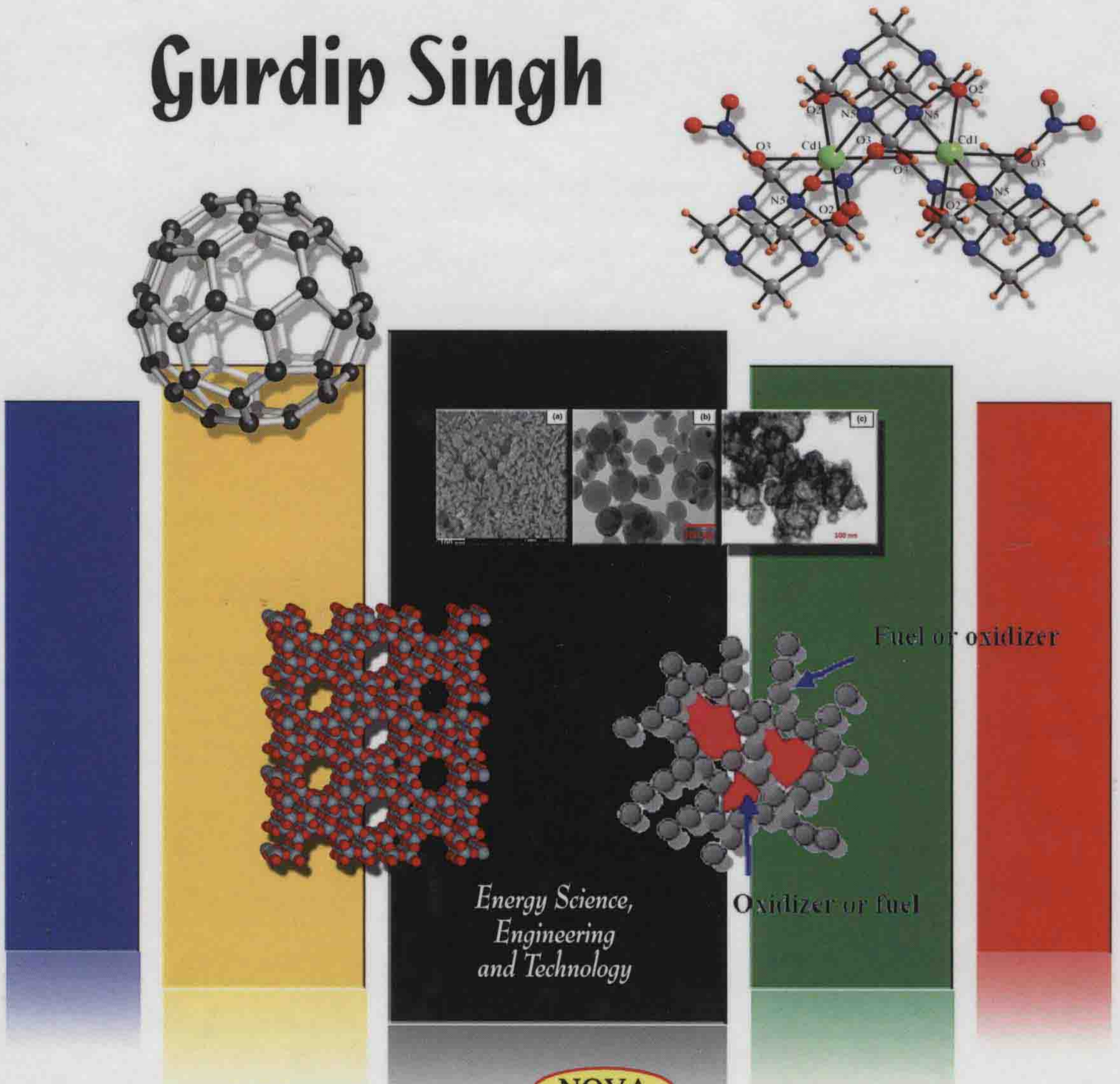
RECENT ADVANCES ON ENERGETIC MATERIALS

Gurdip Singh



Energy Science, Engineering and Technology

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RECENT ADVANCES ON ENERGETIC MATERIALS

