Chapter 1

Introduction to Explosives and Propellants

Part of the text from part-I of this chapter has been presented:

1. S. Venkatachalam, **G. Santhosh,** K.N. Ninan ꞌ
   "High Energy Oxidisers for Advanced Solid Propellants and Explosives"
   *Advances in Solid Propellant Technology, Iˢᵗ International HEMSI
   Workshop, Ranchi, India,* **2002,** *87-106.*

Part-II of this chapter has been communicated:

1. **G. Santhosh**, S. Venkatachalam, K.N. Ninan
   "An Overview on the Synthetic Routes and Properties of Ammonium
   Dinitramide (ADN) and Other Dinitramide Salts"
   Propellants Explosives Pyrotechnics (communicated).

ENERGETIC materials used as ingredients in both propellants and explosive formulations are either high melting crystalline solids or liquids at room temperature. The search for new energetic materials with a given performance, sensitivity and physical properties is one of the major challenges to the chemical industry. New energetic compounds with higher densities are often designed by modifying known substances by addition and/or modification of explosophoric groups ($-NO_2$, NO_3, $-ONO_2$, N_3, $-ClO_4$ etc.,). Solid propellants are widely used in modern rockets and missiles. The solid propulsion looks to the future with enhanced requirements in terms of reduction of costs, increased performance, improved reliability and more friendly environmental impact. In this perspective new generation of solid propellants consisting new oxidizers and binders are needed. This chapter is focused to give a summary on the development and use of various energetic materials. It is divided into two parts. The first part briefly surveys the development of various explosives, oxidizers, polymeric fuel/binder systems used or considered for use in solid propellants. It includes a brief background, requirement for high performance, advantages and shortcomings of the various systems. Special emphasis is placed on the development of dinitramide ($-N(NO_2)_2$) based energetic materials. The second part of this chapter presents a comprehensive review on the methods used for the synthesis of various dinitramide salts and discuses their properties.

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PART-I

1.1. Background and History of Explosives

The earliest energetic material referred to by name is "Greek Fire". It was actually developed by the Byzantines of Constantinopole around the 7th century A.D. and consisted of a petroleum distillate, thickened by dissolving resinous and other combustible materials. Its exact composition is unknown. The development of explosives began with the formulation and use of black powder, which is also known as gunpowder in about the middle of the thirteenth century [1,2]. In 220 BC, Chinese alchemists accidentally made black powder while separating gold from silver. Blackpowder was introduced in 14th century by Roger Bacon and in 1320 a German Berthold Schwartz made black powder and studied its properties. The fuel is a powdered mixture of charcoal and sulphur, which is mixed with potassium nitrate (KN, KNO_3) oxidizer. At the end of the 18th century and at the beginning of the 19th century the composition became more or less standardised KNO_3/C/S (75/15/10 w/w). In 1654, Glauber introduced ammonium nitrate (AN, NH_4NO_3), but it was not until the beginning of the 19th century when AN was considered for use in explosives by Grindel and Robin as a replacement for potassium nitrate in black powder.

Later in the nineteenth century the nitration of many compounds to produce high-energy explosives were realized. Research on explosives greatly intensified during World War II. Much of the interest in the early part of the 19th century was in the effects of nitration of relatively common materials, such as silk, wool, resins, wood, cotton etc., Table 1.1 provides a reference guide to the chemical formulas and structures of some of the more common explosives in use now. There has been enormous growth in the explosives field in the latter half of the twentieth century with the advent of modern electronic instrumentation, characterization techniques, computational analysis etc.,

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Table 1.1: Names and formulas of some of the explosives in use

