.

93. The Synthesis of Hexanitrohexaazaisowutzitane by Oxidation, Pang Si-ping, [School of Life Science & Technology Beijing Institute of Technology Beijing 100081, China], Yu Yong-zhong, [School of Material Science & Technology, Beijing Institute of Technology, Beijing100081, China], Zhao Xin-qi, [School of Material Science & Technology, Beijing Institute of Technology, Beijing100081, China], Chinese Journal of Explosives and Propellants. 2004,27(1):9-11.

Abstract: The way of synthesizing hexanitrohexaazaisowutzitane (HNIW) by oxidation was studied. HNIW was prepared by hydrolysis and nitration of the oxidation products of hexabenzylhexaazaisowurtzitane in 70% HNO₃/AN, system with the yield being 21%. The reaction mechanism of the nitration of N-benzoyl group on hexaazaisowutzitane as the parent ring of HNIW was discussed.

94. Synthesis of Keto-RDX Using Dinitrogen Pentoxide as the Nitrating Agent, Cao Duan-lin, Cao Ming-bao, Li Yong-xiang, [Dept.of Chemical Engineering, North China University of Technology, Taiyuan030051, China], Chinese Journal of Explosives & Propellants.2004,27(1):12-15.

Abstract: The synthesis of Keto-RDX with Urotropine, Urea as raw materials, the mixture of nitric acid and dinitrogen pentoxide as nitrating agent was studied. The best process conditions were concluded. Under the conditions the yield of Keto-RDX can be more

than 120%. By contrast, with the mixture of nitric acid and dinitrogen pentoxide as nitrating agent, mild reaction condition, higher yield and less contamination are the major advantages.

95. Synthesis and Characterization of Nitrocellulose Azidonitrate Glycidyl Ether, SHAO Zi-qiang, WANG Wen-jun, WANG Fei-jun, CHEN Fan-geng, TAN Hui-ming, [School of Materials Science and Engineering, Beijing Institute of Technology, Beijing 100081, China], Chinese Journal of Explosives & Propellants. 2004, 27(1):36-39.

Abstract: A kind of new high energetic binder—nitrocellulose azidonitrate glycidyl ether (NCAGE) for solid propellant was synthesized based on cotton cellulose pretreated by steam explosion. The process of preparing NCAGE included the following steps: (a) alkalization of the treated cellulose; (b) etherification of the alkali cellulose; (c) nitration of the water-soluble cellulose ether; and (d) azidation of nitrocellulose glycidol ether. The nitrogen content, structure and properties of NCAGE were measured and characterized by elementary analysis, DSC, FTIR and X-ray Diffraction. The results indicate that the nitrogen content of NCAGE can arrive at 15%~21% due to the presence of $-\text{ONO}_2$ and $-\text{N}_3$, and the product can absolutely dissolve in solvents such as acetone, decompose at the temperature of 204°C and has lower degree of crystalline compared to original cellulose.

96. Nitrosolysis-debenzylation to Tetraacetyldibenzylhexaazaisowurtzitane, Lu Lian-ying, Ou Yu-xiang, Wang Jian-long, [Beijing Institute of Technology, Beijing 100081, China], Chinese Journal of Explosives & Propellants. 2003, 26(4):41-43.

Abstract: Two benzyls were removed at mild conditions (at room temperature or at 30°C) from tetraacetyldibenzylhexaazaisowurtzitane (TADBIW) molecule through three methods by using inorganic materials as the nitrosolysis reagent to convert tetraacetyldinitrosohexaazaisowurtzitane (TADNSIW), the precursor for synthesis of hexanitrohexaazaisowurtzitane (HNIW). The structure of TADNSIW was determined by FT-IR, MS, (^1H) NMR and element analysis. The mechanism of debenzylation to TADBIW was put forward. The enamine is the intermediate of the nitrosolysis-debenzylation to TADBIW, which was approved by benzaldehyde being the by-product of the reaction.

97. The Synthesis of Large Particle Size TATB, Huang Ming, Luo Shun-huo, Tian Ye, [Institute of Chemical Materials, CAEP, Mianyang 621900, China], Chinese Journal of Explosives & Propellants.2003, 26(4):44-46.

Abstract: The influence factors on synthesis of TATB were described. The parameters affecting particle size of TATB, such as reaction temperature, ammonia flow rate, TCTNB concentration, stirring rate were optimized. The large particle size TATB was produced by the replicate experiment according to the optimized parameters and its average diameter of the particle exceeded 70 μm .

98. Study on HTPB Based PU/PIMA Interpenetrating Polymer Networks, GAO Tong zhai, TAN Hui min, [Beijing Institute of Technology, Beijing 100081, China], Chinese Journal of Explosives & Propellants.2003, 26(3):9-11.

Abstract: A new kind of interpenetrating polymer network (IPN) was synthesized by introducing IMA monomer into polyurethane (PU) based on hydroxy terminated polybutadiene in this paper. FTIR results demonstrated that the two monomers reacted completely. Tensile test indicated that the mechanical properties of IPNs were evidently enhanced with the introduction of PIMA. The microstructure of IPN was also investigated by TEM. The results revealed that the two phases interpenetrated proportionally and possessed preferable compatibility.

99. Synthesis and Properties of 3-Azidomethyl-3-nitratomethyloxetane and Its Polymer, Gan Xiao xian, Qiu Shao jun, Lu Xian ming, [Xi'an Modern Chemistry Research Institute, Xi'an 710065, China], Chinese Journal of Explosives & Propellants.2003, 26(3):12-15.

Abstract: 3-Azidomethyl-3-nitratomethyloxetane (AMNMO) was obtained by the cyclization, substitution and nitration of 2, 2-dibromomethyl-1, 3-propanediol. Through the cationic polymerization of the monomer AMNMO, a liquid high energetic binder (PAMNMO) was synthesized. The possibility of PAMNMO used as a plasticizer or binder in solid propellants was studied.

100. The Inhibitor of Epoxy Resin with Isocyanurate Group, Gao Chao, Gan Xiao xian, Qiu Shao jun, [Xi'an Jiaotong University, Xi'an710049,China], Chinese Journal of Explosives & Propellants.2003, 26(3):27-31.

Abstract: A novel epoxy resin containing isocyanurate group (ISEP) and a novel flexible curing agent (TPA) are synthesized. The mechanical properties of the composite by using biurea as filler are studied. Its tensile strength and elongation are 6.44 MPa and 124.15% at 20°C, 2.68 MPa and 85.24% at 50°C, 7.38 MPa and 24.09% at -40°C, respectively. A propellant is inhibited by this composite. The three-way smoke signature results of the inhibitor show that the transmit ratio of visible light and laser exceeds 80 percent, while 90.4% for IR. The thermal stability of the inhibitor is also studied by TGA.

101. A New Way to Synthesize Spherical KDNBF, Li Yu feng, Zhang Tong lai, Miao Yan ling, Zhang Jian guo, [State Key Lab of Prevention & Control of Explosion, Beijing Institute of Technology, Beijing 100081, China], Chinese Journal of Explosives & Propellants. 2003, 26(3):53-56.

Abstract: A new way was introduced to synthesize spherical crystal of potassium 4, 6-dinitrobenzofuroxanate (KDNBF). Crystal modifiers, such as PVA, Tween 80, Span, Na-CMC, Dextrin and Triton X were used to control the shape of KDNBF. Of all the crystal modifiers, Tween 80 behaved most satisfying. The product was characterized by using FT-IR, DSC and elemental analysis techniques.

102. Nitrosation of the Oxidation Products of Hexabenzylhexaazaisowurtzitane, Liu Jiang qiang, Chen Shu sen, Yu Yong zhong, Zhao Xin qi, [Beijing Institute of Technology, Beijing 100081, China], Chinese Journal of Explosives & Propellants. 2003, 26(3):60-61, 75.

Abstract: With 65% nitric acid / sodium nitrite system on the 6-benzyl-6 hexaazaisowurtzitane oxidation product 4-benzoyl-2-benzyl-6 hexaazaisowurtzitane and 5-benzoyl-1-benzyl-6-aza different alkyl Woods to nitrite solution, the remaining benzyl off will be converted to nitroso benzyl, and the four-benzoyl-2-nitroso-6 hexaazaisowurtzitane and 5-benzoyl-1-nitroso-6 hexaazaisowurtzitane.

103. Hydrolysis of Nitriles with Microwave Irradiation, ZHANG Qingshan, LU Baoping, GUO Bingnan, [Beijing Institute of Technology, Beijing 100081, China], Chinese Journal of Explosives & Propellants. 2003, 26(3):73-75.

Abstract: The hydrolysis of nitriles (benzyl cyanide (1), 4-hydroxybenzotrile (2) and 5-cyanoindole (3)) to give the corresponding acids (phenylacetic acid (4), 4-hydroxybenzoic acid (5) and 1H indole-5-carboxylic acid (6)) in the present of alkalis in water coupled with microwave irradiation was investigated. The optimum reaction conditions were determined through the test results. The optimum power of the microwave is 530 W and the optimum time of the reaction is 4 min for 1, 4.5 min for 2 and 7 min for 3, respectively. The yield is 87.9% for 4, 85.8% for 5 and 89.6% for 6 respectively.

104. Nitration of Toluene with NO₂-O₂ System, CAI Chun, LU Chun xu, [Nanjing University of Science and Technology, Nanjing210094, China], Chinese Journal of Explosives and Propellants.2003, 26(2):1-2,21.

Abstract: Toluene can be nitrated effectively with the system consisted of nitrogen dioxide and pressurized oxygen in the presence of inorganic oxides as catalysts, the partial pressure of oxygen has considerable effect on reaction results. The ratio of p-MNT in the product could be increased when the pore size of catalyst is similar to the diameter of benzene ring.

105. Synthesis and Properties of 1,7-diazido-2,4,6-trinitro-2,4,6-triazheptane, ZHANG Zhi zhong, WANG Bo zhou, SHI Zun chang, [Xi'an Modern Chemistry Research Institute, Xi'an 710065, China], Chinese Journal of Explosives & Propellants.2003, 26(2):3-4,7.

Abstract: 1, 7-diazido-2, 4, 6-trinitro-2, 4, 6-triazheptane was synthesized with urotuopine as primary substance by nitration, chlorization and azido substitution steps in turn, the yield is 75.3%. the properties of DATH have been experimentally studied, its density 1.71 g/cm³, melt point 135 ~ 137°C, detonation velocity 8300 m/s(1.64), heat of combustion 1.08×10⁴ kJ/kg, temperature of decomposition 192°C, friction sensitivity 12% (25 kg/cm², 66°) impact sensitivity 95% (2 kg, 25 cm).

106. Synthesis of Poly(aminotrinitropolyphenylene), Yu Zhan long, Wu Xiao qing, [North China Institute of Technology, Taiyuan 030051, China], Chinese Journal of Explosives & Propellants.2003, 26(2):22-23.

Abstract: Using polytrinitropolyphenylene (PNP) as initial materials, poly (aminotrinitroPhenylene) (PATNP) has been synthesized. The

structure and nature of prepared PATNP has been characterized by FTIR, DTA. The stability of PATNP is better than that of PNP and the sensitivity of PATNP is less than that of PNP. PATNP has potential applications in heat resistant explosives.

107. Oxidation of Derivatives of Hexaazaisowurtzitane, Liu Jiang qiang, Chen Shu sen, Yu Yong zhong, Zhao Xin qi, [Beijing Institute of Technology, Beijing100081, China], Chinese Journal of Explosives & Propellants.2003, 26(1):5-7,19.

Abstract: The oxidative debenzoylation of tetraacetyldibenzylhexaazaisowurtzitane in the system of ammonium peroxydisulfate/cerium ammonium nitrate/acetic anhydride has been studied. The benzyl group of hexabenzylhexaazaisowurtzitane is removed and tetraacetyldibenzylhexaazaisowurtzitane is successfully synthesized by this method.

108. Synthesis of Nanocomposite $\text{Bi}_2\text{O}_3\cdot\text{SnO}_2$ and Its Effect on Thermal Decomposition of RDX, Hong Wei liang, Zhao Feng qi, Liu Jian hong, [Shenzhen University, Shenzhen518060, China], Chinese Journal of Explosives & Propellants.2003, 26(1):37-39,46.

Abstract: Nano-composite oxide $\text{Bi}_2\text{O}_3\cdot\text{SnO}_2$ was synthesized by co-precipitation method using BiCl_3 and $\text{SnCl}_4\cdot 5\text{H}_2\text{O}$ as the reactant. The particle size, crystal form and phase were determined with XRD and TEM. Average particle size of samples was about 5 nm. The effect of nano-composite oxide $\text{Bi}_2\text{O}_3\cdot\text{SnO}_2$ on the thermal decomposition characteristics of RDX was investigated by DSC. The results show that due to the effect of nano-composite oxide $\text{Bi}_2\text{O}_3\cdot\text{SnO}_2$, the peak temperature of thermal decomposition of RDX shifts 13.7°C downward, the decomposition enthalpy ΔH of RDX increases 665 J/g (about 59.9%), and the apparent activation energy of the thermal decomposition of RDX decreases 48.42 kJ/mol.

109. Characterization of the Structure of Large Particle TATB, Huang Ming, Luo Shun Huo, Tian Ye, [Institute of Chemical Material, CAEP, Mianyang 621900, China], Chinese Journal of Explosives & Propellants. 2002, 25(4):23-24.

TATB is synthesized in the enclosed high pressure reactor. Anhydrous gaseous ammonia with a feed pressure of 0.42 MPa is allowed to enter the reactor at 155°C . Trichlorotrinitrobenzene is

gained in toluene on the liquid vapor interface after 8 hours. The average particle size of the production is above 40 μm , and sixty percent of the particles surpassed 40 μm . The production is proved to be TATB with FT IR, MS, elementary analysis and items defined in GJB3292 98. Its SEM photograph indicates obviously edges, corners and layers structure.

110. Nitrosation of the Oxidation Products of Hexabenzylhexaazaisowurtzitane, Pang Si Ping, Yu Yong Zhong, Zhao Xin Qi, [Beijing Institute of Technology, Beijing 100081, China], Chinese Journal of Explosives & Propellants. 2002, 26(4): 27-28.

Nitrosation of the oxidation products of hexabenzylhexaazaisowurtzitane monoacetyltribenzoyldibenzylhexaazaisowurtzitane (3), diacetyltribenzoyldibenzylhexaazaisowurtzitane (4) and triacetylmonobenzoyldibenzylhexaazaisowurtzitane (5) by 65% $\text{HNO}_3/\text{NaNO}_2$, the remained benzyl groups were removed successfully and gave the corresponding nitrosamine products monoacetyltribenzoyldinitrosohexaazaisowurtzitane (6), diacetyltribenzoyldinitrosohexaazaisowurtzitane (7) and triacetylmonobenzoyldinitrosohexaazaisowurtzitane (8).

111. Synthesis of TNAZ via Nitromethane, Bi Wei yu, Liu Qian, Zhang Zhi zhong, [Xi'an Modern Chemistry Research Institute, Xi'an 710065, China], Chinese Journal of Explosives & Propellants. 2002, 25(4):31-32.

Abstract: The title compound, a known melt castable high performance explosive, was synthesized starting with commercially available nitromethane and formaldehyde via a 5 step process. The overall yield was above 40%. Also, the mechanisms of ring closing/dehydration and oxidative nitration were elucidated in light of literatures.

112. Novel Development of Syntheses and Properties of 1,3,3-Trinitroazetidine (TNAZ), Ding Li, Li Ying bo, [Xi'an Modern Chemistry Research Institute, Xi'an 710065, China], Chinese Journal of Explosives & Propellants. 2002, 25(4):42-44,65.

Abstract: Review of routes for TNAZ synthesis since 1990 is presented. Properties of TNAZ such as physic chemical properties are introduced also. It is stated that TNAZ is highly energetic material more powerful than RDX, and which is suitable for

application as a castable explosive as well as a plasticizer.

113. Synthesis of Lead(II) and Copper(II) Salts of 4-Hydroxy-3,5-dinitropyridine Oxide, Zheng Yu mei, Deng Min zhi, Zhao Feng qi, Yuan Chao, [Shanghai Institute of Organic Chemistry Chinese Academy of Sciences, Shanghai 200032, China], Chinese Journal of Explosives & Propellants. 2002, 25(4):51-52, 13.