GURDIP SINGH

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PREFACE

This book is based on our recent researches in the field of high energetic materials. We have published more than 140 papers during 1990-2014. The principal reasons for this interest is that many of these materials are widely used as source of oxidizers in composite solid propellants (CSPs), explosives and pyrotechnics. The interest in insensitive munitions is still one of the biggest and most important challenges in the research of new high energetic materials. Therefore, we have decided to publish a book entitled, "Recent advances on energetic materials", because we wanted to include most of our published papers along with the work of other authors. We do not give comprehensive historical overview and also refrained from extensive mathematical deductions. This book provides the readers: an introduction of propellants and explosives, mechanism of thermal decomposition of ammonium perchlorate (AP), synthesis, characterization and role of nanomaterials in the thermal decomposition of AP, nanoenergetic compounds along with thermites. It also comprises synthesis, characterization and thermal decomposition of nitrate, perchlorate and NTO salts with various amines. Transition metal, lanthanide metal nitrates and perchlorates complexed with various aliphatic and aromatic amines ligands have also been discussed.

Nanotechnology deals with materials or structures in nanometer scale, typically ranging from sub nanometers to several hundred nanometers. Nanomaterials have found a wide range of applications in many disciplines of science and technology e.g., electronics, catalysis, sensors, medicines, advanced functional materials. The nanoparticles (NPs) as additives in composite solid propellants (CSPs) has many inherent benefits. First, the increase of surface area-to-mass ratio produced by the reduction in diameter has been shown to be favorable for affecting the combustion process through catalytic activity. Second, NPs can be synthesized to have specific surface chemistry and crystal structure. This ability to engineer particles allows for more customization and tailing of propellant formulations when compared to conventional, micron scale additives.

Nanoenergetic compounds offer the promise of much higher energy densities, faster rate of energy release, greater stability, higher burning rates, lower impact sensitivity and more security compared to conventional energetic materials of large size. Nitrate, perchlorate, NTOate salts of amines have been found to dissociate to parent amine and acid molecules (HNO_3, $HClO_4$ and NTO) respectively and proton transfer (NH bond heterolysis) seems to be the primary rate controlling step. The metal amine complexes having ClO_4^- & NO_3^- as counter ion undergoes self-propagative decomposition reaction due to presence of both oxidizing and reducing groups in the same molecules. These complexes at higher temperature decompose to form metal oxide with evolution of gaseous products. These ultrafine or nano metal oxides have interesting electrical, magnetic and catalytic properties. Hence, metal amine complexes have been found to be potential burning rate modifier for HTPB-AP propellants.

This book will be of immense help to everyone involved with energetic materials irrespective of their background; Universities, Institutes, R&D laboratories, Quality assurance, Production agencies, Forensic laboratories, Armed forces (Army, Navy and Air Force), Homeland securities, Chemical Industries etc. It is hoped that this presentation will serve to stimulate more research interest in high energetic, nanoenegetic and nanomaterials.

It is a pleasure to acknowledge my appreciation for the help that I have received from my Ph.D. students. I can only mention a few here. I want to thank Dr. Pratibha Srivastava, Dr. Shalini Dubey, Dr. Dinesh Kumar, Mrs. Reena Dubey, Mrs. Supriya Singh, Mrs. Sunita Singh & Nibha for their assistance. Thanks are also due to Dr. J.K.Sharma for technical assistance. I am also thankful to DST for providing me financial assistance under USERS scheme No. SB/UR/08/2013. Thanks are also due to the Head of Chemistry Department, DDU Gorakhpur University, Gorakhpur, India for providing me space and other administrative facilities.