Name	Structural formula	Molecular formula
Nitrocellulose		$[C_6H_7N_3O_{11}]_n$
Nitroglycerine		$[C_3H_5N_3O_9]$
Pentaerythritol Tetranitrate (PETN)		$[C_5H_8N_4O_{12}]$
Trinitrotoluene (TNT)		$[C_7H_5N_3O_6]$
Trinitrophenol (Picric acid)		$[C_6H_3N_3O_7]$
Triaminotrinitrobenzene (TATB)		$[C_6H_6N_6O_6]$
Cyclotrimethylene-trinitramine / Research & Development Explosive (RDX)		$[C_3H_6N_6O_6]$
Cyclotetramethylene-tetranitramine/ Her Majesty's Explosive (HMX)		$[C_4H_8N_8O_8]$

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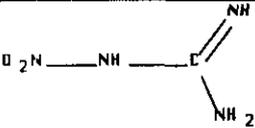
Nitroguanidine (NQ)		$[CH_4N_4O_2]$
Lead azide		PbN_6
Silver azide	AgN=N=N	AgN_3
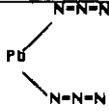
1.1.1. Nitro Explosives

In 1846 the Italian Professor Ascanio Sobrero discovered liquid nitroglycerine (NG). A few years later the Swedish inventor, Immanuel Nobel developed a process for manufacturing nitroglycerine. Nitroglycerine has a great advantage over black powder since it contains both fuel and oxidizer elements in the same molecule. Due to its unpredictability and the dangers of handling it in normal liquid state it was not used. Nitration of cellulose to nitrocellulose (NC) was undertaken by different workers, notable Schonbein at Basel and Bottger at Frankfurt-am-main during 1845-47. Until 1868, nitrocellulose was not used in military and commercial explosives because of its high explosive nature. E.A. Brown discovered that nitrocellulose could be handled under wet conditions. Wet compressed NC when mixed with small quantity of dry NC could be exploded, whereas dry compressed NC with high extent of nitration could be detonated using a detonator.

In 1875 Alfred Nobel discovered that on mixing nitrocellulose with nitroglycerine a gel was formed. This gel was developed to produce blasting gelatine, dynamite and later in 1888, ballistite, the first smokeless powder. It was a mixture of nitrocellulose, nitroglycerine, benzene and camphor. The Swedish chemists Ohlsson and Norrbin found that the explosive properties of dynamites were enhanced by the addition of ammonium nitrate. In 1885 Turpin has found that Picric acid

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(Trinitrophenol) to be a suitable replacement for black powder. In 1888 black powder was replaced by picric acid in British munitions under the name Liddite. In Russia, Panpushko prepared picric acid in 1894 and soon realized its potential as an explosive. Eventually, picric acid was accepted all over the world as the basic explosive for military uses.

Around 1902, the Germans and British had experimented with trinitrotoluene (TNT), first prepared by Wilbrand in 1863. Pure 2,4,6-trinitrotoluene was prepared in 1880 by Hepp and its structure established in 1883 by Claus and Becker. By 1914, TNT became the standard explosive for all armies during World War I. Use of a mixture of TNT and ammonium nitrate, called amatol became widespread to relieve the shortage of TNT. Other explosives with superior characteristics were also developed. Cyclotrimethylenetrinitramine (RDX) was first prepared in 1899 by Henning for medicinal use. Its value as an explosive was not recognized until 1920 by Herz. Herz succeeded in preparing RDX by direct nitration of hexamine, but the yields were low and the process was expensive and unattractive for large-scale production. RDX was not used as the main filling in British shells and Bombs during World War II, but was added to TNT to increase the power of the explosive compositions.

Research and development continued throughout World War II to develop new and more powerful explosives and explosive compositions. Octogen or Cyclotetramethylenetetranitramine (HMX) became available at the end of World War II. The detonation performance of HMX was found to be superior to that of RDX. Other explosives viz., pentaerythritoltetranitrate (PETN), Triaminotrinitrobenzene (TATB), hexanitrobenzene (HNB) etc., was developed later for various applications. The flow sheet in Figure 1.1 gives the general classification of explosive materials with relevant examples [3]. It shows the breakdown of energetic materials into families designed for the specific purposes associated with different types of weapon applications and civilian uses of explosives.