Abstract: The paper describes that synthesis of lead(II) and copper(II) salts of 4 hydroxy 3, 5 dinitropyridine oxide in good yields from pyridine via the multiple steps. The salts were characterized by M.S and microanalysis. DSC and TG experimental results of the salts showed that the salts could effectively catalyze the thermal decomposition of RDX, AP and NC+NG. Meanwhile, the decomposition heats of mixtures containing different salts were larger than those of the corresponding pure RDX, AP and NC+NG. The all facts suggested the salts might be better energetic burning catalysts.

114. Effect of Synthesis Method on Crystal Phase of Iron Oxide Nanocrystalline Powders, Liu Xiang xuan, Wang Xuan jun, Liu Zhen yu, Zhu Ming, LI You, [Xi'an Institute of high technology, Xi'an 710025, China], Chinese Journal of Explosives & Propellants. 2002, 25(4):85-86.

Abstract: Iron oxide Nano-crystalline Powders were prepared respectively by precipitation, stearic acid gel, polyethylene glycol gel, and citrate gel and iron citrate combustion. The influence of synthesis method on the final product, such as the crystal structure, crystalline grain size, dispersivity was studied. XRD results show that the pure α Fe₂O₃, Fe₃O₄ were synthesized respectively by precipitation, ionic citrate combustion, and mixture of α Fe₂O₃ γ Fe₂O₃ were gained by Sol gol method.

115. Fluorodenitration Using Tetramethylammonium Fluoride for Synthesis of Aromatic Fluorine Compounds, Cai Chun, Lu Chun xu, [Nanjing University of Science and Technology, Nanjing 210094, China], Chinese Journal of Explosives & Propellants. 2002, 25(3):31-32.

Abstract: Tetramethylammonium fluoride (TMAF) could be used as fluorodenitration reagent in synthesis of aromatic fluorine compounds from nitroaromatics. This process has the advantages of

mild reaction condition, high yield and little by reaction.

116. Synthesis and Properties of 3,3'-dinitroxazafurazan, Shi Yan shan, Li Zhan xiong, Ou Yu xiang, [Beijing Institute of Technology, Beijing 100081, China], Chinese Journal of Explosives & Propellants.2002, 25(2):14-15,27.

Abstract: dinitroxazafurazan (DNOAF) was synthesized from 3, 4 dinaminofurazan as a non hydrogen energetic compound. Its structure has been identified by IR, NMR, MS and elemental analysis .The standard formation enthalpy, detonation velocity and detonation pressure of DNOAF was calculated to be 640 kJ/mol, 9390 m/s and 40.5 GPa respectively. Calculation shows that the specific impulse is 269.2 s⁻¹ of NEPE propellant by substituting 20% of HMX with the title compound (if HNIW was substituted for HMX, the specific impulse is 268.7 s⁻¹).

117. Synthesis of O,O-Bis (β-azidoethyl)-α-(p-toluenesulfonamido) -Substituted-benzyl Phosphite Esters, Ye Ling, Zhou Yu lan, Xu Rui xing, [Capital University of Medical Science, Beijing 100054, China], Chinese Journal of Explosives & Propellants.2002, 25(2):16-18.

Abstract: A serial of Mannich compounds, including O,O bis(β azidoethyl) α (P toluenesulfonamido) substituted benzyl phosphite esters and O,O bis(β, β' diazidoispropyl) α (p toluenesulfonamido) m nitrobenzyl phosphite ester, were firstly synthesized and their structures were verified by IR, 1H NMR and element analysis respectively. In addition, the thermo stabilities of Mannich bases were analyzed by DTA.

118. Study on the Synthesis of Ultrafine Powder of Lead Carbonate, Ma Feng guo, Zhou Gui zhong, Liao Shuang quan, [Beijing Institute of Technology, Beijing 100081, China], Chinese Journal of Explosives & Propellants.2002, 25(2):12-16.

Abstract: Study on the synthesis of ultrafine powder of lead carbonate. The Ultrafine powder of lead carbonate crystallites was synthesized by chemical precipitation method. The influences of reaction temperature, reaction time and the ratio of reactants on the formation of lead carbonate crystallites were investigate. The TEM was used to characterize the samples. The graph TEM shows the product was hexagonal crystal and the size ranges from 1 to 15

micron. The results show that with chemical precipitation method, ultrafine powders of lead carbonate can be achieved.

119. Study on the Lab. Synthesis of HMX Using Dinitrogen Pentoxide as the Nitrating Agent, Ge Zhong xue, Li Gao ming, Hong Feng, Song Xin chao, [Xi'an Modern Chemistry Research Institute, Xi'an 710065, China], Chinese Journal of Explosives & Propellants.2002, 25(2):45-47.

Abstract: The method of synthesizing HMX is presented in this paper. Using DADN (1, 5 diacetyl 3, 7-dinitro 1, 3, 5, 7 tetranitrotetra-cyclooctane) as reactant, the HMX was synthesized in the nitrating agent of the mixture of dinitrogen pentoxide and nitric acid. The yield of HMX was more than 96%, mp 272.0 - 272.8. In addition, factors that affecting the yield of HMX were discussed preliminary.

120. Study on the Preparation Technique of M-cresol From M-toluidine, Hao Yan xia, Chen Shu sen, [Nanjing University of Science and Technology, Nanjing 210094, China], Chinese Journal of Explosives and Propellants.2002, 25(2):64-66.

Abstract: A new thought for preparing m cresol from m nitrotoluene via reduction, diazotiation and hydrolysis is proposed in this paper. The procedure of synthesizing m cresol from m nitrotoluene is researched mainly and the better reaction condition was acquired by the orthogonal. The yield of m cresol is above 77% under this reaction condition. Moreover, the effect of copper salt on the hydrolysis procedure of diazonium salt is discussed.

121. New Synthesis of TATB in USA, Wang Zhen-yu, Guo Hui-li, [Xi'an Modern Chemistry Research Institute, Xi'an 710065, China], Chinese Journal of Explosives & Propellants.2001, 24(4):68-70.

Abstract: Two kinds of new synthesis method of TATB are introduced. Picramide was used as reactant in one method, sonochemically-aminated TATB was synthesised in the other method.

122. Synthesis of Nanometer PbO,Bi₂O₃ and Their Effect on Burning Properties of Solid Propellants, Hong Wei liang, Zhao Feng qi, Liu Jian hong, Tian De yu, [Department of Chemistry and Biology, Normal College, Shenzhen University, Shenzhen 518060, China], Chinese Journal of Explosives & Propellants.2001,24(3):7-9.

Abstract: Nanometer PbO and Nanometer Bi₂O₃ were synthesized by solid state reaction using Pb(NO₃)₂, Bi(NO₃)₃ with NaOH at room temperature. The crystal form, particle size and morphology of nanometer PbO and Bi₂O₃ were characterized by XRD and TEM. The effect of two nanometer catalysts on burning Properties of RDX CMDB propellant was investigated. The results show that nanometer Bi₂O₃ can increase the burning rates of the propellant and lower burning rate pressure exponent.

123. Study on Nitrolysis of TADCIW, Liu Li hua, Ou Yu xiang, Wang Jian quan, Cheng Bo ren, Lei Xiang yang, [Beijing Institute of Technology, Beijing 100081, China], Chinese Journal of Explosives & Propellants.2001, 24(3):16-19.

Abstract: The effects of nitrolysis agents and reaction conditions on the purity and yield of nitrolysis product of tetraacetyldichloroacetylhexaazaisowurtzitane (TADCIW) were investigated, and the related reaction mechanism was discussed. Tetranitrodichloroacetylhexaazaisowurtzitane (TNDCIW) with high purity could be obtained in high yield (94%~98%) by nitrolysis of TADCIW using a mixture of fuming nitric acid and concentrated sulfuric acid or a mixture of alkali metal nitrate and concentrated sulfuric acid as nitrolysis agents. Besides, the mixture acid from fuming acid and concentrated sulfuric acid could be reused. In the case of nitrolysis agent of a mixture of fuming nitric acid and phosphorus pent-oxide or a mixture of concentrated nitric acid and concentrated sulfuric acid, the yield of TNDCIW was quite low (13%~40%).

124. The Improvement of Synthetical Techniques of Tetranitrodibenzo-1,3a,4,6a-Tetrazapentalene, Li Zhan xiong, Ou Yu xiang, Chen Bo ren, [Beijing Institute of Technology, Beijing 100081, China], Chinese Journal of Explosives & Propellants.2001, 24(2):32-34.

Abstract: TACOT was synthesized by the improved techniques, the time of reaction was shortened to a half, and the operation was predigested. Moreover, the total yields have been increased from 26.7% to 52.0%. These methods reduced the cost of TACOT greatly.

125. Synthetic Principle and Application of Lubricant G for Glass Fiber, Ren Chuan rong, Li Tao qi, Yao Yi lun, [Xi'an Modern Chemistry Research Institute, Xi'an 710065, China], Chinese Journal of Explosives & Propellants.2001, 24(2):69-72.

Abstract: This paper describes a new idea on condensation reaction principle of dicyanodiamide and formaldehyde according to manufacture of lubricant G for glass fiber, and the synthetic technology and the application are discussed.

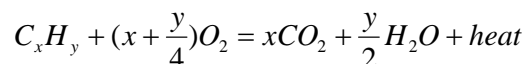
126. Synthesis of 2,4,6-Trinitro 2,4,6-triazacyclo-hexanone (Keto RDX), Zhang Yue jun, [Nanjing University of Science and Technology, Nanjing 210094, China], Chinese Journal of Explosives & Propellants. 1999, 22 (4):1-3,6.

Abstract: This paper reports the method of synthesizing 2, 4, 6 tri-nitro 2, 4, 6 triazacyclohexanone (Keto RDX) from DPT (or PHX) and urea (or nitrourea) in several kinds of nitrating agents. There are primary investigations on reaction forms of nitrolysis fragments of DPT, PHX and BSX, and on the mechanism of forming by products. Experimental results showed that the nitrolysis fragments N, N dihydroxymethylamines that were not directly substituted by nitro groups condensed with urea or nitrourea to form Keto RDX, while N, N dihydroxymethylnitroamine did not. Using DPT as a reactant, the yield of Keto RDX was 69% (one mole Keto RDX per mol reactant), and by products were HMX, RDX and small molecule fragments. Using PHX, the yield was 36%, and by products were HMX and small molecule fragments. While using BSX, no Keto RDX product and no cyclonitroamine by products were obtained.

Chapter 5

Combustion

Combustion, a reaction involving the production of heat, is one of the most common topics in the energetics field. Combustion is defined as the sequence of exothermic chemical reactions between a fuel and an oxidant accompanied by the production of heat and conversion of chemical species. The release of heat can result in the production of light in the form of either glowing or a flame. Fuels of interest often include organic compounds (especially hydrocarbons) in the gas, liquid, or solid phase. The most common combustion reactions involve hydrocarbons and oxygen, reacting to produce water and carbon dioxide, as shown in the stoichiometric chemical equation below:



One of the most simple combustion reactions can be in the reaction of hydrogen and oxygen, which is a commonly used combustion in rocket engines. This reaction will result in water vapor, as illustrated in the stoichiometric chemical reaction:



However, most combustion processes involve multiple chemical reactions with a complicated series of heat and mass transfers. Every combustion reaction is governed by the First and Second Laws of Thermodynamics: the conservation of energy and the existence of entropy, respectively. During a combustion reaction, the final temperature will always exceed the initial temperature. The amount of heat produced will be directly related to the change in internal energy of the system.

The fuels in combustion can be in a solid, liquid, or gaseous form. Combustion of a liquid fuel in an oxidizing atmosphere actually happens in the gas phase. The vapor burns, not the liquid. Therefore, a liquid will normally catch fire only above a certain temperature: its flash point. The flash point of a liquid fuel is the lowest temperature at which it can form an ignitable mix with air. It is also the minimum temperature at which there is enough evaporated fuel in the air to start combustion. Solid fuel combustion consists of three relatively distinct but overlapping phases:

- Preheating phase: When the unburned fuel is heated up to its flash point and then fire point, flammable gases start being released.
- Gaseous phase: When the mix of flammable gases released and oxygen is ignited, energy is produced in the form of heat and light. Flames are often visible. Heat transfer from the combustion to the solid maintains the evolution of flammable vapors.
- Solid phase: When the output of flammable gases from the material is too low for the persistent presence of flame, the charred fuel does not burn rapidly anymore but just glows and later only smolders.

Combustion, however, requires an oxidizer as well as fuel. The oxidizer involved in the combustion process is most often air, because it contains oxygen, though alternatives exist, such as thermal oxidizers, which are more environmentally friendly.

There are multiple types of combustion, including turbulent combustion, microgravity combustion, smoldering combustion, slow combustion, and rapid combustion. However, rapid combustion is really the only combustion of interest in the energetics field due to the large amount of heat released when it occurs. Rapid combustion is defined as a form of combustion in which large amounts of heat and light energy are released, which often results in a flame. This is used in machinery such as internal combustion engines and in thermobaric weapons. Sometimes a large volume of gas is liberated in combustion besides the production of heat and light. The sudden evolution of large quantities of gas creates excessive pressure that produces a loud noise. Such combustion is known as an explosion. Rapid combustion does not necessarily require oxygen; e.g., hydrogen burns in chlorine to form hydrogen chloride with the liberation of heat and light characteristic of combustion.

Combustion reactions are often difficult to study due to high pressures and temperatures as well as the speed of the reaction. However, there are many ways that scientists and engineers can measure and

extract information from combustion reactions. Differential scanning calorimetry (DSC) is a thermal analysis technique used to measure the amount of energy an exothermic reaction produces. It is extremely useful in the energetics field, as the technique can be used to study not only combustion reactions, but also crystallization and fusion processes [24, 26, 32, and 117]. In an experiment using DSC, the difference in the amount of heat required to increase the temperature of a sample and reference is measured as a function of temperature. Both the sample and reference are maintained at nearly the same temperature throughout the experiment. DSC is also useful in measuring the burning rate of a reaction using the linear combustion rate of a compound [32]. Higher pressures and temperatures will increase the burning rate of a compound substantially. Recent articles have shown, however, that although the flame temperature increases with a pressure increase, this does not necessarily imply a relationship between the flame temperature and the burning rate.

Other techniques used to study combustion include thermogravimetric analysis (TGA) and differential thermal analysis (DTA) [100]. TGA measures changes in the weight of a sample versus changes in temperature. It is useful for determining the decomposition points and degradation temperatures of a reaction. This method can also be used in conjunction with DSC to improve results even further. DTA is similar to DSC as it also records changes in temperature versus time. DTA is useful for measuring enthalpy change during a reaction. Other testing methods will be discussed specifically with their applications in the research of rapid combustion of energetic materials.

Many improvements can still be made regarding combustion in the energetics field. Efficiency is always of primary concern. A more efficient combustion system means less fuel wasted and thus more energy output. One method of improving efficiency is to alter the content of the substance added [67, 83, 88, 141]. In addition, the composition of fuel can have a major effect on efficiency [43, 131, 137, 173]. Changes in the oxidant can also have similar effects on efficiency. Safety operation is another area that needs further exploration in the energetics field. For instance, there may exist accidental firing or explosion of an industrial electric detonator during manufacture, storage, or transportation or in use. In order to prevent accidents and avoid the resulting damage and losses, the various causes of the accidents have been analyzed and corresponding preventive measures were recommended by Hao Jian-chun [16]. Other concerns beyond efficiency in rapid combustion include environmental concerns, safety operation, as well as economical utilization. Environmentally, combustion of energetic

materials is actually beneficial, as it helps to dispose of harmful material, such as asbestos and chlorine.

5.1 Research in Combustion

Combustion has always been a topic of interest to Chinese researchers. Publications reached a peak in 2004, representing 25% publications in the energetics field. Recently, combustion and detonation research has been in decline, though it still accounts for over 8% of research publications in China's energetics field.