Prof. Gurdip Singh
M.Sc., Ph.D.
Emeritus Scientist (DST)
Department of Chemistry
DDU Gorakhpur University
Gorakhpur – 273009, India

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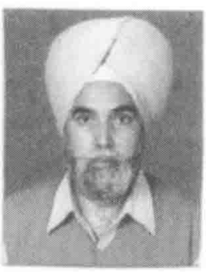
ABOUT THE AUTHOR



Prof. Gurdip Singh retired from the Department of Chemistry, DDU Gorakhpur University, Gorakhpur in 2008. He worked as an Emeritus Scientist (CSIR) during 2008-2011 and Emeritus Fellow (UGC) during 2011-2013. Presently he is working as an Emeritus Scientist (DST) in DDU Gorakhpur University Gorakhpur. He has long research experience in the field of nanomaterials, high energetic materials, essential oils & oleoresins and solid state sulfonation. He has published over 250 research papers and 21 review articles in national and international journals with high impact factors. Three of his books have already been published. He has one patent on "Optical technique for measurement of flame temperature of solid propellant using the sodium-line reversal technique". He has participated and delivered invited lectures at various national and international symposia and conferences. He is an honorary editor of Green and Sustainable Chemistry (USA), Journal of Essential Oil Bearing Plants (India) and also reviews many of the research papers of reputed journals. He is leading a big research group and has completed 16 research projects funded by various agencies and one in hand. Twenty two students have already been awarded their Ph. D. degree under his supervision.

Dr. Singh is a life member of High Energy Materials Society of India, Indian Thermal Analysis Society, Catalysis Society of India, Indian Science Congress Association, Essential Oil Association of India, Indian Society of Chemists and Biologists and Association of Food Scientists & Technologists (India). He is a recipient of the Dr. Dhingra Award (1991) by EOAI and the NETZSCH-ITAS award (2004). He had visited Czech Republic during 2002 under INSA-ASCR exchange of scientist programme.

Prof. Gurdip Singh)
M.Sc., Ph.D.
Emeritus Scientist (DST)
Department of Chemistry
DDU Gorakhpur University
Gorakhpur – 273009, India
E-mail: gsingh4us@yahoo.com

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Chapter 1

EXPLOSIVES AND PROPELLANTS

Gurdip Singh
DDU Gorakhpur University, Gorakhpur, India

ABSTRACT

High energetic materials can broadly be classified into three classes- explosives, propellants and pyrotechnics. This chapter is focused to give a summary on the explosives and propellants. It is divided into two parts. The first part briefly surveys the classification, properties and application of explosives while the second part includes classification and properties of propellants, basic requirement for high performance and ingredients for solid propellants.

1.1. EXPLOSIVES

An explosive may be defined in one of the following ways:

1. An explosive is a material, either a pure single substance or a mixture of substances, which is capable of producing an explosion by its own energy.
2. An explosive is a substance which, when suitably triggered, releases a large amount of heat and pressure by way of a very rapid self-sustaining exothermic decomposition reaction. The entire phenomenon takes place in a few microseconds, accompanied by a shock and loud noise.
3. An explosive is a chemical substance or a mixture of chemical substances, which when subjected to heat, percussion, detonation or catalysis, undergoes a very rapid decomposition accompanied with the production of a large amount of energy. A large volume of gases, considerably greater than the original volume of the explosive, is also liberated.
4. An explosive is a substance or device which produces, upon release of its potential energy, a sudden outburst of gases thereby exerting high pressure on its surroundings.

Explosives must be inert to substances with which they may come into contact, including air and moisture, and they must be thoroughly stable under the expected conditions of storage and uses. At the same time, they must be sufficiently sensitive to be initiated by convenient means. Explosives are thought to have been discovered in the seventh century by the Chinese and the first known explosive was black powder (gunpowder) which is a mixture of charcoal, sulfur and potassium nitrate. Subsequently, with the development of nitrocellulose (NC) and nitroglycerine (NG) in Europe, a new class of explosives viz. low explosives came into existence. As this new class of explosives burn slowly in a controlled manner giving out a large volume of hot gases which can propel a projectile, these low explosives were termed as propellants. The discovery of high explosives such as picric acid, trinitrotoluene (TNT), pentaerythritol tetranitrate (PETN), cyclotrimethylene trinitramine (research department explosive RDX), cyclotetramethylene tetranitramine (high melting explosive HMX) etc. which are more powerful but relatively insensitive to various stimuli (heat, impact, friction and spark), advocated their use as explosive fillings for bombs, shells and warheads etc. [1-2].