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                        ┌─────────────────────┐
                        │  Explosive Matter   │
                        └─────────────────────┘
                                  │
              ┌───────────────────┴───────────────────────┐
              │                                            │
      ┌───────────────┐              ┌──────────────────────────────┐
      │  Explosives   │              │  Industrial Chemical Products │
      └───────────────┘              │    for non-explosive Purpose  │
                                     └──────────────────────────────┘
                                        Fertilizer grade AN,
                                        Organic peroxides
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Explosives → High Explosives, Propellants, Pyrotechnics

High Explosives → Primary Explosive, Secondary Explosive

Primary Explosive

Lead azide
Lead styphnate
Tetrazene

Secondary Explosive → Military Explosives, Industrial Explosives

Pyrotechnics

Flashes
Flares
Fume generators
Fire works

Propellants → Gun propellants, Rocket Propellants

Gun propellants

Single base
Double base
Black powder

Rocket Propellants

Composites
Liquid fuels &
Oxidizers

Military Explosives

TNT, RDX
PETN,
Tetryl, HMX

Industrial Explosives

Gelatins
ANFO
Emulsion slurries

Figure 1.1: Explosive Materials and their Application

1.1.2. Liquid Oxidizers and Explosives

Liquid oxygen explosives (LOX) came into use in 1926 and their use was continued into the 1960s. Two problems exist with LOX; they lose their explosiveness as the liquid oxygen evaporates (b.p. -183°C); and they are easily inflammable. The combination of liquid oxygen with the detonable fuel acetylene (acetylene 25%/ O_2 75%) produces an explosive with detonation velocity 6000 m/s.

Nitrogen tetroxide (N_2O_4) is another liquid oxidizer capable of forming powerful explosives. It exists over the narrow temperature range between its freezing point (-11°C) & 21°C, where it dissociates into NO_2. Explosives made with liq.N_2O_4 and combustible liquids (CS_2, nitrobenzene, nitrotoluene, gasoline, halogenated hydrocarbons) were considered in the 1880s. Mixtures of N_2O_4 with 64% nitromethane have a detonation velocity of 6900 m/s. N_2O_4 explodes on contact with a number of fuels: acetic anhydride, liquid NH_3, methyl & ethylnitrate, propene, hydrazine-type fuels.

Peroxides with oxygen bonded to oxygen, can be violent oxidizers in the presence of fuel. Pure H_2O_2 decomposes violently above 80°C. Solutions of 90.7% H_2O_2 have reported detonation velocities of 5500 m/s to 6000 m/s. H_2O_2 when mixed with organic materials is readily detonable. One of the propellant systems on the space shuttle uses the combination of H_2O_2 & unsymmetrical dimethyl hydrazine (UDMH).

1.2. Solid Rocket Propellants

Propellants are mixtures of chemical compounds that produce large volume of gas at controlled, predetermined rates [4]. Their major applications are in launching projectiles from guns, rockets, and missile systems. Propellant-actuated devices are used to drive turbines, move

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pistons, operate rocket valves, start aircraft engines, eject pilots, pump fluids and act as sources of heat in special devices. Solid propellants are compact, have a long storage life, and may be handled and used without exceptional precautions. These are substances containing fuel and oxidizer in a single molecule or those which contain suitable molecular configurations which on appropriate initiation, burn slowly - a few mm to about a hundred mm/s, resulting in deflagration or burn up very fast – at about a few km to 10 km/s, resulting in explosion or detonation [5,6].