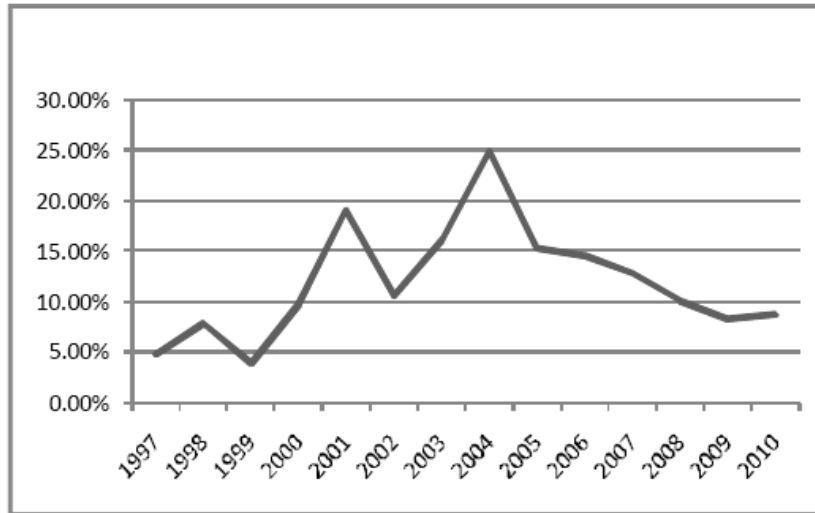


Figure 5.1: Research in combustion and detonation

Recent work in combustion has been conducted by Wang Qiong-lin, Wei Lun, Guo Feng, Zhang Yuan-bo, and Li Ji-zhen. In particular, Wang Qiong-lin, Wei Lun, and Guo Feng, all at the Xi'an Modern Chemistry Research Institute, have done extensive research on gun propellants. Both multilayer gun propellant and controlled burning gun propellant have been examined, with particular attention to progressive burning behavior. Li Ji-zhen, also from the Xi'an Modern Chemistry Research Institute, has recently conducted research involving the effects of ammonium perchlorate and aluminum powder on the burning rates of certain propellants. He has particularly done research involving composite modified double-base propellants (CMDDB) and high-energy modified double-base propellants (HEMDB).

Explosives and propellants usually exhibit characteristics of rapid combustion. Therefore, the topic has been widely studied in the energetics research field. This research focuses on explosives and propellants and is discussed in more detail in the following sections.

5.1.1 Detonation and Deflagration

Explosive and propellant materials can be categorized by the speed at which they expand. Materials that detonate (explode faster than the speed of sound) are said to be high explosives, and materials that deflagrate are said to be low explosives. Detonation is a supersonic exothermic front accelerating through a medium that eventually drives a shock front propagating directly in front of it. They are observed in both conventional solid and liquid explosives, as well as in reactive gases. The velocity of detonations in solid and liquid explosives is much higher than in gaseous ones, which causes far clearer resolution of the wave system in the latter. Gaseous detonations normally occur in confined systems, but they are occasionally observed in large vapor clouds as well. A variety of fuels may be present as gases, as droplet fogs, or as dust suspensions. Other materials, such as acetylene, ozone, and hydrogen peroxide are detonable in the absence of oxygen. Oxidants include halogens, ozone, hydrogen peroxide, and oxides of nitrogen and chlorine.

Deflagration is used to describe subsonic combustion that usually propagates through thermal conductivity (hot burning material heats the next layer of cold material and ignites it). Most “fire” found in daily life, from flames to explosions, is technically deflagration. Deflagration is different from detonation (which is supersonic and propagates through shock compression). Deflagrations are easier to control than detonations in engineering applications. Consequently, they are better suited when the goal is to move an object (a bullet in a gun, or a piston in an internal combustion engine) with the force of the expanding gas. Typical examples of deflagrations are the combustion of a gas-air mixture in a gas stove, a fuel-air mixture in an internal combustion engine, the rapid burning of gunpowder in a firearm, or pyrotechnic mixtures in fireworks. Tan et al. [165] originated the concept of using steady deflagration as a propelling energy source of traveling charge, which can be applied in gun propulsion techniques.

5.1.1.1 Detonation

Studies on detonation properties are a major topic in detonation research. Detonation property parameters such as detonation velocity, time of detonation development, detonation pressure, detonation wave emissivity, and detonation temperature, etc., have been used to describe the detonation process and evaluate detonation reliability. For example,

Xu et al. conducted an experimental study on continuous detonation velocity of modified ANFO [18]. Their studies showed that the energy of explosives with priming is larger, and the time of detonation development and run distance are shortened, i.e., the modified ANFO with priming has steadier detonation. Other studies [6, 59, 80, 139, and 166] have been conducted to investigate detonation parameters, including pressure, detonation temperature, and detonation wave emissivity for different explosives. Ding and Yuan [6] studied the characteristics of detonation waves in dual explosives under asymmetrical initiation. The shape of the detonation front, the t vs. d coordinates, and the shape distribution of the detonation wave was gained by the slit scan technique of the rotating mirror camera. The velocity distribution, the reason of the concave detonation front developed, and the spread rule of the detonation convergence wave were analyzed. In a study by Gao, et al. [80], ionization probes and a manganin gauge were used to measure detonation velocity and pressure, respectively. Generally, detonation wave emissivity and detonation temperature measurements cannot be carried out simultaneously. Yuan et al. [166] applied the method of detonation wave emissivity and detonation temperature measurement by imaginary auxiliary source reflection to measure the detonation wave emissivity and detonation temperature of liquid explosive nitromethane (NM). Zhou et al. [68] studied detonation velocity to develop a two-directional energy-focusing cutter in which low-cost industry dynamite with low detonation velocity is used to form the main detonator, and two high explosive strips are used to form a supporting detonator to boost the main detonator to produce strong focusing gas and metal shoot. This two-directional cutter has actually been used in demolition engineering for fore-splitting and smoothing blasting.

In addition, the explosive particle size and shape exerts an influence on the detonation properties. Miao et al. [134] studied the mechanism of aluminum size and shape influence on the aluminized explosives by means of the secondary reaction theory and the heat dilution theory, which indicated that the fundamental factor is the specific surface area modified with different shape and particle sizes of aluminum. Similarly, the effect of aluminum particle size on the expansion process of NM was studied by Luo et al. [82].

Detonation transfer reliability is another topic that has been investigated in recent years. Wen Shang-gang [35] developed a testing method to evaluate the reliability of detonation transfer performance. This analysis method is useful for designing an interlayer initiation train or to evaluate the reliability of a train. Fei et al. [79] evaluated the reliability of detonator components used in a nuclear warhead stored for

several decades by adopting a GSJ high-speed video camera and a spark detonator synchronous explosive device.

5.1.1.2 *Deflagration-to-Detonation Transition*

It is important to distinguish between detonations and deflagrations in terms of external damage. In deflagration, the exothermic wave is subsonic and the maximum pressures are at most a quarter of those generated by detonations. Processes involved in the transition between deflagration and detonation are covered thoroughly in the field of energetic materials and are generally known as deflagration-to-detonation transition (DDT). DDT is the phenomenon where deflagration turns into detonation. It is practical mainly because detonation provides much higher combustion efficiency than deflagration.

Experiments on DDT for different explosives have been conducted in numerous studies. Specifically, studies have been carried out on the DDT of granular HMX and JOB 9003 explosives [131], fine flake aluminum dust-air mixtures [8], high density explosives [11], modified double base (DB) propellants [51], nitrate ester plasticized polyether (NEPE) propellants [53], and composite B [58]. In the research conducted by Huang et al. [131], the effects of the composition, density, and confinement of explosives on the DDT process were studied and the principles of explosive DDT were analyzed. Their experimental results illustrate the compositions and the charge conditions of explosives that have an influence on DDT behavior.

Li et al. [8] studied the DDT of fine flake aluminum dust-air mixture under weak ignition of 40J in a horizontal tube with an inner diameter of 199mm and length of 29.6m and equipped with 40 sets of a special dust dispersion system. The influences of aluminum dust concentration and ignition delay time on the DDT process of aluminum dust-air mixture were discussed. The experimental results show that the whole DDT process of aluminum dust-air mixture can be divided into a slow reaction compression stage and a fast reaction shock stage.

The characteristics of DDT in pressed high-density explosives are another interesting topic in the research field of DDT. For instance, Wang et al. [11] studied the effect of the amount of black power and confinement conditions on the DDT process of pressed high-density explosives. Composite B, which is widely applied in conventional weapons, is another topic that has been examined carefully in the DDT field. Wen et al. [58] conducted an experimental study to explore the different mechanisms at work in the DDT of three kinds of 40/60-TNT/RDX-composition B with different densities. Their results demonstrated that there is a critical density for transition to detonation at

certain confinement conditions. Transition from deflagration to detonation is easier for low-density explosives.

As with explosives, DDT of propellants has also been studied in recent years in China. The characterization parameters and factors influencing DDT of propellants are introduced in various studies. An example of such studies is an investigation conducted by Zhao [53]. The transition characteristics of the deflagration to detonation of NEPE propellant slurry in the mixing process was studied by means of a DDT tube, a photoelectric cell, a strain gauge, and a witness board. They concluded that NEPE propellant slurry has the possibility of deflagration to detonation transition because the vertical mixer is hermetic and the propellant slurry is inhomogeneous in the mixing process. Another study on the DDT of propellants was carried out to evaluate the effect of 4,4'-azobis(4-cyanopentanol) (ACP), a fast burning energy material, on a modified double-base propellant under the condition of porous charge [51]. The results showed that the fast burning material ACP could increase the transition tendency of the modified double base propellant to DDT.

5.1.2 Combustion Ignition

Ignition generally refers to the heating of a compound or mixture to the point of combustion, as by electric current, friction, or mechanical shock. It can also refer to an electrical system that provides the spark to ignite the fuel mixture.

5.1.2.1 Plasma Ignition

The application of plasma ignition systems in explosives and propellants is a topic that has been studied extensively in recent years. Although most studies have been carried out on its application to propellants, a few have been conducted with primary explosives. One such study was an investigation of the relationship between semiconductor bridge (SCB) plasma ignition energy and the chemical characteristics of primary explosives including lead azide (LA), lead styphnate (LTNR), nickel hydrazine azide (NHA), nickel hydrazine nitrate (NHN), tetrazene (Tz), and lead picrate (LP) [1]. The experimental results demonstrated that there is a correlation between plasma ignition energy and explosive characteristics, such as critical temperature.

Some studies on propellants have compared plasma ignition with regular ignition (e.g., [21]) and have demonstrated propellant performance improvement with plasma ignition. In an interrupted combustion experiment of SF-3 propellant with plasma ignition conducted by Zhang et al. [21], two comparative tests related to

combustion performance and interruption combustion were carried out with a vented chamber under the conditions of plasma ignition and regular ignition. The changes to the burned surface were examined with a scanning electron microscope (SEM). The results indicated that there were many micro holes on the burned surface after the propellant had been ignited by a plasma generator. The existing micro holes increased the burning area on the surface of the propellant and led to the deviation of the SF-3 propellant burning with plasma ignition from the geometric burning rule to a certain extent. This difference showed that the combustion performance of SF-3 propellant could be affected by the high temperature C and Cu particles that were produced by the plasma generator.

Furthermore, some propellants have a long delay time for ignition and difficulty in ignition, such as energetic thermoplastic elastomer (ETPE) propellant. In order to solve the problem of the long delay time of ignition and the difficulty in ignition, the ETPE propellant was ignited by the electrical arc plasma, which was generated by a plasma producer via high power pulse electrical power in a study conducted by Zhao et al. [22]. The ignition and combustion characteristics of ETPE propellant were studied under the effect of plasma. The results indicated that in comparison to the usual method of ignition, the plasma effect made the burning rate of the ETPE propellant enhance significantly. In addition, the delay time of ignition was shortened, and the consistency of ignition was improved. These improvements were caused by the strong effect of plasma flow with high temperature and high speed. This effect causes RDX grain leaping over the process of heat absorption and liquation and entering into the process of decomposition and rapid heat release. Liu and Zhang [31] developed a semiconductor bridge ignition model that can be used to obtain the ignition delay time by the input energy, pellet radius, and plasma temperature.

Finally, it has been proved that plasma can be successfully used to optimize and control the propellant ignition process in the solid propellant electro thermal chemical (SPETC) propulsion concept. However, to date, the mechanisms have not been very clear on how plasma could modify propellant gas generation. Many scholars have tried to explain the plasma propellant interaction mechanisms by a series of tests [151, 140]. These experimental studies and their results provided evidence for the study of the mechanism of plasma interior ballistic ignition.

5.1.2.2 Ignition of Explosives

Studies of the ignition of explosives have been carried out to characterize different ignition systems, such as thermal ignition [157],

laser ignition [155, 162, 36], boron ignition [169], shock waves [90], and flyer-initiating devices [84, 146, 52]. In an experimental study conducted by Du and Feng [157], thermal ignition of black powder and single-base powder by an electrically heated wire was experimentally studied. The critical ignition current through the wire and the time-to-ignition were measured, and the temperatures of the wire when the ignition of the powders occurred were determined.

Duan and Wang [169] conducted a study to improve the ignition and combustion performance of boron. Studies on laser instruments for ignition have become more popular in recent years (e.g. [162 and 36]). Zhao et al. [162] carried out an experiment on the ignition properties of solid energetic materials using a laser that was generated by powerful laser instrument: ND YAG. The influence of the laser on the ignition properties, such as different energy levels, pulse width, different frequencies of laser instruments, and different webs of propellants, was studied and analyzed.

To investigate the characteristics of solid explosives initiated by shock waves, the Card Gap Test was carried out for JO-9195 explosives and recorded with a high speed camera in a study by Chen et al. [90]. The critical thickness of the Plexiglas clapboard to initiate the explosion was predicted and the shock initiation model of the explosives was given. Numerical simulations of explosive initiation were conducted. The pressure histories inside explosives under shock wave loading were calculated. The threshold pressure to initiate the explosive and the run distance of detonation were discussed. In order to improve the design of exploding foil initiation systems, the velocity of Mylar flyer driven by exploding foil was measured using a velocity interferometer system for any reflector (VISAR) [52]. The principle of VISAR and the experimental setup and measuring method to determine the velocity of Mylar flyer were introduced. The velocity history of Mylar flyer was given at different charging voltages and various exploding bridge sizes. The discharge circuit parameter, electromagnetic interference, and emission of light from shock and reflectivity affecting the velocity measurement were discussed. The velocity of Mylar flyer was successfully measured by VISAR.

In addition, studies have been conducted to improve ignition performance, such as those by Duan and Wang [169] and Hu et al. [93]. To improve the initiating capacity of booster pellets, Hu et al. [93] applied a multi-point synchronous explosive circuit to initiate the booster ring. A “one in four out” and “one in eight out” synchronous explosive circuit was designed. The experimental results indicated that the initiating capacity of the booster pellet ring was significantly improved by applying the multi-point synchronous explosive circuit. Similarly, in

order to develop a new civil ignition powder with better efficiency, Al, Mg, KNO_3 , and S were used as major elements to form a new type of ignition composition in a study conducted by Tian et al. [73]. The orthogonal design method was used to optimize the formulations. The igniting efficiency of the selected optimal powder was tested by Bruceton's method. The results indicated that the ignition performance of the optimal new ignition powder is better than that of black powder. The new ignition powder can ignite the thermite reliably.

The sensitivity of ignition systems obviously has safety issues. Duan and Zhang [25] designed a transient ignition system along with a testing system to study ignition sensitivity. Transient ignition devices are based on high-voltage discharge, and the ignition energy testing system is based on the DPO5054 oscillograph. Through igniting the fuel air explosive (FAE), fifty percent of an ignition energy of 2.443J is obtained. This offers a new method for accurate testing of the ignition energy of a sample.

5.1.2.3 Ignition of Propellant

The study of the ignition of propellant is well established, just as is the study of explosives. Some specific studies concentrated on propellants include [153, 107, and 136]. In these studies, the ignition and combustion behaviors were investigated by experimental means and/or combined with theoretical analysis. For example, Yu and Du [153] used a six-channel instantaneous optical pyrometer to determine the temperatures of ignition and combustion of two propellants at different pressures. Optical devices were also used in a study conducted by Yu et al. [154] in which optical computerized tomography and multimedia computer techniques were used to visualize and analyze the ignition process of an energetic droplet LP1846 under atmospheric pressure. The time series interference graphs of the droplet from heat decomposition to combustion were showed dynamically. The ignition temperature of the droplet was also calculated. Yang et al. [107] conducted closed vessel experiments to study the ignition and combustion behavior of a type of

LOVA propellant based on RDX. The interaction mechanism of plasma and LOVA (Low Vulnerability Gun Propellants) propellant was discussed for further research into the configuration of propelling charge and enhanced combustion effect in electrothermal-chemical (ETC) firing. Yu Bin conducted experimental studies and theoretical analysis of ignition and flame spreading, as well as interior ballistic cycles in guns with modular charges in his thesis [136]. Lei et al. [81] conducted clapboard experiments to study the influence of shock waves on the detonation performance of hydroxy-terminated polybutadiene (HTPB) / ammonium perchlorate (AP) composite propellant used in a plus

penetrator. The results show that the HTPB/AP composite propellant can be detonated reliably by means of reasonably controlling the shock wave intensity. This new method can be used for the initiation of other propellants. To design the igniter of similar solid rocket motors, celluloid was adopted as the igniter case and black powder as the amorcer (a cap that consists of a paper envelope containing explosive composition) and ignition pressure was chosen as the criterion for igniting the propellant in a study conducted by Zhang et al. [69]. A simulation combustion container was made to obtain the ignition characteristics of the igniter, such as the ignition peak, the delay time, and the opening manner of the nozzle closure. The ignition tests of the primer's ignition and electric-squib ignition at different conditions were studied, respectively.