1.1.1. Classification of Explosives

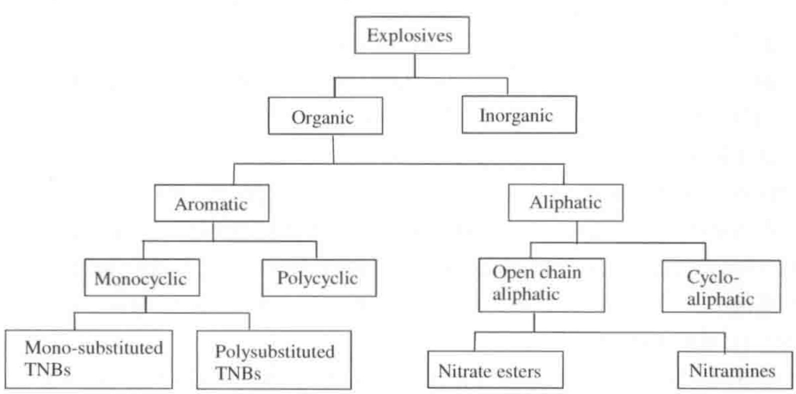
Explosives can be classified on the basis of several ways.

(i) Classification on the Basis of Different Groups / Chemical Nature

Explosives can be classified (Scheme 1.1) both on the basis of their chemical nature and uses. From chemical point of view, these are individual substances or mixtures [3].

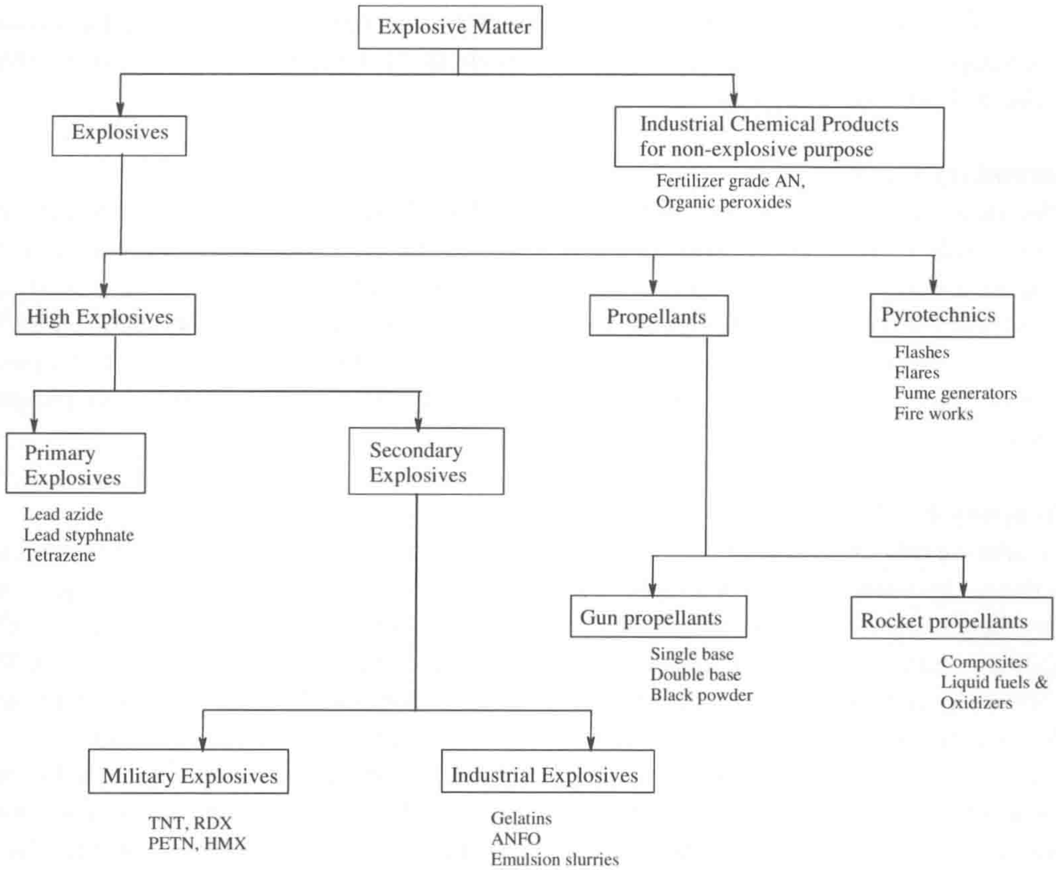
The individual substances are further divided into