In the initial years, a composite mixture of carbon (fuel), sulphur (binder) and potassium nitrate (oxidizer) was used in the solid propellant rocket motors [7]. In 60's and early 70's propellants based on either nitrocellulose or on synthetic cross-linked polymeric binders such as polysulfides, polyurethanes or polybutadienes were used. Propellants containing only plasticized nitrocellulose as energy source are referred to as single-base propellants. Propellants, which contain both NC and a liquid explosive plasticizer such as nitroglycerin, are called double-base propellants. Multiple or triple base propellants incorporate a crystalline explosive such as nitroguanidine in the double-base formulation. Composite-modified double-base rocket propellants generally contain an inorganic crystalline oxidizer such as ammonium perchlorate (AP, NH_4ClO_4) and a metallic fuel, e.g. aluminium in a double-base matrix.

Polymer-based rocket propellants, generally referred to as composite propellants, contain cross-linked polymers that act as a viscoelastic matrix for holding a crystalline inorganic oxidizer such as ammonium perchlorate and for providing mechanical strength. Many other substances may be added including metallic fuels, plasticizers, extenders, and catalysts to improve the mechanical, storage and ballistic properties.

A typical composite propellant used in solid rocket motors consists in general 1) organic polymeric binder 2) solid oxidizer 3) metal powder

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4) plasticiser 5) anti-oxidant 6) burning rate catalyst and 7) curing agent. The propellant is thus a composite mixture of finely ground solid particles of an oxidizer and a metal in a matrix of combustible polymeric fuel binder. The finely suspended solids have a good adhesion with the surrounding polymeric binder to impart strength to the propellant.

1.2.1. Propellant Types

Chemical propellants provide a simple and effective way of creating propulsion for flight [8]. The rocket propellant gained importance during World War I and II with the use of various types of propellants. The classification is given below.

1.2.1.1. Single Base Propellants

Single base propellants are mainly used as gun propellants and are not used in rocketry. As there is no plasticizer in single base formulations, the nitrocellulose is not plasticised properly and hence the propellant has a horny structure and poor mechanical properties. Only thin webbed charges are processed as single base propellants.

1.2.1.2. Double and Triple Base Propellants

Double base propellants contain two energetic ingredients viz., nitrocellulose and nitroglycerine. Nitroglycerine is used to plasticise the high molecular weight nitrocellulose to yield thermoplastic materials. Both nitrocellulose and nitroglycerine are high explosives each capable of undergoing detonation with a detonation velocity of 6-7 km/s. Other nitrate esters like glycol dinitrate, diethylene glycol dinitrate, metriol trinitrate etc., can also be used in place of nitroglycerine as explosive plasticisers for nitrocellulose. A triple base propellant contains nitrocellulose, nitroglycerine and an energetic ingredient nitroguanidine (NQ). NQ is an aliphatic nitramine with characteristic $N-NO_2$ group. Incorporation of ultra fine grade NQ yields grains with reasonably good mechanical properties.
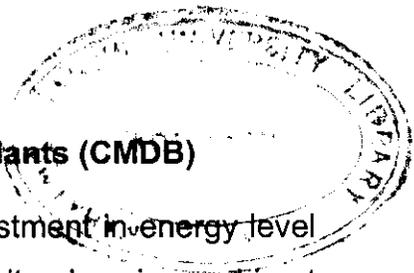
1.2.1.3. Composite Modified Double Base Propellants (CMDB)

In conventional double base propellants, adjustment in energy level is made by varying the percentage of nitrocellulose, nitroglycerine and inert components. The energy level of the double base propellant can be increased by incorporating a crystalline inorganic oxidizer like ammonium perchlorate (AP). Significant amount of metallic fuel, viz. aluminium powder can also be added to exploit maximum energy and such a high-energy version is called composite modified double base propellant. In the CMDB formulations double base matrix is approximately 60% (by weight) and the rest AP and aluminium powder.

1.2.1.4. Composite Propellants

These are solid rocket fuels, consisting of oxygen donating inorganic salts and a binder made of plastic. The polymeric binders include polysulfides, polybutadiene-acrylic acid (PBAA), polybutadiene-acrylonitrile-acrylic acid (PBAN), polyurethane (PU) and carboxyl or hydroxyl terminated polybutadiene (CTPB or HTPB). Nitrates and perchlorates are used as oxidizers.