Improvements on different ignition materials applied on propellants have been made in the past few years, such as those used in explosives. Examples include the new formulas developed by Du et al. [130] and the pyrotechnic composition Mg·Al Ba(x)n 308A proposed by Hao Jian-chun [171] to improve the ignition efficiency of regular black powder. The different ignition agent formulas were composed with the usual ignition materials such as NC, NH_4ClO_4 , BP, and so on, and their ignition capabilities igniting nitramine propellants were examined. The new type of ignition agent formulas, which could improve nitramine propellant ignition properties, were obtained through the ignition simulated tests comparing the single base propellants.

Tan et al. [146] studied the effect of a barrel on a flyer initiating system. The key parameters of the barrel, such as the material, length, and diameter, were determined to ensure the effect of a small flyer initiating system. Some other examples include the two ignition methods investigated to reduce the pressure wave in a large caliber gun propelling charge with high loading density by Xiao et al. [150]. The first ignition method is to add a crosswise igniter and upper ignition bag on the base of a standard igniter. The second ignition method is to use a low velocity detonation igniter instead of a standard igniter while at the same time adding a crosswise igniter. The firing test results of the propelling charge with high loading density showed that both of the two methods could meet the requirements for ignition. Compared with the standard igniter, the first ignition method could ignite the charge simultaneously and entirely, but the pressure wave phenomena in barrels are significant. The flame spreading velocity of the second ignition method is faster than that of the first ignition method. The ignition pressure could be established quickly, and the ignition delay time of propelling charge is short. The frequency spectral analyses show that the second ignition method could weaken and restrain the high frequency vibration and improve the characteristics of vibration in a high loading density charge.

Gun propellant ignition and combustion performance can be improved using energetic binders, as demonstrated by Zhang et al. [109]. Two kinds of LOVA gun propellants with different binders were prepared in their study: L15A (RDX: 76%, NC: 4%, DOP: 8%) and L13A (RDX: 76%, NC: 4%, CAB: 12%, ATEC: 8%). The ignition and combustion behaviors were investigated with a closed bomb and a simulator of ignition and combustion. The results indicated that the LOVA gun propellants are difficult to ignite; however, its ignition behavior can be improved by adding AP into the igniter. The results showed that the LOVA propellant with an energetic binder has a better ignition ability compared to LOVA propellant with an inert binder. Furthermore, the results indicated that the characteristics of low burning rate in lower pressure will improve the dynamic conditions in bore and bring preferable adaptabilities of interior ballistics so that RGD7 propellant can be safely used in guns. However, its mechanical performance in lower temperatures could be further improved.

5.1.3 Combustion Catalyst

Catalysis is the change in rate of a chemical reaction due to the participation of a substance called a catalyst. Unlike other reagents that participate in the chemical reaction, a catalyst is not consumed by the reaction itself. A catalyst may participate in multiple chemical transformations. Catalysts that speed the reaction are called positive catalysts. Catalysts that slow the reaction are called negative catalysts, or inhibitors.

Catalysts generally react with one or more reactants to form intermediates that subsequently give the final reaction product and in the process regenerate the catalyst. Catalysts work by providing an (alternative) mechanism involving a different transition state and lower activation energy. Consequently, more molecular collisions have the energy needed to reach the transition state. Hence, catalysts can enable reactions that would otherwise be blocked or slowed by a kinetic barrier. Numerous studies have been carried out to investigate the effect of a catalyst on rapid combustion, because catalysts may increase the reaction rate or selectivity or enable a reaction at lower temperatures. In addition, the exhaust from the burning of fuels can be treated via catalysis. Catalytic converters, which are typically composed of platinum and rhodium, can break down some of the more harmful byproducts of exhaust. Catalytic combustion is especially valuable in the field of propellants.

Investigations have been conducted to study the catalytic combustion of various propellants. The focus is mainly on the reaction mechanism, rules of combustion, and enhancements in burning rates while decreasing

the pressure exponent [143]. Different types of catalysts have different effects on the combustion properties of propellants, as demonstrated by various studies [e.g., 143, 64, 156, 41, and 119]. Wang et al. [64] studied the effects of catalysts (carbon black, C(60), fullerene soot, carbon fiber, and carbon nano-tubes) in solid propellants. It was found that the carbon black and C(60) in double base (DB) or composite modified double base (CMDB) propellants could enrich catalysts and prevent catalysts from conglomerating. These two catalysts can reduce the pressure exponent of double base systematic propellants and enhance the burning rate at low pressure of double base systematic propellants. The carbon fiber improves the conduction of heat exchange, increases the intensity of propellant, enhances the burning rate of propellant, and prevents the propellant from cracking. The carbon fiber and carbon nano-tube in propellants promote the decomposition of energetic materials and enhance the burning rate of composite propellants.

Metal oxides are a type of catalyst that has been widely used in propellants. An et al. [156] used metal oxide in hexanitrohexazaisowurtzitane (HNIW) to study the catalytic combustion. The burning rate of HNIW was compared with that of HMX monopropellant. The results indicated that the burning rate of HNIW monopropellant could be changed by adding metal oxide, but the pressure exponent of a burning rate is not changed by metal oxide. In another study conducted also by An et al. [138] the combustion property of HNIW monopropellant was studied by adding some additives. The results of the experiments indicated that the decomposition products of HNIW affected the burning behaviors of HNIW monopropellant. The burning rate of HNIW monopropellant was decreased through adding the products of the decomposition of HNIW. The catalysts used in the experiment have catalyzed the combustion property of HNIW monopropellant. Liao et al. [41] studied the influence of nine catalysts in terms of decreasing the burning-rate pressure exponent of DB propellants. The burning-rate pressure-exponent of double-base propellants containing catalysts was measured in terms of segments. The depression of the burning-rate pressure exponent of double-base propellant with different catalysts at different pressure intervals was discussed. It was found that the general trend is that the effects of catalysts are more significant at lower pressure intervals. Among the nine catalysts studied, nano-MCuO and Pb_3O_4 catalysts are more effective in decreasing the burning-rate pressure-exponent of DB propellants.

Besides metal oxides, metal salts are a second type of catalyst that has been studied extensively. Zhao et al. [45] put various metal salt catalysts into triethyleneglycol dinitrate (TEGDN) gun propellants, and the effect of these catalysts on the combustion properties of TEGDN gun

propellants were studied through a closed bomb test. The results indicated that lead phthalic acid could shorten combustion time, improve burning rate, and increase the combustion gas generation brisance of TEGDN gun propellants. Copper salt can depress the combustion gas generation brisance of TEGDN gun propellants.

Research on metal salts in double-base propellants has been extensively studied, with numerous studies presenting improvements in DB propellant performance. For example, Liu et al. [133] studied the catalytic activities of eight Pb salts and four Cu salts, which could be used as combustion catalyst ingredients of elastomer-modified cast double base (EMCDB) propellants. Experimental results showed that some Pb salts had stronger catalytic activity in the cross-linking reaction than others, and almost all Cu salts and carbon black had no catalytic activity.

Li et al. [30] studied the influence of metal salicylates on the combustion characteristics and thermal behaviors of AP-CMDB propellants. The results showed that the pressure exponents of the AP-CMDB propellants decreased to a certain extent with the increase in burning rates of the propellants at low pressures and the decrease in burning rates at high pressures. The peak temperature of thermal decompositions of a binary system NC/NG in the AP-CMDB propellants were affected by all the metal salicylates, and the peak temperature of thermal decompositions of AP at high temperature were brought forward by CuSa and Cu₂ Sa₂. It was also found that the pressure exponents of the AP-CMDB propellants in a wide pressure range of 1–20 MPa could be decreased efficiently by the copper (II) salts of salicylate (CuSa, Cu₂ Sa₂ and PbCuSa₂). Fu et al. [26] conducted similar studies on the effects of three organic lead salts on combustion characteristics and thermal decomposition of high energy modified double-base (HEMDB) propellant. A study conducted by Zhao et al. [125] studied the effect of six kinds of energetic lead or copper salts of hydroxypyridines on the combustion properties of RDX-CMDB propellant.

Furthermore, efforts have also been made to develop some composite energetic catalysts to improve the combustion performance of propellants [49, 164, and 161]. Zhao et al. [49] prepared various energetic composite catalysts through a non-solvent extrusion technique. The effects of these composite energetic catalysts on the minimum smoke propellant, the RDX-CMDB propellant, were investigated. The results showed that lead salt of 2-hydroxy-3, 5-dinitropyridine (2HDNPPb)/copper salt of 2-hydroxy-3, 5-dinitropyridine (2HDNPCu), and lead salt of 4-hydroxy-3, 5-dinitropyridine (4HDNPPb)/2HDNPCu composite catalysts possess better catalytic effect and better ability to reduce pressure exponent for the propellant, when compared to single

energetic lead salt or copper salt. In addition, the mixtures of lead and copper salts of hydroxypyridines had higher catalytic efficiency when the total amount of the catalysts added is constant.

As mentioned above, catalysts that slow a reaction are called negative catalysts, or inhibitors. Inhibitors are very important in studying the application of very high burning-rate propellants. For example, Li et al. [96] prepared a novel propellant that had a porous structure and had a very high burning rate (above 1000 mm/s). Propellant grains with size Φ 25×25 mm were inhibited using polyvinyl chloride (PVC) as an inner layer and cellulose acetate added flake asbestos as an outer layer. Experiments were conducted to determine the thickness of the coating layer, termination burning and indirect proof. Experimental results showed that the convection burning of very high burning rate (VHBR) propellant is stable with no flame-leak.

Cao et al. [65] studied the curing mechanism of unsaturated polyester resin (UPR) and the inhibition mechanism of DNT to UPR. Two composite primers DT-1 and DT-2 were developed and used in DB propellants. Li et al. [141] investigated a low burning rate NEPE propellant by means of adding some burning rate inhibitors and adjusting its composition. It was observed that the burning rate of the propellant could be depressed by the presence of burning rate inhibitors. Wei et al. developed a deterrent B that is suitable for 1,5-diazido-3-nitroazapentane (DIANP) propellant [104]. The combustion properties of deterrent-coated DIANP propellant were tested with a closed bomb. The experiment results indicated that using a deterrent coating technique could reduce the initial pressure rate of DIANP propellant result in progressive combustion. The coated thickness is the most important factor in deterrent-coated propellants for adjusting combustion performance.

Zheng et al. [46] studied the de-bonding between the propellant and the inhibitor at high-pressure and the erosive burning of the propellant grain. It was found that the modified propellant grain inhibited with an inorganic inhibiting layer appears to generate reliable inhibition and steady combustion at high pressure. It was pointed out that the application of the inhibiting materials with a low thermal conductivity coefficient and a reliable bonding effect is the key technique for ensuring the measurement accuracy of the burning rates of the propellant in the high-pressure range.

5.1.4 Explosive Combustion

An explosive is a substance that contains a great amount of stored energy that can produce an explosion. An explosion is a sudden expansion of a material after initiation, usually accompanied by the

production of light, heat, sound, and pressure. An explosive charge is a measured quantity of explosive material.

Explosives may also be categorized by their sensitivity. Sensitive materials that can be initiated by a relatively small amount of heat or pressure are primary explosives, and materials that are relatively insensitive are secondary explosives. An explosive booster acts as a bridge between a low energy explosive and a low sensitivity (but typically high energy) explosive such as TNT. It increases the explosive shockwave from an initiating explosive to a degree sufficient to detonate the secondary charge. Note that not all explosives can be detonated simply by inserting a detonator and firing it. An initiator such as a shock tube, a cannon fuse, or even a conventional detonator does not deliver sufficient shock to detonate charges comprising TNT, Composition B, ANFO, and many other high explosives. Therefore, some form of “booster” is required to amplify the energy released by the detonator so that the main charge will detonate.

Explosive boosters are widely studied in the research field due to their wide range of applications. There are two reasons for the wide application of explosive boosters. First, there is a major safety issue: detonators are by definition more sensitive to shock and heat than an explosive booster, so minimizing the amount of detonators that users must store or carry greatly reduces the likelihood of accidents. Second, chemical compounds used in detonators (e.g., lead styphnate) are more expensive to produce and encapsulate compared to the manufacturing costs of explosive boosters.

Preparation methods of various booster explosives have been provided in many research studies. For example, Chen et al. [5] discussed the preparation process of an ϵ -HNIW booster explosive. HNIW was used as the base explosive to make the ϵ -HNIW booster explosive using a water slurry method in order to obtain a high-performance, low-sensitivity booster explosive. An orthogonal experiment for the optimizing process was designed, and the main factors affecting the coating effect were investigated through single factor tests. FT-IR, SEM and impact sensitivity testing methods were used to characterize the coated samples. The result indicated that the order of influencing factors for the coating effect was as follows: temperature, agitating rate, adding rate, and degree of vacuum.

Wang et al. [13] prepared and characterized a membranous RDX/SiO₂ booster in one of their studies. The white sub-transparent membranous RDX/SiO₂ booster was prepared with the pulley and manual spin coating methods by sequentially adding the definite solution of N, N-dimethylformamide (DMF) dissolving RDX, and the definite solution of water dissolving polyvinyl alcohol (PVA) in the process of

the silica (SiO₂) sol transformation into the gel. The detonation velocity of the membranous composite showed that the performance of the booster was mainly affected by the thickness and particle size of the composite, especially at low charge densities.

Another example presenting a preparation method is a study conducted by Dong et al. [7]. They prepared a booster explosive by using an ethylene propylene diene monomer (EPDM) as a binder and 2, 6-diamino-3, 5-dinitropyrazine (LLM-105) as the main explosive using the solution-water suspension method. Chai and Zhang [127] prepared explosive HMX using two different particle sizes of 1–2 μ m and 20–30 μ m by the spraying ultrafine method. The effect of the ratio of the two samples on the compressibility of typical booster explosives was studied.

Other studies in the field of booster explosives include investigations of the dynamic response performance of a booster explosive [3], component analysis of a booster explosive [12], vulnerability of a booster explosive [4], and shock pressure [121]. Zhang et al. conducted an experimental study on the dynamic response of the booster explosive JH-14C. In their study, JH-14C under different strain-rate (from 1400s⁻¹ to 4000s⁻¹) impact over-loading conditions was studied using the split Hopkinson pressure bar technique. The macro failure-forms of the booster explosive JH-14C and failure-modes of the recovery specimen were observed and analyzed by SEM, and corresponding stress-strain curves were obtained.

Wang et al. from North University of China used an optimizing chemical analysis method to analyze the components of a certain kind of booster, JO-9Cl [12]. The experiment results indicated that the consumption of acetic ester, the mass fraction of sodium hydroxide (NaOH) solution, and alkali hydrolysis time affect the analytical results. In order to assess the vulnerability of booster explosives, Zhi et al. [4] designed seven sealing types of cook-off bomb. The cook-off tests of passive RDX cylinders with shells are used to study the response characteristics of passive RDX in different sealing conditions and analyze principal factors affecting the characteristics.

Various research methods have been applied in explosive studies, and progress has been made in advancing the technology and overcoming the difficulties of high pressure and high temperature. Testing methods include the cylinder test [27], the X-ray method [95, 106], the pelleting test [106] and the low amplitude shock test [132]. Han et al. [27] conducted cylinder tests on two aluminized explosives with diameters of 50mm and 100mm using a slit scanning photography technique with a high speed rotating camera to study the deviation extent from the similarity law about the energy release process of aluminized

explosives with different diameters. The experimental results demonstrated that the similarity law of cylinder expansion velocity did not recur for the two aluminized explosives, which is true for ideal explosives.

X-ray experiment can be used to study the reaction mechanisms in solid explosives. Huang and Wang [95] used X-ray experimentation to investigate the reaction mechanism of Ti-Ni metalized explosives. The results of the X-ray experiments showed that there were oxides and alloys in the detonation products. The amount of titanium that oxidized into oxide was 57.0%, which was more than that turning into alloy. There was not only an alloy reaction in the reaction of the metalized explosive containing Ti-Ni metal powder, but also an oxidization reaction. The oxidization reaction is faster than the alloy reaction, which is in line with chemistry kinetics. Yan Ji-sheng [106] characterized the pelleting characteristics of two CH-6 composite explosives composed of pressure-cooked RDX and RDX refined with acetone by the pelleting characteristics test and the X-ray inspection method. The results concluded that the pelleting characteristics of CH-6 composite explosive containing pressure-cooked RDX were better than those of CH-6 composite explosive containing RDX refined with acetone.