- Nitro compounds
- Nitrate Esters
- Nitramines
- Chlorates and perchlorates
- Azides
- Various compounds capable of producing an explosion (fulminates, acetylides, tetrazene, peroxides etc.)



Scheme. 1.1. Classification of Explosives on the basis of different groups / chemical nature.

(ii) Classification on the basis of their application



Scheme. 1.2. Classification of Explosives on the basis of their application.

1.1.2. Brief Description of Explosives

1.1.2.1. Low Explosives or Deflagrating

A low explosive is a combustible substance that decomposes rapidly (deflagrate) but does not explode under normal conditions. They burn slowly and regularly. The action is therefore less shattering. On combustion, low or deflagrating explosives evolve large volume of gases but in a controllable manner. Examples are black powder, smokeless powder, propellants: single-base (SB), double-base (DB), triple-base (TB), composite, composite modified DB, fuel rich etc. and pyrotechnics such as flares and illumination devices.

1.1.2.2. High Explosives or Detonating

These explosives are characterized by very high rates of reaction and generation of high pressures on explosion. They are usually sub-divided into (i) primary or initiatory explosives, (ii) secondary explosives and (iii) tertiary explosives. High explosives undergo detonation at rates of 1000 to 9000 meter per second. Such explosives are normally employed in mining, demolition and military warheads. Most of the low explosives are mixtures whereas most of the high explosives are compound, but to both there are some exceptions.

i) Primary Explosives

Primary explosives are extremely sensitive to shock, friction and heat, they will burn rapidly or detonate if ignited. They are generally used in primers, detonators and percussion caps. Examples of primary explosives are lead azide (LA), mercury fulminate (MF), silver azide, basic lead azide (BLA) etc.

ii) Secondary Explosives

Secondary explosives or base explosives are relatively insensitive to shock, friction and heat but explode with greater violence when set off by an explosive shock obtained by detonating a small amount of a primary explosive in contact with it. These are sometimes added in small amounts to blasting caps to boost their power. Dynamite, TNT, RDX, PETN, HMX and others are secondary explosives. PETN is often considered as benchmark compound; the materials which are more sensitive than PETN being classified as primary explosives.

iii) Tertiary Explosives

Tertiary explosives, also called blasting agents are so sensitive to shock that they cannot be reliably detonated by practical quantities of primary explosives, and instead require an intermediate explosive booster of secondary explosive. Examples are ammonium nitrate (AN, NH_4NO_3), ammonium perchlorate (AP, NH_4ClO_4), ammonium dinitramide [ADN, $NH_4N(NO_2)_2$] and mononitrotoluene (MNT), fuel oil mixture (ANFO) and slurry or 'wet bag' explosives. These are primarily used in large scale mining and construction operations.

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

1.1.2.3. Military Explosives

Military explosives comprise explosives and explosive compositions or formulations that are used in military munitions (bombs, shells, torpedoes, grenades, and missile or rocket warheads). The bulk charges (secondary explosives) in these munitions are insensitive to some extent and are, therefore, safe for handling, storage and transportation. They are set off by means of an explosive train consisting of an initiator followed by intermediates or boosters. Military explosives must be physically and chemically stable over a wide range of temperatures and humidity for a long period of time. They must be reasonably insensitive to impact, such as those experienced by artillery shells when fired from a gun or when they penetrate steel armor. They are used for a number of applications. They are fired in projectiles and dropped in aerial time bombs without premature explosion. The raw materials necessary to manufacture such explosives must be readily available for production in bulk during wartime.