1.3. Development of Composite Propellants

The development of castable composites started in 1942 at the Guggenheim Aeronautical Laboratory with the formulation of mixes containing ca. 25% (by weight) asphalt and 75% potassium perchlorate [7]. These were rapidly superseded by a variety of cross-linked elastomer-based propellants with superior mechanical properties and increased available energy, which contained as much as 90% crystalline filler in the polymeric matrix. The most widely used binders include polysulfides, polyurethanes, and polybutadienes. The polysulfides, developed in the late 1940s and early 1950s, start with low viscosity partially polymerized mercaptyl (-SH) terminated compounds, which are cured by oxidation by compounds such as p-quinone dioxime or PbO_2.

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Other ingredients are sulfur as a cure catalyst, dibutyl phthalate as plasticizer, magnesium oxide to improve thermal stability, iron oxide and ferrocene as burning rate catalysts, and copper phthalocyanine as a burning rate suppressor. Polysulfide based propellants have been replaced for most purposes by binders with superior characteristics. The polyurethanes were developed during the 1950s to take advantage of the long-chain polyalcohols, which were becoming available in a wide molecular weight range. With diisocyanates these form stable network polyurethanes , which are used in large, case-bonded rocket motors. The polybutadienes were first made during the late 1950s by curing the liquid copolymer of butadiene and acrylic acid (PBAA) with epoxides and/or polyfunctional imines. The PBAA binders were replaced during the 1960s by superior terpolymers of butadiene, acrylonitrile and acrylic acid (PBAN). The PBAN has been extensively used in high performance rockets. During the early 1960s, polybutadiene prepolymers were developed with terminal carboxy groups. These were cured with epoxides or aziridines to form polymers that have better low temperature mechanical properties than the PBAN. Hydroxy-terminated polybutadienes (HTPB) cured with isocyanates were also developed during this period; they have superior processing properties and low temperature properties. Figure 1.2 gives an overview of the evolution of composite and double base propellants through the major improvements brought to the various families of materials [9].

1.4. Major Components of a Composite Solid Propellant

Composite propellants are made of a polymeric matrix, loaded with a solid oxidizer, and possibly a metal powder that plays the role of a secondary fuel component. A certain number of properties such as burning rate, rheology and mechanical behaviour are directly related to this composite character.

1.4.1. Oxidizer

All energetic materials contain oxygen, which is needed for the explosive reaction to take place. Oxygen can be introduced by chemical reactions (nitration) or by mechanical incorporation of materials containing bound oxygen. The most important solid oxidizers are nitrates – AN, sodium nitrate, potassium nitrate; chlorates – potassium chlorate, ammonium perchlorates.

The characteristics of a good oxidizer are the capability of supplying oxygen to burn the binder and other fuels with maximum heat of combustion and highest enthalpy of formation.

1.4.2. Binder

Binders are compositions that hold together a charge of finely divided particles and increase the mechanical strength of the resulting propellant grain. These are usually functionally terminated prepolymers such as hydroxy-terminated polybutadiene (HTPB), carboxyl-terminated polybutadiene (CTPB), resins, plastics, or asphaltics used dry or in solution. The enthalpy of formation (ΔH_f, discussed later) should be more positive and the binder must have suitable structure, which on combustion produces low molecular weight gases, thereby leading to high specific impulse (I_{sp}, discussed later).