Progress has also been made in the development of novel experimental methods. Zheng et al. [23] developed a method to study the formation and propagation of defect-induced hot-spots in explosives. The optical radiation and temperature of the hot-spots were measured by pyrometer, which can be used to analyze the formation and propagation of hot-spots.

In addition, theoretical model analysis is sometimes combined with experimental methods in studies of the explosion process [37, 59]. Zeng et al. [37] applied a theoretical model for the electric power of exploding foils, which was based on the non-linear resistance model of foils in the process of explosion, to estimate the ratio of energy for accelerating flyers to that absorbed by foils. The simulated curves of flyer velocity history coincided well with those measured by VISAR. Theoretical analyses can also be applied to studies of mechanisms of radiation in each phase of an explosion of condensed explosives [59] when combined with high speed photography. The results showed that the process of radiation of firelight from an explosion consists of two phases: detonation and afterburning. The detonation pressure, detonation temperature, detonation velocity, and oxygen balance of condensed explosives have an effect on the maximum intensity of radiation during explosion. The duration of firelight from the explosion of condensed explosives is influenced by the oxygen balance and the mass of the condensed explosives.

5.1.5 *Propellant Combustion*

Propellants are a type of product that incorporates combustion. They contain pure or mixed products containing both the oxidant and fuel necessary to combust without requiring a supply of air. The process of combustion is then used for propulsion purposes. These solid propellants can be classified into homogeneous and heterogeneous.

A propellant is a material that is used to move an object. The material is usually expelled by gas pressure through a convergent-divergent nozzle. The pressure may be from a compressed gas, or a gas produced by a chemical reaction. The exhaust material may be a gas, liquid, plasma, or, before the chemical reaction, a solid, liquid, or gel. Common chemical propellants consist of a fuel—such as gasoline, jet fuel, or rocket fuel—and an oxidizer. There are three different types of solid propellant compositions: single-base propellants, double-base propellants, and composite propellants.

Ding et al. [40] reported on progress in the methods and equipment to study the thermal decomposition of energetic materials and combustion wave structure of propellants. There are numerous testing methods available to characterize the combustion performance of propellants. Among them the closed bomb test is the most widely used technology [74, 17, 78, 34, 47, 105]. Ying et al. [44] observed that two factors resulting in pressure loss in a closed bomb test. An established method can interpret the effects of gas thermo-dynamic parameters and the co-volume on pressure loss in a closed bomb. Compared with the conventional correcting methods for pressure loss, the new method can obtain not only the propellant force and co-volume, but also the pressure curves and burning rate curves in the whole burning process of propellants.

Based on a soft-sensing model and its corresponding solution, and combined with an example, the in-wall temperature of a closed bomb has been studied with the soft-sensing method in a study by Huang and Yu [94]. The results showed that the in-wall temperature of a closed bomb could be measured with the given model and its solution. The obtained curve of the in-wall temperature vs. time before the peak value is smooth. Other testing methods include SEM [102, 124, 60], the 30mm interior ballistic test [34], the high-pressure test [74], the strand burner method [67, 75], VST [17], the W-Re micro-thermocouple and flame photo technique [102], the extrusion technique [70], the closed vessel technique [76, 135], the high-pressure differential scanning calorimetric (PDSC) technique [32], rupture combustion tests [34], and coherent anti-Stokes Raman scattering (CARS) spectroscopy [91,113]. Detailed applications of some of these methods are discussed below.

Lin et al. [75] used the strand burner method in air at normal pressure to measure the apparent mass burning rate of the oblate propellant to investigate its combustion properties. Experimental results showed that the bulk density, grain size, test temperature, and loading conditions have significant effects on the mass burning rate of oblate propellant with micro-pores. Similarly, to investigate the combustion performance of a new propellant with polyether polyurethane binder plasticized by a mixed nitrate ester, the combustion characteristic of the JMZ propellant in the range of different pressure was studied by the closed bomb normal test and high pressure test [74]. The test results indicated that the JMZ propellant had good burning performance in the initial stage, which would be beneficial for barrel weapon. Wei et al. [17] used a closed bomb test and VST to study the influence of CL-20, DNTF, and ADN on the compatibility, energy, and burning behavior of nitramine propellant RGD7A. The results of this study could be used to widen the application of the high energy density compounds (HEDCs) in high energy and high burning rate propellants. Fan et al. [78] studied the effects of three kinds of lead compounds on the combustion characteristics of smokeless NEPE propellant by the Crawford bomb test and elemental analyses of the quenched surface of propellant samples. The W-Re micro-thermocouple and flame photo techniques were applied in a study conducted by Wang et al. [160] to measure wave temperature profiles and the flame structures of NEPE propellant samples.

Theoretical and mathematical models have been established to study the fundamentals of propellants. Lu et al. [33] developed a correctional model of a relative pressure impulse format by analyzing and correcting the geometric combustion law to study the propellant actual energy release law. Theoretical and experimental analysis under the conditions of various loading densities, propellants, constant volumes, and variation volumes were made. The granular diffusion flame (GDF) combustion model was used to calculate the burning rates of a certain AP propellant with various particle sizes and concentrations of oxidizer. The results gave a reference for avoiding cone burning in the engineering of propellants.

Pressure sensitivity is a topic that is very important to the application of propellants. Many studies have been carried out to reduce the pressure exponent of propellant combustion to improve performance. Li et al. [115] theoretically analyzed the pressure sensitivity of ultra-high burning rate propellant (UHBRP). Based on the theoretical analysis, when the densities of UHBRP pellets increase gradually from one end to another, the pressure sensitivity will be reduced greatly, and the pressure exponent can be reduced to zero theoretically. Li et al. [116] observed that decreasing the particle size of HMX could reduce its burning rate

and pressure exponent. Energetic catalysts have been used widely in studies to reduce the pressure exponent of propellants. Liu et al. [117] studied the effect of $B_{12}H_{12}[N(C_2H_5)_4]_2$ (YL 6) on the combustion properties of NEPE solid propellant. They concluded that when YL 6 was applied to NEPE solid propellant, the burning rate of propellant increased and the pressure exponent was effectively brought down to 0.13 in high pressure.

Zhao et al. [125] studied the effect of six kinds of energetic lead or copper salts of hydroxypyridines on the combustion properties of RDX-CMDB propellant. It was found that the lead salts of hydroxypyridines containing nitro groups possess better a catalytic effect and a better ability to reduce the pressure exponent for the propellant, especially for the lead salt of 2-hydroxy-3, 5-dinitropyridine, which has the highest catalytic efficiency. The catalysis of the energetic copper salts of hydroxypyridines in the propellant is insignificant. The catalytic difference between lead salt 2-hydroxy-3, 5-dinitropyridine and 4-hydroxy-3, 5-dinitropyridine is due to their different thermal decomposition mechanisms and their different carbon contents formed in the decomposition process.

Fan et al. [78] studied the effects of three kinds of lead compounds on the combustion characteristics of smokeless NEPE propellant. The lead compounds were LF (an energetic lead compound), LP (an organic lead compound), and LC (an inorganic lead compound). The propellant samples, containing LF, LP, and LC, were prepared by a slurry casting process. It was found that those lead compounds could all decrease the pressure exponents of the propellant to 0.33–0.48 in the pressure range of 3–5Mpa and to 0.18–0.58 in the pressure range of 5–12MPa, respectively. LP, which also had no side effect on the curing process of the propellant, can obviously improve the combustion characteristics of smokeless NEPE propellant in the pressure range of 3–12MPa. The results of elemental analyses indicated that the content of lead on the combustion surface of propellant containing LF or LP was more enriched than that of the propellant containing LC. Zhang et al. [88] conducted a similar study with two copper compounds (AD and BC) and three carbon blacks to study their effects on the pressure exponent of non-smoke NEPE propellant. Other studies on the pressure exponent reduction of DB propellants by using catalysts include [24, 119, 41, 48, 66, 71, 77, and 170].

5.1.5.1 Single-Base Propellant

Single-Base Propellant: A single-base propellant has nitrocellulose as its chief explosive ingredient. Stabilizers and other additives are used to control the chemical stability and enhance the propellant's properties.

Due to the rapid development in the field of DB and composite propellants, comparatively fewer studies have been carried out in the field of SD propellants, among which most have focused on the effect of additives on SD propellants. For instance, He Wei-dong [54] studied the low temperature coefficient mechanism of poly-(ethylene glycol dimethacrylate) (D1) deterred SD propellant. The physicochemical properties, linear expansion coefficient, and mechanical performance of polymer D1 and SD propellant at different temperatures were studied by a dynamic mechanical analyzer and material tester. Combustion performances of deterred multi-perforation single-base propellants were studied by a closed bomb test and interrupted-burning test. The study concluded that the low temperature coefficient effect of SD propellant deterred by polymer D1 is caused by two reasons. The first reason is that the differences in the coefficient of expansion between the propellants and polymer D1 lead to some spaces between polymer D1 and propellant surface and increase the burning surface area at low temperature. In addition, the increase in the burst ratio of deterred multi-perforation propellants at low temperatures reduces the temperature coefficient. Tests conducted by Xong [152] showed that adding fine KNO_3 grains and deterrent to the SB oblate spherical propellant powder could improve its inner burning area and affect its burning rate efficiently.

5.1.5.2 Double-Base Propellant

Double-base propellants consist of nitrocellulose (NC) with nitroglycerin (NG) or other liquid organic nitrate explosives added. Stabilizers and other additives are used also. Nitroglycerin reduces smoke and increases the energy output. Double-base propellants are used in small arms, cannons, mortars, and rockets.

The majority of the studies conducted on DB propellants are concentrated on the effects of different additives, which include catalysts, oxidizers, and binders. The varieties of catalysts include metal oxides, metal salts, carbon blacks and others. These catalysts have different effects on propellant burning rates and pressure exponents, and combined catalysts generally have better performance in improving combustion performance [119]. Qin et al. [119] used lead salts, copper salts, carbon black, and assistant plasticizer to adjust the combustion performances of low flame temperature and low burning rate propellants. Liao et al. [41] studied the effects of nine catalysts in decreasing the burning-rate pressure-exponent of DB propellant.

The effect of the catalyst bismuth 2, 4-dihydroxybenzoate (β -Bi) on the catalyzing burning of propellant was investigated in a study by Song et al. [70]. The results showed that β -Bi has a good catalytic effect on the combustion of double-base propellant and has an excellent ability to

enhance burning rates and reduce pressure exponents. Furthermore, when β -Bi together with a little carbon black (CB) and copper salt is used, the catalytic effect is better. Qin and Wang [83] studied the general Pb-Cu catalyst effect on the combustion performance, thermal decomposition, and quenched surface appearance and element distribution of double-base (DB) propellants. They concluded that general Pb-Cu salt catalysts used in common DB propellants had a catalytic effect not only on DB propellant, but also on DB propellant with a low burning rate and low flame temperature. However, Wang and Sun [66] compared the effects of Pb-Cu catalysts and non-lead salt catalysts on the propellant combustion performance and concluded that the propellant containing non-lead salt catalysts showed better combustion performance, indicating that non-lead salt catalysts had a higher catalyzing efficiency than Pb-Cu catalysts.

Besides catalysts, other additives can also improve the combustion performance of DB propellant performance. Wang and Sun [66] added an energetic additive (PQ, a nitramine product) to a CMDDB propellant containing HMX to decrease the burning rate and flame temperature of low flame temperature and low burning rate double-base propellant. The results revealed that the PQ-HMX composite energetic additives were able to efficiently decrease the theoretical flame temperature to lower than 1200K and the burning rate was lower than 2.5mm/s at 10MPa and 200°C. The decrease in the burning rate and flame temperature by adding energetic additive PQ is due to the reduction in energy level of the propellant and the decrease of the chemical reaction rate by the endothermic melting of PQ. Wang et al. [71] achieved the extraordinary effect of improving the burning rate of modified double-base propellant (AP based composite propellant and N-15D propellant) with fast-burning energetic material ACP. The burning rates of propellants were all substantially improved, but the pressure exponent was not changed. Wang and Li [148] studied the influence of azide nitrate ester PDADN [1, 3 propanediol, 2, 2 bis(azidomethyl), dinitrate (ester)] on the combustion property of nitramine modified double-base propellant.

A few studies have been conducted to apply mathematical models to investigate combustion behaviors of DB propellant. Liao et al. [97] established four mathematical models describing the combustion of smokeless modified double-base propellant, which contains fast burning energetic substances with different shapes (cubes, globes, cuboids, and slices). The mathematical equations of burning rate and the available size of fast-burning energetic substances in the direction of combustion were deduced. With the help of the established mathematical model, the burning rates of propellants containing 5% and 7% ACP were calculated under different pressures. Wang Yi [101] used theoretical computation,

which was based on a one-dimensional gaseous phase reaction flow model, to investigate the influence of the main chemical components of double-base plateau propellants on their combustion properties. The computation results were not only in agreement with domestic and international practical experience, but also explained the chemical mechanism of the propellant burning process. Cai and Wang [76] also applied theoretical analysis to the grain distribution and thermal decomposition characteristics of RDX in RDX-modified double-base spherical small-size propellants.

Composite modified double-base propellants (CMDB) are comprised of nitrocellulose, an energetic plasticizer, and solid organic or inorganic oxidizers. Various stabilizers are employed in CMDB to improve the thermal stability of propellants. In preparation of CMDB by the slurry casting process, it is desirable to crosslink the nitrocellulose binder in order to obtain improved and reproducible mechanical properties for the cured propellant. Resorcinol, the most commonly employed thermal stabilizer for CMDB, has not proved to be satisfactory as a stabilizer in cross-linked CMDB because of the reaction of resorcinol with diisocyanate cross-linking agents. Accordingly, considerable research effort has been undertaken to find a suitable replacement for resorcinol in diisocyanate cross-linked CMDB. One class of compounds found to be satisfactory stabilizers for diisocyanate cross-linked CMDB are urethane compounds such as 1,3-bis-N-m-methoxyphenyl urethane benzene.

Other research efforts on CMDB have been undertaken to investigate combustion properties such as sensitivity, burning rate, and pressure exponent. In a study by Dang and Zhao [77], the mechanical sensitivity and combustion properties of CMDB propellant using phase-stabilized ammonium nitrate (PSAN) as oxidizer were investigated through the burning rate, impact sensitivity, and friction sensitivity measurements. It was proved in the experiments that PSAN is effective for improving the sensitivity of CMDB propellant. Experimental results also showed that the burning rate of CMDB propellant with PSAN is lower than that of CMDB propellant with RDX, and the pressure exponent of CMDB propellant with PSAN is higher than that of CMDB propellant with RDX.

Li et al. [29] studied the influences of particle size and the content of AP and aluminum powder (Al) on the combustion characteristics of AP-CMDB propellant by determining the burning rates and pressure exponents of the propellants at different pressures. Furthermore, Chen et al. [129] introduced the concept of critical pressure for RDX CMDB propellant steady burning. More interestingly, Chen et al. [168] studied the effects of different processing conditions on the combustion characteristics of casting CMDB propellants. Such processing conditions

include ways of treating and adding to the catalyst, the pre-dry and kneading time, the curing time, and temperature. The results showed that processing conditions have a significant effect on the burning rate and pressure exponent of casting CMDB propellants.

Zhang and Tan [38] studied the effects of aluminum powder content on the exhaust signature of CMDB propellant, such as visible, infrared, and laser transmission and infrared radiant temperature and radiance by using a transmitter, a thermal-image instrument, an FTIR spectrum device, a high-speed camera, etc. The results showed that the visible, infrared, and laser transmission of the exhaust plume of CMDB propellant were greatly decreased, while the infrared radiant temperature, radiance, and dimensions of the flames were obviously increased as the content of the aluminum powder increased in the formulation of CMDB propellant. It was also observed that the content of aluminum powder had a slight influence on the types of final combustion products of CMDB propellants.

Finally, Zhang et al. [124] studied the combustion characteristics of smokeless XLDB propellant at different pressures by analysis of flame structure, combustion waves, and SEM. They proposed that the model of the combustion process of smokeless XLDB propellant was transferred from that of the double-base propellant type to the composite propellant type, which will be discussed below.