1.4.3. Metallic Fuel

Most explosives and pyrotechnic compositions are prepared by mixing of oxidizers and fuels. Fuel means any substance capable of reacting with oxygen and oxygen carriers with the evolution of heat. Aluminium is virtually the universal fuel for composite propellants. It is available in spherical powders, with small diameters and it is well suited for high solid loading. Aluminium is safe to handle because of the fine layer of aluminium oxide, which inactivates the grains in humidity. Apart from

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aluminium, boron, beryllium and lithium have also been used in very specific applications. Because of the increased cost, toxicity, long-term instability and toxic combustion products, the latter fuels are not used.
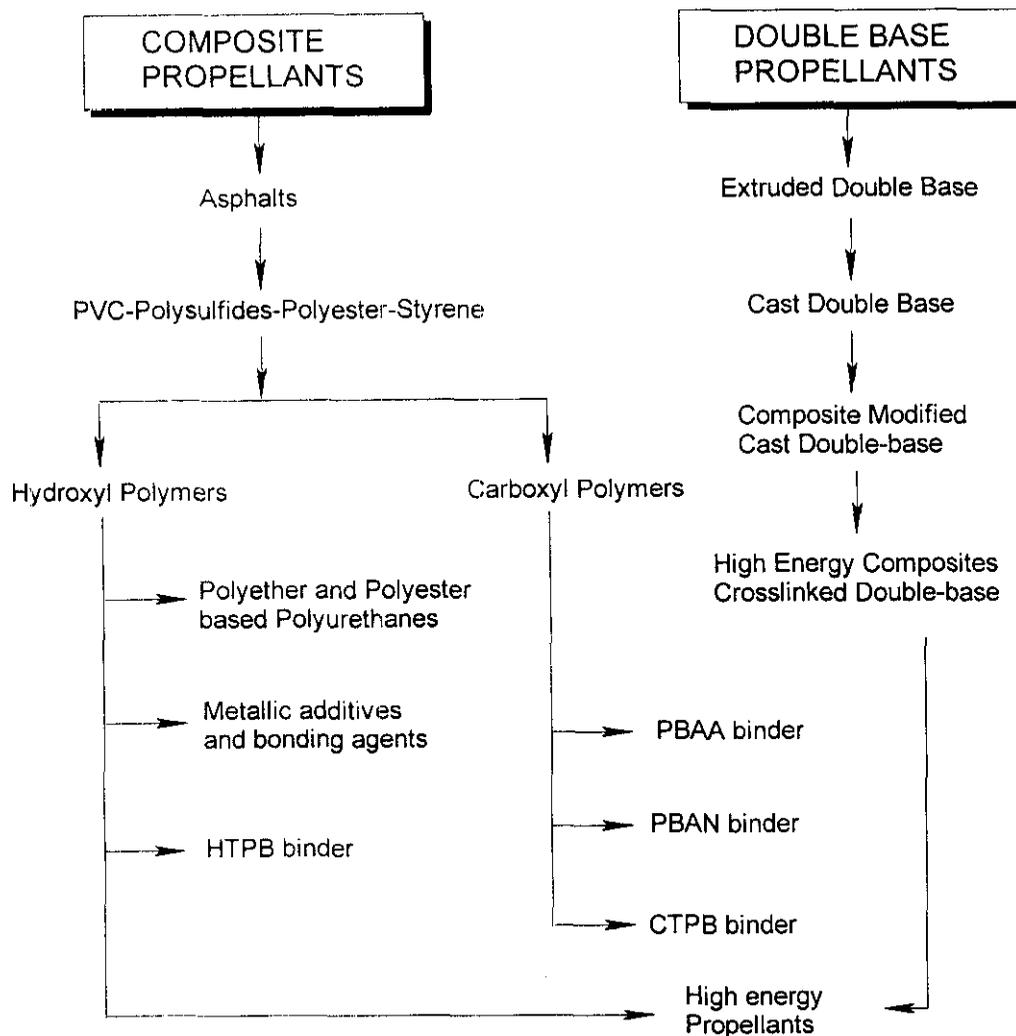
Figure 1.2: Chronological development of double base propellants and composite propellants

1.4.4. Cross-linking Agents and Curing Agents

The function of a cross-linking agent is to facilitate curing of the prepolymer molecules by forming a cross-linked network. It plays a critical role in kinetics of the crosslinking reaction and in achieving the desired

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mechanical properties of the propellant. Examples are trimethylol propane (TMP), glycerol etc., In addition to cross-linking agents, curing agents like toluene diisocyanate (TDI), isophoronediisocyanate (IPDI) or hexamethylene diisocyanate (HMDI) are used, which react with the terminal functional groups of the binder and crosslinking agent to give rigid matrix with very good mechanical properties to the propellant.