5.1.5.3 Composite Propellant

Composite propellants contain no nitrocellulose, nitroglycerin, nitroguanidine, or any other organic nitrate. Composites usually consist of a fuel such as metallic aluminum, a binder such as synthetic rubber, and an oxidizer such as AP. Composite propellants are used in large rocket motors.

Studies on composite propellants have mainly been concentrated on binders and oxidizers, with very few studies on the fuels [e.g., 10, 173, 137], probably due to its maturity in understanding the behavior of metallic aluminum. Zhang et al. [173] studied systematically the combustion characteristics of magnesium/aluminum fuel rich propellant and optimized the fuel rich propellant composition. The experimental results showed that the contents of the AP and the magnesium in the metal additives have the most effective action on the combustion characteristics of the propellants. The greater the contents of AP and magnesium are, the higher the burning rates of the propellant and the broader the flammability limit.

Pang et al. [67] studied the influence of agglomerated boron on the burning rate of solid fuel rich propellant. The burning rate and pressure index of propellant samples, with different AP gradations and Mg/Al

(particle size) combinations, and agglomerated boron with different particle sizes were determined by the strand burner method. It was found that the processing of fuel-rich solid propellants become less difficult when the agglomerated boron was introduced to replace ordinary boron powder. In addition, increasing the content of fine AP in composition led to the significant enhancement of the burning rate and pressure index of propellant samples, but the effects of particle size of Mg/Al and agglomerated boron were rather minor.

HTPB propellants refer to those composite propellants containing an inert hydroxy-terminated polybutadiene (HTPB) binder. These formulations generally contain 86–88% solids and use an ammonium perchlorate oxidizer [118]. They may also use an inert plasticizer such as dioctyl sebacate (DOS) or dioctyl adipate (DOA), aluminum fuel, and solid cyclic nitramines, cyclotetramethylene tetranitramine (HMX), or cyclotrimethylene trinitramine (RDX). The HTPB propellants are useful because they are less expensive and safer to use than DB propellants, which are Department of Defense (DoD) class 1.1 (mass-detonable).

HTPB propellants also have low electrical conductivities (or high resistivity), which makes them susceptible to catastrophic dielectric breakdown and other electrostatic hazards. Electrostatic discharge has caused disastrous fires that have occurred during the handling and manufacture of rocket motors containing HTPB bound propellant. HTPB propellants require high depressurization rates to extinguish. Consequently, they are not suitable for use in applications where thrust termination through rapid motor depressurization is required.

Studies on HTPB propellant have focused mainly on the combustion properties and mechanical properties. For example, the combustion properties and mechanical properties of HTPB propellant with a 90% solid mass fraction were studied by changing the content and particle size of oxidizer AP and the bonding agent and the value of R, in a study conducted by Chen et al. [39]. The results showed that the energy of HTPB propellant increases with the increase of the solid content, and the combustion and mechanical properties remain in good conditions. Under the condition of high solid mass fraction, the combustion and mechanical properties of HTPB propellant display some distinct rules as the change of direction for producing chemicals. The propellants combust steadily and the burning rate and pressure exponents can be controlled. Lei and Wu also prepared damaged samples of HTPB/AP CCCF composite propellant charge by four kinds of methods, which may simulate the different damage states of high-energy gas fracturing applications [112]. In order to improve the combustion properties of HTPB propellants, the effects of carbonate composites, ferrocene derivative G, high-nitrogen energetic material M, nanometer metal oxide particles, and

nano-aluminum on combustion characteristics of HTPB propellants were studied by Song et al. [42].

Jing Zhen-yu studied the damage characteristics of the propellant charge of a composite perforating device [28]. The HTPB/AP composite propellant loaded in the composite perforating device was taken as the main object. Damage to the propellant charge samples were simulated under different loads. The damage levels of the samples were analyzed and the combustion characteristics of the damaged propellant charges were studied with the measuring technique for the density of propellant grain and closed bomb test. The results showed that as different loads acted on the HTPB/AP composite propellant, microcosmic change and damage occurred in its internal structure. Its damage level was successively after high velocity impact, low velocity impact, quasi-static compression, and high temperature impact. The more serious the damage level, the greater the change of the combustion characteristics. Under the high velocity impact and low velocity impact, the combustion characteristics of the composite propellant became convective combustion or compressive combustion. Under the condition of a certain environmental restriction, it is possible that DDT will occur.

Different methods have been applied in the studies of composite propellants. The hermetic bomb test and the DDT tube test were used to study the influence of HTPB/AP on combustion stability and DDT behavior [112]. Ran and Yang used a Crawford test and firing test of a neutral burning $\Phi 64\text{mm}$ motor to investigate the effects of the fast-burning energetic compound ACP with various contents in propellants on the combustion properties of low-burning rate, medium-burning rate, and high-burning rate HTPB propellants [61]. The results showed that the ACP made the burning rate of the above-mentioned three kinds of HTPB/AP/Al propellants, and the pressure exponents of the propellants in the pressure range of 6.86-15MPa increased obviously. The primary evidence of non-parallel layer combustion in the motors by the fast-burning energetic compound ACP was obtained. Wu et al. [43] prepared propellant samples via a mix of compositions in a mixing machine, pouring in a vacuum, and curing at a constant temperature to evaluate the main factors that affect the pressure exponent. The standard target method was applied to determine the burning rate of propellants. The experimental results indicated that the pressure exponent was affected by HTPB content, AP content, AP gradation, and catalyst content to a certain extent. The pressure exponent increased as the HTPB content and AP weight mean diameter decreased, while the AP content and catalyst content increased.

5.1.5.4 Gun Propellants

The combustion of gun propellants has been an important topic for many years, and studies are still conducted extensively these days. Therefore, the research of gun propellant will be discussed in this section in detail. Test methods such as the closed bomb test and the interior ballistic test are applied in the studies on gun propellant. Wang et al. [14] used these test methods to develop a new concept of gun propellant and charge (controlled burning gun propellant [CBGP]) to enhance the burning progressivity and total energy of gun propellant. Three formulae were obtained in the study, which showed that a gun propellant with a high muzzle velocity should satisfy the requirements of high energy and high burning progressivity at the same time. The closed bomb test method was also utilized in a study conducted by He et al. [72] to evaluate the low temperature sensitivity of variable burning-rate gun propellants. The burning area of the propellant was changed by changing thickness of the crazes with temperature. Besides the closed bomb test, SEM was also used to observe the craze, and the thickness changes in the craze with temperature were observed by means of SEM. A compensating system was applied in a two-layered variable-burning rate propellant, and the low temperature coefficient of the propellant was estimated. The results indicated that using the thickness changes of craze with temperature changed the burning area of the propellant and could change the rate of gas production of the propelling charge. The closed bomb test showed that the combustion performance was about the same at different temperatures. The interior ballistics performance showed that variable-burning rate propellant has a low temperature coefficient. Similarly, Zhao et al. [110] designed a low temperature-sensitivity charge with improved stability. The closed bomb test and 30 mm gun-shooting test were used to characterize the burning properties, chamber pressure wave, and physical stability of the charge at different temperatures. He et al. [92] used the same methods, i.e., closed bomb test and 30 mm gun shooting test, to study the principle and realizable approach of variable-burning rate propellants. They concluded that the burning rate of the inner layer was higher than that of the outer layer, which is consistent with the concept of variable-burning propellant given by Xiao et al. [86].

In addition, in order to develop an ideal gun propellant with special progressivity distribution, the closed bomb test was used by Wang et al. to compare the combustion process of gun propellant by a dynamic interior ballistic cycle [15]. Based on the difference of progressivity distribution between an ideal and a real gun propellant, a quantitative assessment method of gun propellant progressivity based on a

closed-bomb test was proposed and the assessment results were proved to be reliable. Zhang et al. [109] used the closed bomb and a simulator of ignition and combustion to evaluate the ignition and combustion performance of two kinds of LOVA gun propellants with different binders: L15A (RDX: 76%, NC: 4%, DOP: 8%) and L13A (RDX: 76%, NC: 4%, CAB: 12%, ATEC: 8%). The results indicated that the LOVA gun propellants were difficult to ignite; however, its ignition behavior can be improved by adding AP into the igniter. In a study conducted by Zhang et al. [50], the effects of physical dimension (inner diameter and length-to-diameter ratio) on the combustion performance of a tubular variable-burning-rate gun propellant were investigated by the closed bomb test. The experimental results showed that this gun propellant would not present good progressive combustion performance if its inner diameter is too large or too small. The combustion properties of LOVA propellant can also be investigated by the closed vessel test [98], which can be used to evaluate the effect of particle geometry and the grain size of nitramine on combustion properties. The nitramine treated by chemical re-crystallization was needle-like and was not good for improving burning properties. The nitramine treated by ball grinding was cobblestone-like and was efficient for combustion properties.

The testing methods for the combustion remains of gun propellants include fume-box tests, nitrogen-bomb tests, and TG tests. For example, Wang et al. [62] studied the characteristics of gun propellant combustion remains and their negative effects on interior and exterior ballistics using these three testing methods. It was suggested that gun propellant combustion remains could be sorted into three categories: adhesive remains, floating remains, and sinkable remains, out of which adhesive and floating remains are most harmful. Tests have revealed that different gun propellants have dramatically different adhesive remains, and the greater the amount of adhesive remains, the greater the amount of floating remains.

Deterred propellants often result in muzzle smoke. Progress has been made to introduce a new clear-burning double-base gun propellant containing polymer deterrent and stabilizer [120]. One newly developed propellant has low muzzle smoke, low maximum pressure, high muzzle velocity, low temperature sensitivity, and excellent safe life. This improvement in interior ballistic performance was achieved by a combination of high oxygen-containing and diffusion-stable deterrent, slightly increased energy content, and very progressive burning behavior.

As with other solid propellants, studies have been focused on the characterization and stability of gun propellant combustion. One example of such studies is a study conducted by Huang and Liao [111]. In their study, the characteristics of pressure wave, the adaptability of interior

ballistics, and dynamic burning at lower temperatures of RGD7 propellant in high pressure guns were studied and analyzed using a 30 mm high pressure simulated gun test. The results were compared to those for a single base propellant. The burning rate of some gun propellants can be increased by the method of desensitization, although with the potential risk of being less stable. Li et al. [114] evaluated the combustion stability of three main types of gun propellants (single-base propellant, double-base propellant, and nitramine propellant), which were desensitized with two different methods. It was shown that the burning rate of the propellants increased through both of the two desensitized methods, but the instability of the combustion and the burning rate-pressure exponent also increased. Zhao et al. [110] designed a low temperature-sensitivity charge with relatively low temperature-sensitivity, stable chamber burning properties, excellent physical stability and shooting security. The charge was composed of loose flat-ball gun propellants and dense flat-ball gun propellants. The temperature-sensitivity of designed charge was controlled by adjusting the proportion of loose propellant.

Investigation into variable-burning rate gun propellants is another topic that has been studied extensively. Various studies have been conducted to improve the performance of gun propellants in this category. Ma et al. [63] manufactured a variable-burning rate gun propellant with glue and consolidation. The gun propellant was made with the grains of variable-burning rate gun propellant as the base propellant with energetic glue firmly pressed to surface. This charge has resolved the problem of progressive combustion of consolidation charges. The issue of burning gas release of high charge density gun propellant was effectively controlled by combining the high charge density and progressive combustion performance of the variable-burning rate gun propellant. The combustion performance of base propellant and the variable-burning rate gun propellant with glue and consolidation were analyzed comparatively by the p - t and L - B curves from the traditional closed bomb test. The results indicated that the variable-burning rate gun propellants with glue and consolidation kept high progressive burning of the variable-burning rate gun propellant and have high charge density and burning reappearance. Zhang et al. [57] studied the gas generation rule about tubular gun propellant with two different burning rate layers. The theoretical analysis showed that this tubular gun propellant with two layers, with the proper geometric size and burning-rate ratio, can present progressive combustion in its early stages with a step of Γ in the intermediate or late stage.

In the gun propellant field, researchers sometimes refer to two layer gun propellants as multilayer disc gun propellants. Wang et al. [34]

developed a new multilayer disc nitramine gun propellant, and the effect of slow burning materials on the burning rate of high energy nitramine gun propellant was studied by the constant-pressure burning rate test and closed bomb test. The combustion stability of a multilayer disc nitramine gun propellant was studied by rupture combustion tests. The results showed that slow burning materials could decrease the burning rate of propellant and enhance its progressive combustion performance effectively. The 30mm interior ballistic test showed that compared to the reference nitramine multiperforated propellant, multilayer disc nitramine gun propellant can increase muzzle kinetic energy of 15%. Zhang et al. [20] prepared sheet multilayer charge. The inner of the charge was made of high energy propellant with higher burning rate, and the outer one was made of low burning rate propellant containing macromolecular deterrent material.

Due to the complexity of the investigation of multilayer disc gun propellant, mathematical combustion models of multilayer gun propellant disks were established. Wei et al. [2] adopted such a model to study the influence of the structures on the progressive burning of multilayer gun propellant disks. The theoretical Γ - Ψ curves were obtained by the established combustion model of the multilayer gun propellant disk, and the static burning behaviors of the multilayer propellant with different structures were studied by the closed bomb test. Wei et al. [15] developed a combustion model of multilayer disc high energy nitramine propellant to simulate its interior ballistic properties and burning behavior. Three parameters—the burning rate ratio of the slow layer to the fast layer of the disc (K), the ratio of the initial thickness of the slow layer to the fast layer of the disc (X), and the ratio of the internal diameter and external diameter difference to the initial thickness of the disc (W)—were defined. The Ψ - Z curves describing the shape functions of the multilayer disc gun propellant with different parameters were obtained, and the combustion model was validated by the interrupted-burning test. The interrupted-burning test results proved that the combustion model is simple and hypotheses are reasonable and the theoretical calculation is much closer to the test results.

5.1.6 Others

High burning rate propellant (HBRP) is a novel addition to the family of propellants. Ma et al. [99] introduced the grain structure and combustion characteristics of a novel high burning rate propellant. Base on motor test results, it was found that HBRP exhibits three types of combustion manners at different motor loading parameters. The combustion manners include parallel layer burning, limited convection burning, and convection burning. Sha et al. introduced [145] the

processing technique of grain binding HBRP. The burning rates of both small grainy propellants and fast burning binders were calculated by means of the burning rate-calculated characteristic chemical group method of propellant. Wang et al. [85] summarized the research process and the status of the applications of the new high-energy polymer GAP. The experimental studies of the thermal decomposition and the combustion of GAP were introduced. Some new effective investigating methods, such as GCMS, pyrolytic MS, MBMS, IR/UV/CO₂ laser-induced decomposition, laser-supported decomposition, etc., were presented.

Various aspects of the cartridge case have been studied. Zhang et al. [123] calculated the ultimate characteristic parameters and ballistic performance of an ejection cartridge by analyzing its action and operational requirements. Through ballistic calculation and analysis, the charge configuration was preliminarily fixed and verified by tests. These efforts laid a good foundation for cartridge design and production. Li et al. [9] studied the combustion properties and energy release properties of a combustible cartridge case. The effects of different charge densities, different ignition pressures, and different moisture were studied using the closed-bomb test. The results showed that as the charge density and the ignition pressure increased, the cartridge burning rate and the maximum pressure increased. The combustion stability also improved, and the energy of cartridges was released more effectively. The effect of charge density on energy release decreases with increases in the ignition pressure.

The strong hygroscopicity of combustible cartridges was verified through an absorption experiment with moisture [9]. When samples contain moisture, the burning rate and the combustion stability of low charge density decrease significantly. The combustion duration extends; however, the influence on impetus is weak. Zhang Yi-Le [167] discovered that the internal ballistic performance of a countersunk caseless cartridge could be improved by adjusting the weight of the combustibility primer or adding ignition composition. A device for testing the performance of the cartridge's primer was designed [149]. The performance of the press-loading small primer could be measured with the testing device. A new way was suggested for the study of the reliability of stored ammunition and the analysis of accidents.

Some progress has also been made in research on flame retardants. Chang et al. [89] reported on the progress of flame-retarded polyurethane materials containing phosphorus and halogen flame retardants. Currently, most of the research focus has been on developing new additive flame retardants, reactive flame retardants of organic phosphate, and flame retarded binders for flame retarded polyurethane materials. It was

suggested that future work should focus on improving the comprehensive properties of flame-retarded polyurethane materials and going deep into the study of the flame-retarding mechanism. Shi and Wang [100] studied the flame-retardant mechanisms of two phosphorated flame retardants, P1 and TCP, in isocyanurate-modified polyurethane elastomer (IMPUE). Qiao et al. [144] studied the influence of two kinds of additives on the flame temperature of EBM extinguishing agent. It was found that the flame temperature could be lowered by additives, and the combination of two kinds of additives was found to be more effective for lowering the flame temperature of an aerosol generating agent.

Surface treatment in the combustion field is another topic that has been widely covered. Yang et al. [108] studied the characteristics of initial combustion of surface-treated azidonitramine propellants in a gun chamber. The surfaces of azidonitramine propellants were treated with desensitizing and coating. Yu Xian-han [122] introduced the surface treatment method of pentaerythritol tetranitrate (PETN) by means of a surfactant. The results showed that the static electricity of PETN greatly decreased after it was treated with the surfactant. Lu et al. [158] used a surfactant (expanding agent) in compulsory crystallization for a saturated solution of ammonium nitrate (AN). Chen and Song [174] presented an application for surface-active agents in determining the azide ion in wastewater from sodium azide workshop of a primary explosive plant using the UV spectrophotometric method.

Finally, to evaluate the signature of solid propellant formulation based on the framework of signature characterization facility (SCF), Zhang et al. [87] established a signal (including visible light and near-mid-far infrared radiation) transmittance measuring system and a smoke-box. A standard to characterize the signals transmittance of primary and secondary smoke has been established. The results indicate that the signal transmittance decreases with increases in the content of Al powder for primary smoke and closely relates to the content of AP in propellant formulation for secondary smoke. The occurrence of secondary smoke is related to the temperature and humidity in the smoke-box.

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Chapter 6

Modeling and Simulation

The process of testing energetic materials can be costly and time-consuming. Modeling and simulation provide a way to predict the effects that an energetic material will produce without the physical process of testing. The data produced by modeling and simulation can be used to make decisions that save time and money.

A model takes the form of a set of mathematical equations representing chemical and physical processes. Within the model, assumptions must be made. Making assumptions can simplify the solution of a set of equations, but can also lead to erroneous results if the assumptions are unrealistic. On the other hand, not making enough assumptions can complicate the model to the point that it is difficult to use. Mathematical equations, often partial differential equations, are solved by discretizing the equations. This can be done by a finite element method, a finite difference method, or (particularly in engineering) a finite volume method. This reduces the problem to the solution of algebraic equations. In the end, a model must accurately simulate the processes it is representing.

Numerical modeling and simulation in the energetics field can be one-dimensional [16, 18, 29], two-dimensional [22, 30, 46] or three-dimensional [6,10]. Various software codes have been developed for numerical modeling and simulation. A popular software code is the finite element hydrodynamic code LS-DYNA [10, 11, 25, 36, 46]. LS-DYNA uses a general-purpose physics simulation. The code is useful in military applications, such as predicting warhead trajectories after detonation. It is also useful for simulating nonlinear materials such as thermoplastic polymers. Other codes used in the energetics field include solid propellant burning rate models [16]; Computational Fluid Dynamics software such as ANSYS [43], POLYFLOW [6], Gaussian 03

software [1], Gaussian 98 software [24, 45]; and simulation programs produced with MATLAB (e.g., [17, 33]).

Due to their value, modeling and simulation have comprised an average of 10% of China's overall research publications in the energetics field over the last fourteen years. From 2005 to 2006, there was a major decline in modeling and simulation publications, comprising less than 6% of the research publications (see Figure 6.1). Recently, there has been renewed interest in modeling. It has comprised more than 10% of research publications in the last four years.

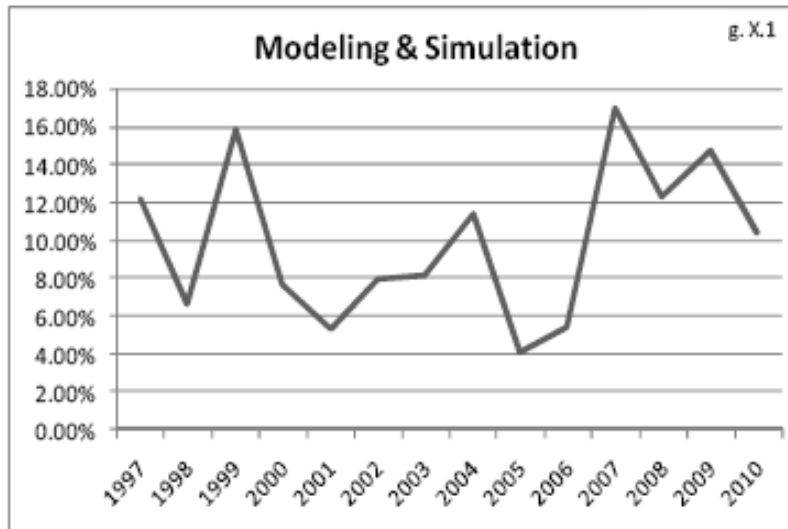


Figure 6.1 Percentage of China's overall energetic material research publications represented by modeling and simulation.

6.1 Modeling and Simulation Methods in Energetic Field

One popular modeling and simulation methodology is based on density functional theory (DFT). DFT is one of the more frequently used computational methods for predicting the properties of atoms and molecules, particularly molecular geometries. The name comes from the use of the functionals of the electron density of the material being studied. DFT is used to create and simulate a model of the structure of the atoms and molecules. Examples of the application of the DFT method include developing high energy density materials with good properties [14], theoretical studies of bonds [50], optimization of the

molecular geometries of energetic ionic salts [7], and investigations of the thermodynamic properties of combustion products [12, 21]. One example of applying DFT methods in thermodynamic studies is a study conducted by Tan et al. [39], in which the C-N bond dissociation energies, the average C-N bond dissociation energies, and the average nitril binding energies of fourteen kinds of polynitrofullerenes were calculated.

Another computational method used in the field of energetics is smoothed-particle hydrodynamics (SPH), a popular method known for fluid simulation. SPH differs from DFT in that it is a mesh-free Lagrangian method where the co-ordinates move with the material. SPH divides the fluid into a set of particles, thus guaranteeing the conservation of mass in the simulation. It is extremely useful for obtaining the density of a substance, though, for SPH to be accurate, because a large number of particles are required in the simulation. For simulating the detonation of high explosives, SPH is favored over DFT because it is a grid-free method. Zhou et al. [19] conducted a simulation, based on an SPH method, to investigate the non-ideal propagation of detonation waves in the spherical shell of a charge surrounding a spherical metal body. In this study, a simple engineering approximate calculation method was given to compute the propagation time of waves in the metallic spherical shell of the charge. The results showed that the characteristic detonation time obtained by simulation is consistent with that obtained by theoretical analysis, indicating that the modified SPH method is feasible and reasonable for numerical simulations of detonations.

Computational fluid dynamics (CFD), another simulation method, is similar to SPH. However, unlike SPH, it uses a mesh grid. It has been found most useful in problems involving fluid flow. An example of the application of the CFD method is a study conducted by Zhang and Wang [43] in which the fractal model (FM) of turbulent chemical reaction was developed based on the phenomenological concept of vortex cascade and fractal theory. The numerical simulation of a Steckler's room fire was carried out with a fractal model of the turbulent combustion chemical reaction and the eddy-dissipation-concept (EDC) model by the CFD software, ANSYS CFX 10.0.

The minimum free energy method is a method used in combustion studies. The concentration of gaseous combustion products can be calculated using this method. He et al. [4] used the minimum free energy method to obtain the CO concentration in the combustion products of propellant while varying the ammonium nitrate content. Using the same method, He et al. also conducted a study to calculate the combustible gas concentrations in the combustion products of propellants while varying

oxygen balances [20]. Both studies used closed-bombs and gas chromatography to analyze the combustible gas composition of the propellants.

Molecular dynamics (MD) is useful for simulating diffusion in the energetics field. This method, as the name implies, simulates the individual molecules interacting with each other. The interactions follow approximations of the laws of physics, which are complex at the atomic level. For this reason, “force fields” are formulated to simulate the structural, vibrational, conformational, and thermo-physical properties [28, 38].

One of the latest force fields used in the study of energetics is the Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies (COMPASS) force field. COMPASS accurately simulates these properties for molecules in isolation and in condensed phases. The application of molecular models under COMPASS can overcome the difficulties of experimental methods and be used in the study of the compatibility and the diffusibility of the plasticizer and the bond system of HTPB propellants [26]. Other examples of molecular dynamics using COMPASS include studies conducted by Li et al. [8, 13] and Huang et al. [35]. Li et al. [8, 13] explored the effect of aluminum powder oxidation on interface properties for binding agents of HTPB propellant. Molecular dynamics and a COMPASS force field were adopted to simulate the adsorption energy and mechanical properties (elasticity coefficient, moduli, and Poisson ratio) of the interfaces between HTPB, Al, and Al_2O_3 . By analyzing the adsorption energy and the pair correlation function, the nature of the interface interaction was simulated. Huang et al. [35] evaluated the performances of nitrocellulose (NC) and the nitric acid ester of cellulose glycidyl ether (NGEC) by molecular simulation using a COMPASS force field and the Synthia module of Materials Studio. Synthia calculates polymer properties using advanced Quantitative Structure-Property Relationships (QSPRs). It allows researchers to rapidly screen candidate polymers for a wide range of properties. It determines the properties of copolymer blends.

Finally, a mathematics-based (as contrasted to physics-based) modeling and simulation approach uses the Monte Carlo method [38]. This method relies on repeated random sampling and computation algorithms to obtain results. It is most useful in applications where there is uncertainty in some aspects of the problem and where a clear answer is not available. This type of modeling makes few assumptions and is thus able to make estimations for problems that have significant uncertainty in their input.

6.2 Modeling and Simulation Research in the Energetics Field

In the energetics field, some of the most recent research involving modeling and simulation has been done by Hu Rong-zu, Xiao Zhong-liang, Ma Zhong-liang, Liu You-ping, and Zhao Feng-qi. In particular, Hu Rong-zu, one of the top researchers from the Xi'an Modern Chemistry Research Institute, has created prototypes to model the decomposition reaction of energetic materials. Hu has also done extensive research utilizing DFT. Xiao Zhong-liang, from the North University of China, is also a top researcher in modeling and simulation. Xiao has done models of volume flow rate, oxygen balance, and the amount of energy released. He has also conducted numerous studies involving gun propellants.

6.2.1 Modeling and Simulation in Phase Transformations of Energetic Materials

Models can simulate condensed phase energetic materials that undergo phase transformations. Such materials are often used in explosive and pyrotechnic systems and are commonly referred as solid explosives. Explosives are usually stable solids at room temperature and pressure. When subjected to sufficiently strong mechanical and thermal stimuli, they undergo phase transitions to liquid and gas before releasing by chemical reactions their stored energy, mainly in the gas phase. Numerical modeling is often used to simulate the phase transitions from solid to liquid to gas and estimate the energy release due to chemical reactions. For example, Hou et al. [23] calculated the intermolecular interaction energy with basis set superposition error correction (BSSE) and zero point energy correction (ZPE). The interaction energies predominately come from hydrogen bonds. Natural bond orbital (NBO) analysis was performed to reveal the origin of the interaction. Numerical modeling [22, 37] has also been extensively used to simulate the initiation and detonation process of a plastic bonded explosive (PBX). As demonstrated by Liang et al. [47], numerical simulations can be used to calculate detonation parameters and predict detonation products. In their study, Liang et al. designed a series of new furazan (furoxan) explosive molecules with 3,4-bis (aminofurazano) furoxan (BAFF) as the structural units. The detonation parameters of this explosive were calculated using Rothstein's method for estimating detonation velocity and Cooper's method for estimating C-J pressure. These explosives molecules were predicted to have favorable stability.

6.2.2 *Modeling and Simulation in Molecular Geometry Optimization*

Another numerical modeling technique in the energetics field is the optimization of the molecular geometry of energetic materials. For example, Li et al. [7] employed the DFT-B3LYP method to optimize the molecular geometries of five kinds of picric energetic ionic salts: ammonium; aminoglycoluril; carbonylhydrazide; aminoguanidinl; and diaminotetrazole. Their IR vibrational frequencies and heats of formation were investigated. Based on their heats of formation, the detonation properties (detonation velocity and detonation pressure) of the title compounds were estimated using the Kamlet-Jacobs equations. Similar studies were also conducted by Fan et al. [15], Hou et al. [23], and Du et al. [28]. Fan et al. [15] optimized the geometrical structures of the super-molecular systems of nitroglycerin (NG) with polyethylene glycol (PEG), hydroxyl-terminated polybutadiene (HTPB), glycidyl azide polymer (GAP), poly(3-azidomethyl)3-methyl-oxetane (AMMO) and poly(3,3-bis(azidomethyl)-(oxetane) (BAMO) by the semi-empirical molecular orbital theory PM3 method. In the study by Du et al. [28], geometry optimizations and frequency calculations were carried out for five nitroaniline explosives using density functional theory (DFT). Vibrational analyses have shown that the optimized structures have no imaginary frequencies, which indicates that the structure of each molecule corresponds to a local minimum on the potential energy surface. Using Gaussian 98 software, the structure of β -octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) was optimized at the levels of HF/6-31G, DFT-B3LYP/6-31G and MP2/6-31G, respectively [45].

Models are used to obtain stable geometric configurations of energetic materials, such as a simulation conducted by Ge et al. [38]. In this research, the molecular geometry of FOF-18 was optimized by the B3LYP method with the basis set 6-31G to obtain stable geometric configuration. The infrared vibrational frequencies and the IR spectrum of the system were obtained on the basis of vibration analysis. The density was estimated by the Monte-Carlo method, and the enthalpy of formation was estimated by designing reactions, which have equal bonds and equal electronic pairs. The detonation velocity, detonation pressure, and detonation heat were estimated using the Kamlet-Jacobs equations. Lai et al. [14] did a simulation to obtain high energy density materials, resulting in the design of picryl furazan compounds with oxy bridges.

6.2.3 Modeling and Simulation in Theoretical Thermodynamics Investigations

Theoretical investigation of the thermodynamic properties of energetic materials is another area for numerical modeling. Hu et al. [12] investigated 4-amino-1,2,4-triazol-5-one (ATO) using the DFT/B3LYP method to determine the thermodynamic properties and evaluate the adiabatic time-to-explosion of ATO. In a study by Xu et al. [21], the thermodynamic properties of rocket propellants containing chlorides and fluorides of Cu, Pb, B and Al were studied using density functional theory (DFT) at B3LYP/6-311G(d,p) and B3LYP/SDD levels. The thermodynamic properties of diatomic molecules were calculated by a statistical mechanical method based on the Morse potential. This showed that the statistical mechanical method based on the Morse potential can be used to calculate the thermodynamic properties for the combustion of a rocket propellant.

The study of the thermodynamics of the thermal decomposition of energetic materials is another area where numerical modeling and simulation can be used. For example, Huang et al. [36] investigated the thermal decomposition trajectories of an s-tetrazine molecule and its five derivatives using ab initio molecular dynamics (AIMD) to obtain the possible decomposition pathways and identify their relative importance. The reaction channels were studied by DFT at the B3LYP/6-311G(d,p) level to locate the local minimum points and transition structures and to verify the results of AIMD in terms of energy. New conclusions regarding the effects of intermolecular reactions on the thermal decomposition mechanisms of tetrazines were reported. Another example of a numerical modeling application in thermal decomposition is the development of a method for determining the chemical kinetic parameters [E, A, and $f(\alpha)$] of the exothermic decomposition reaction of energetic materials [5]. Using this method, the chemical kinetic parameters of the exothermic decomposition reaction of energetic materials such as 2,6-bis(trinitromethyl)-4,8-dinitro-glycoluril, 1,4,5,8-tetranitro-1,4,5,8-tetrazadelin and bis (1,3-dinitro-1,3-diazacyclohexanone-2) were obtained [5].

In the numerical modeling and simulation of thermodynamics, some models, such as the CJ and ZND models, have the shortcoming of not being able to attain thermodynamic equilibrium. This is not consistent with the basic principles of thermodynamics. In order to overcome this flaw, Hu [52] developed a new detonation model, called the conjugate detonation model. Thermodynamic equilibrium is assumed to be the final state of the detonation process. In this detonation model, the chemical reaction is initiated by the shock wave front, and the released energy

makes the particles of explosion products move in different directions. Every pair of particles, with one particle moving forward and the other moving backward, is called a conjugate pair. By correlating the detonation wave propagation with the conjugate pairs appearing in micro-explosion and disappearing in expansion, the conjugate detonation model is produced.