1.4.5. Plasticizers

Plasticizer plays the essential role of complementary element to reduce the viscosity of the slurry and to improve the mechanical properties by lowering the T_g and the modulus of the binder. Typically, it is oil that is non-reactive with the polymer chains, thereby reducing their interaction in the liquid state as well as in the cross-linked state. Examples include diisooctyl azelate, diisooctyl sebacate, isodecyl pelargonate, dioctyl phthalate and dioctyl adipate.

1.4.6. Other Additives

These are liquid or solid products added in small quantities (a few %) of the binder. Their function is to modify the characteristics of the propellant. Burning rate modifiers are used to modify the propellant burning rate and to adjust the pressure exponent "n" of the burning rate-pressure curve in the pressure zone where the propellant grain will be operating (discussed later). Examples include ferrocene, n-butylferrocene, copper chromate etc.,

Antioxidants are essential to ensure satisfactory ageing of the propellant in ambient conditions. Examples are ditertiary butyl paracresol, 2,2-methylene bis(4-methy-6-tertiary-butyl phenol) etc.,

Catalysts are often necessary to reduce the curing time of the propellant. They have a significant impact on the mechanical properties by facilitating some favourable reactions, thereby giving direction to the

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formation of the polymer network. They are usually salts of transition metals. Examples include dibutyltindilaurate, lead octoate, iron acetyl acetonate, lead chromate etc.,

1.5. Basic Requirements for High Performance

A solid propellant develops thrust or recoil force due to discharge of gaseous products when it undergoes combustion. The burning process in the rocket motor is influenced by the thermodynamic performance values of the propellant, the burning characteristics of the propellant grain, depending on its shape and by the pressure influence of the burning rate. The specific impulse (I_{sp}) is a means of characterizing and evaluating the properties and is viewed as a key measure of propellant performance [10]. It can be interpreted as the thrust derived per unit weight flow of propellant. I_{sp} is a theoretical maximum of the mechanical work that can be derived from the adiabatic decomposition of a unit mass of propellant followed by expansion of the decomposition products into an environment of specified pressure, which is usually the near total vacuum of outer space. In other words, it is the enthalpy release converted into the kinetic energy of the exhaust jet. It is expressed by a simplified relation given by Equation 1.1.

$$I_{sp} = T_c^{1/2} N^{1/2} \qquad\qquad \dots\dots\dots(1.1)$$

where,

T_c is the combustion chamber temperature and N is the number of moles of gaseous products produced. The heat released during the combustion increases the flame temperature T_c, which is given by Equation 1.2.

$$T_c = \frac{-\Delta H}{C_p} \qquad\qquad \dots\dots\dots(1.2)$$

where, ΔH is the heat of reaction, C_p is the specific heat capacity.

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Specific impulse is also defined as the thrust or impulse achieved per unit weight of propellant and is given by Equation 1.3

$$I_{sp} = \frac{F.t}{W} \qquad \ldots\ldots\ldots(1.3)$$

I_{sp} = specific impulse

F = thrust (N)

t = time (s)

W = weight of propellant

The heat of reaction (ΔH) is given by Equation 1.4.

$$\Delta H(T) = \Delta H_f(T)_{products} - \Delta H_f(T)_{reactants} \qquad \ldots\ldots\ldots(1.4)$$

The heat of formation (ΔH_f) depends on the bond energies between the atoms of the various ingredients used in propellant formulations. To get as high a combustion temperature as possible, one must select reactants with large positive heats of formation and products with large negative heats of formation. The maximum energy output is possible from a material when it contains bonds with as small bond energies as possible and products with as high bond energies as possible.