6.2.4 Modeling and Simulation of Detonation Waves in Energetic Materials

Numerical simulation techniques are used to study the propagation characteristics of detonation waves. Studies in this area include those by Li et al. [46], He and Long [48], Chen et al. [10], Lu et al. [29], and Li and Weng [30]. In order to investigate the propagation characteristics of a detonation wave under the point initiation condition, Li et al. [46] used the two-dimensional hydrodynamic code DYNA2D to simulate detonation waves in a TATB-based explosive. Similarly, in a study by He and Long [48] designed to study the propagation characteristics of the detonation wave and the low pressure flow field in corner-turning, the numerical simulation program LS-DYNA3D was used to simulate the detonation wave propagation phenomena for three specific corner-turning (120°, 90°, and 45°) composition B charge structures. Chen et al. [10] studied, both experimentally and by numerical simulations using LS-DYNA, the propagation characteristics of a shock wave generated by a thermobaric column exploding in a confined space that was connected to an open area. The numerical results were in agreement with the experimental results. A software program was developed using one-dimensional reacting flow theory with a particle-trajectory dual-step reaction model to simulate the effects of the detonation wave ignition energy and the initial temperature on the structure and the development of detonation waves [29]. The numerical results were in good agreement with the experimental results, indicating that the method and the resulting software program are practical. Li and Weng [30], using a two-dimensional viscous conservation element and solution element (CE/SE) method, investigated the flow of blast waves in a problem with a gear wave wall around the explosion point. These numerical simulation results have contributed to research on protection from blast waves in the explosives field.

6.2.5 Modeling and Simulation in Chemical Reactions of Energetic Materials

Another application of modeling and simulation is the study of the reaction mechanism of energetic materials. Its application in turbulent chemical reaction simulations is important. Zhang and Wang [43]

developed a fractal model (FM) based on the phenomenological concept of vortex cascade and fractal theory to simulate turbulent chemical reactions. The numerical simulation of Steckler's room fire was carried out with the fractal model of turbulent combustion chemical reaction and the eddy-dissipation-concept (EDC) model using the CFD software ANSYS CFX 10.0. Wang et al. [1], using the DFT and Gaussian 03 software, studied the mechanism for the reaction of TNT with the sulfate radical. In their study, the geometries of all the molecular reactants, transition states, and products were optimized and the harmonic vibration frequencies and the energies were calculated at the level of B3LYP/6-31G(d). The experimental and calculated results showed that the reaction of the sulfuric radical with TNT was mainly controlled by the dynamics, and the major channel of hydrogen abstraction was the reaction of TNT-methyl hydrogen and sulfate radical. The major channel for the addition reaction was the reaction of non-substituted TNT-phenyl carbon and the sulfate radical.

In addition to studying reaction mechanisms, numerical modeling and simulation have also been used in reaction kinetics studies. To analyze the influence of damage on the initiation and detonation behavior of a PBX, Liang et al. [22] built a reaction rate function model. Reaction rate function model parameters were obtained by genetic algorithms. The validation of the model was carried out by comparing the simulation results with those from the Forest-Fire model. This reaction model can be used to analyze the detonation mechanism of damaged explosives where the porosity and grain size have been changed by the impact load.

6.2.6 Modeling and Simulation in Propellants

Modeling and simulation techniques are used in propellant studies where experimental testing can be costly and difficult. Most of the numerical modeling applications in research areas discussed in Sections 4.2.1 through 4.2.5 can be applied to propellant investigations. Additionally, numerical modeling and simulation techniques provide insight into other aspects of propellant behavior. Feng et al. [16] developed the SPRS software to calculate the burn rates and pressure indexes of a propellant when the chemical composition of the propellant and the pressures are given. The composition of the propellant could be determined based on the desired burn rates and pressure indexes. This numerical modeling application is useful for cycle-shortening and cost-savings in the development of solid propellant.

Zhang et al. [17] developed a simulation program based on classical interior ballistics theory to produce an interior ballistics mathematics model of multilayer propellant charges. Other numerical modeling simulations were carried out to investigate the following aspects of

propellants: (1) the effects of the deformation of interior pores due to warhead launch load on the safety of gun propellants [25]; (2) the progressive combustibility of variable burn-rate gun propellants [31]; (3) the influences of the environment temperature, species, and concentration of oxidizers, particle radius, and the oxide layer thickness on boron ignition [32]; and (4) the effect of agglomerated boron powder on the energy release and burn-rate characteristics of boron-based fuel-rich solid propellant [34].

Finally, a mathematical model has been developed to simulate a propellant's combustion behavior under constant volume conditions [40]. The influences of the distribution and variety of web thickness, non-synchronous ignition, and changes in burn-rate coefficient on a propellant's combustion behavior were analyzed. The calculated results agreed with the experimental data, showing that the hypothesis and the scheme established by the mathematical model are reasonable.

6.2.7 Modeling and Simulation in Other Areas of Energetic Materials

Numerical modeling and simulation has also been used to investigate some specialized topics in the energetics field. For example, Li et al. [9], using a thermal-mechanical coupled finite element method, studied the hazards in the truing process of solid propellant. Using methods based on the viscoelastic integral constitutive relation, the heat produced by the pressure and friction in the truing process was determined, and the hazard point was calculated. Numerical modeling simulation can be used to study the trajectories of fragments driven by explosives in directed energy warheads controlled by detonating meshwork and ordinary fragmentation warheads [49]. Another application of numerical modeling incorporates a creep model based on a modified time hardening theory [37]. This model was used to simulate the short duration creep behavior of PBX components. In this study, 15 sets of model parameters were determined by using data from 15 uniaxial compressive creep tests on an HMX-based PBX. The model was used to simulate the creep deformation of HMX-based PBX components subjected to vac-sorb forces for one hour. The results from the numerical simulation and theoretical analysis showed that the modified time-hardening creep model is suitable for the short duration creep behavior of PBX.

Densities of energetic materials are predicted with numerical models. The densities of a series of aromatic polynitro compounds were predicted using an artificial neural network (ANN) based on the erroneous reversed dissemination method [44]. Selecting molecular structure descriptors (MSD) as input characteristic parameters, the relative error between the predicted values and literature values for the densities of aromatic

polynitro compounds are within $\pm 10\%$. In Zhang and Wang's study [42], the densities of polynitroaromatic compounds (PNACs) were predicted by the Boosting algorithm. They concluded that the Boosting algorithm improves the prediction accuracy. The relative error of the prediction is within 8% of measured density.

Finally, numerical modeling and simulation techniques have been applied to projectile studies. In order to improve the design of the solid traveling charge in a projectile, Yang and Yu [18] developed an advanced one-dimensional interior ballistic aerodynamic model of a projectile. Taking into account the changes in the projectile, a numerical simulation of the structural parameters of the traveling charge in the interior ballistic process of 30mm artillery was performed. The position-pressure curves on the traveling charge, for all times after the shell was fired, were obtained. Using a mathematic model based on strength theory, Zhang [27] studied the strength of the base bleed charge in a fired projectile. The factors causing the base bleed charge to be destroyed were studied, and the results showed that an increase in stress was the main factor.

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Chapter 7

Nanoenergetics

Nanoenergetics (often known as energetic nanomaterials) is a new category of energetic materials that are usually measured in nanometers. Because of their diminutive sizes, nanoenergetics react faster and thus are able to release their energy in a shorter period of time. Nanomaterials can also be used as catalysts to control reactions.

One way nanometals are used is through carbon nanotubes (CNT). Carbon nanotubes are extremely thin and their diameters are measured in nanometers. They can be used as a substrate for the coating of materials, such as ferric oxide (Fe_2O_3) or copper oxide (CuO).

Producing nanoenergetic materials can be difficult. One of the most used ways of making them is the sol-gel method. This method is a way to manufacture nanoenergetics in an easy, safe, and cheap manner. It involves the reaction of certain chemicals to produce a solution (sol) that interacts with an integrated three-dimensional network (gel). The nanoenergetic material is then obtained by super-critical or non-super-critical extraction. To obtain an aerogel, super-critical extraction is used to remove all liquid surface tension in the liquid-solid chemical solution (sol). Using non-super-critical extraction or controlled evaporation to create a solid form produces a xerogel. In addition to the sol-gel method, precipitation is also an efficient method for the preparation of nanoenergetics.

Until recently, nanomaterials have been used mostly in the energetic field as catalysts. As catalysts, nanocomposites can provide increased stability and better control over reactions. Nanocatalysts such as Al_2O_3 , TiO_2 , and SnO_2 can induce an increased burn rate and a decreased activation rate.

Results from research on nanoenergetic materials have been similar to nanocatalysts. For example, researchers have noted that the production

of a nano-RDX by the sol-gel method results in particles with dimensions smaller than 90 nanometers with lower activation energies as well as increased explosive probabilities. In other studies, it has been shown that nanoenergetic material always has a favorable increase in burn rate and a decrease in decomposition temperatures. Overall, nanoenergetics provides higher combustion efficiency, reduced sensitivity, and higher controllability in the rate of energy release.

From Figure 7.1, it is clear that the field of nanoenergetics is still an emerging field of study in China. Recently, there has been more research in the field, though it still comprises less than 4% of the total research in the field of energetics in China.

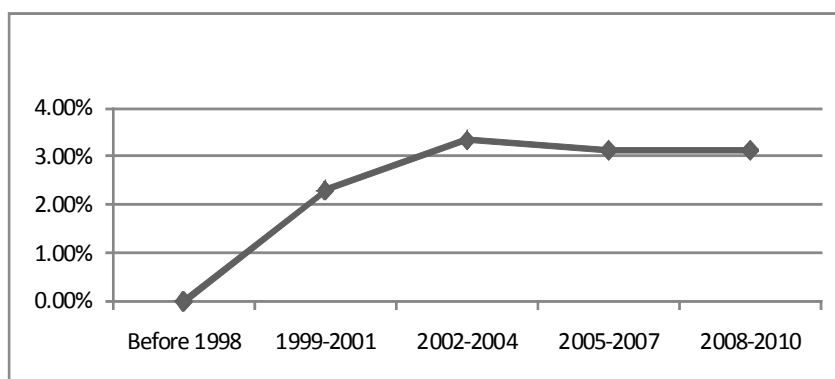


Figure 7.1: Research in nanoenergetics

7.1 Research in Energetic Nanomaterials

Energetic nanomaterials offer the potential for extremely high energy release, extraordinary combustion efficiency, a high degree of tailorability in the rate of energy release, and reduced sensitivity. Nanomaterials can also impact high energy density compounds, metallic explosives, composite explosives, and the application of new polymer binders and reactive materials. Methods of creating and mixing constituents are issues of interest in the nanoenergetics field. One example is the choice between solvent and non-solvent methods. Other issues relate to the uniformity (size) of the elements in a mixture as well as the uniformity of the mixture itself. Research into energetic nanomaterials thus involves preparation, characterization, and the relationships between structure and properties. As a result, researchers [18] have investigated the preparation of nano/micro composite particles for combustion catalyzers, oxidant/combustible composite particles, catalyzer/oxidant composite

particles, and composite explosives using nano/micro particle compounding techniques.

In the area of nanoenergetics, research has focused on the preparation of powders, because a reduction in particle size is known to have a significant effect on detonation properties. For example, by adding 20% superfine (50 nm particle size) aluminum with RDX as the main explosive, the detonation properties and power strength can be significantly improved [22]. Another study [7] investigated the development of 59.3nm average particle diameter α -Al₂O₃ powder for “RDX/nanometer α -Al₂O₃” explosives. In [13], the authors studied the preparation of RDX micro-crystals.

Nanorods and nanotubes have also been studied in the energetics field. In one study, annealed Cr₂O₃ nanorods were developed to accelerate the thermal decomposition process of RDX and decrease the decomposition temperature of RDX [4]. In another study, carbon nanotubes were created to support transition metal oxides, which affect the reaction rate of potassium perchlorate (for fireworks) [5]. The effect of carbon nanotubes on the thermal decomposition of CL-20 was also studied [15].

Nanocatalysts influence detonation properties. Research was conducted on the effects of copper oxides [6, 25, 29] and copper chromite [26, 28], which accelerate the decomposition of ammonium perchlorate, and lead oxide on the burning properties of propellants such as NEPE [23, 27]. In [8], the results of burn-rate tests showed that iron oxide nanoparticles can improve the burn rate of metallic fuel 30 percent more than micrometer-sized iron oxide. Nanometer-sized ferric oxide was synthesized at room temperature by humid solid state reaction [19], and the effects of nanometer-sized ferric oxide on the catalyzing thermal decomposition reactions of absorbent powder (nitrocellulose absorbed nitroglycerin, NC/NG) were studied. In [9], the effects of energetic nanoscale organic lead salt (n-ONPP), nanoscale organic cupric salt (n-PAC), and carbon black on the combustion characteristics of smokeless composite modified double-base propellant were studied. Research has also been conducted on the catalytic performance of ZnTiO₃ nanocrystals on ammonium perchlorate decomposition [1]. Also, spherical CO nanometer powder has been found to significantly reduce the decomposition temperature of ammonium perchlorate, and the burn rate of ammonium perchlorate/HTPB propellant can be increased and its pressure exponent can be reduced with spherical CO nanometer powder [3]. In [14] the authors investigated the effects of ten kinds of nanocatalysts on the combustion properties of DB/RDX-CMDB propellant. In [16] the authors studied the effect of nano-catalysts (Al₂O₃, Fe₂O₃, TiO₂, SnO₂) on the decomposition of amino-nitro-benzo-difuroxane.

The disposal of materials is also an area of research in China. For

example, in order to dispose of the leaking N_2O_4 liquid propellant in an emergency, research was conducted using uniform porous nano-size spherical $Ca(OH)_2$ powder prepared by the CaO hydrolysis-azeotropic distillation method [2]. Here, the grain size of $Ca(OH)_2$ was 200-300nm, the pore diameter was 8-15nm, and the specific surface area was $63m^2/g$. A movable leakage disposal device was constructed by filling a pressure bottle with the prepared powder. Leakage can be controlled by spraying the powder over the leakage. Experimental results showed that the removal rate of NO_2 gas was up to 90%. Through adsorption, absorption, infiltration, and interfacial chemical reactions, $Ca(OH)_2$ powder captured the NO_2 gas and covered the leaking liquid, preventing its evaporation and diffusion.

In [11], it was noted that unsaturated polyester (UP) as a solid propellant inhibitor has deficiencies due to its fragility of solidification, its low coefficient of elongation at low temperature, its poor flame retardant properties, and its resistance to ablation. In order to overcome those deficiencies, methods of modifying an UP inhibitor with nanofillers have been studied.

Because of its novelty, there is no general core of researchers dedicated to this field. However, the Xi'an Modern Chemistry Research Institute is one of the leading institutes studying energetic nanomaterials. Specifically, Zhao Feng-qi and Li Ji-zhen, senior researchers at Xi'an, have conducted research in this area. Zhao Feng-qi has done experimental research with nanocatalysts. The National Special Superfine Powder Engineering Research Center in Nanjing, which in one study was able to synthesize cobalt nanometer powder, is the other facility conducting high quality energetic nanomaterials research.

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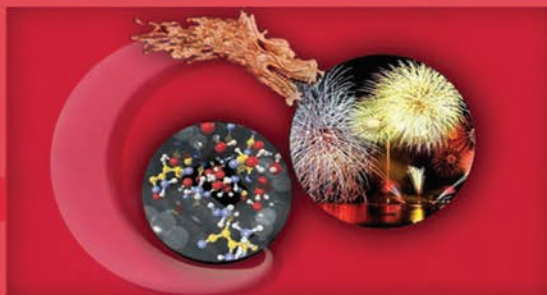
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ENERGETICS SCIENCE & TECHNOLOGY IN CHINA

“As Chancellor of the University System of Maryland, I am especially proud of the extensive number of US / China partnerships that are ongoing within our university communities. The University of Maryland, College Park (UMCP) gives special attention to the emerging strength of China through both its Institute for Global Chinese Affairs and the Confucius Institute. Adding to these impressive partnerships, I am particularly proud of the relationship that The Center for Energetic Concepts Development at UMCP is establishing with the Chinese Scientific Community through the publication of *Energetics Science and Technology in China*. The importance of these-and other-collaborations will only grow in the years to come as we and institutions in China reap the mutual benefits of higher education exchanges and partnerships.”

William E. Kirwan



“As President of City University of Hong Kong, I am delighted that we are working with universities in the United States on fundamental scientific endeavors. This book provides an excellent venue for scientific dialogue with our colleagues in the United States, and especially the University of Maryland. We are also proud to be hosting the first *Workshop on Energetics - Past and Present*. I am sure this will lead to stronger relationships and ensure future partnerships in this important area.”

Way Kuo

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