The linear burning rate of a propellant is the velocity with which combustion or burning process progresses along the length of the propellant grain (at right angles to the current surface of the propellant). It depends on the chemical composition, geometric shape of the grain, the pressure, temperature and the viscoelastic state of the propellant (whether slurry, cured mass, powder or gel).

The burning rate versus pressure law is usually expressed by the formula given by Saint Robert and Vielle and is given in Equation 1.5

$$r = aP^n \qquad \ldots\ldots\ldots(1.5)$$

where, 'n' is the pressure exponent, 'a' is the rate of burning constant and 'P' is the pressure in MPa. For a propellant, generally 'n' values range between 0.2 to 0.7 at a pressure ranging from 3-15 MPa.

Oxygen balance (OB) is important for the propellant/explosive/ oxidizer characteristics. It is expressed as the excess weight % of oxygen present in the molecule after complete conversion of the fuel elements to CO_2, H_2O, CO etc. If the amount of oxygen bound in the explosive is insufficient for the complete oxidation reaction, the material said to possess a negative oxygen balance and if it possess sufficient oxygen it is said to have a positive oxygen balance [11].

Explosives such as nitrate esters, nitro compounds and nitramines contain only the elements carbon, hydrogen, oxygen and nitrogen and are called CHNO explosives[12] having the general formula: $C_aH_bN_cO_d$

Oxygen balance (OB) is given by Equation 1.6.

$$OB = (d-2a-\frac{b}{2}) \times \frac{1600}{M}$$ ....(1.6)

where M is the relative molecular mass of the explosive.

One of the primary ways of improving the I_{sp} of propellants is by increasing enthalpy release and increasing the average molecular weight of the exhaust gases to attain more working fluid. In order to achieve this the propellant should contain sufficient oxygen to maximise the energy release. This is possible when the molecules contain bonds between first row elements i.e., C-N, N-O, N=O, N=N, N-F and O-N in propellant formulations. The presence of more number of such bonds improves the oxygen balance. Examples are ammonium dinitramide (ADN), ammonium nitrate (AN), HNF, Cl-20 etc, (discussed later). Systems that yield high performance can undergo violent reactions on heating, impact or shock. They must be safe enough for handling during production and use.

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The density of the propellant should be as high as possible to store as much energy per volume as possible. Density is far less a critical factor in the performance of propellants than it is for explosives, having a small indirect effect on I_{sp}. In addition to I_{sp}, the density impulse (the product of specific impulse and density) also becomes important for launch vehicle applications such as first stages of launchers, boosters and jet assisted take off vehicle applications where, the propellant mass is much less compared to the total mass of the launch vehicle. Maximizing the density is important because it permits the volume fraction of the particulate within the composition is minimised and improves the flow properties of the mix. In addition to the above the cured propellant has improved energy, absorbing capacity or toughness because of low solid loading in the system. Solid metallic hydrogen expanding into a vacuum would have an excellent I_{sp}, provided one is able to technologically realize such a system.

1.6. Energetic Materials – Currently in Use

In past decades fascinating and novel molecular structures have been synthesized and a number of them are being developed for use in rocket propulsion and ordnance industries [13-15]. Unlike photophysics or biotechnology, the science of energetic materials evolved slowly. It has taken nearly 200 years to reach its current status, because the newly developed energetic materials need years of vigorous field-testing. Number of innovative explosives, oxidizers and binders were explored for use in space propulsion. The investigations on solid propulsion have grown over the years and continue to emerge with special attention on 1) safe handling and operation 2) performance reliability and reproducibility 3) cost minimization and so on.

The first oxidizer used in composite propellants was potassium perchlorate (KP, $KClO_4$). It is stable, compatible, and relatively insensitive but contributes little energy. Thus it was soon replaced by AP, which is

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more energetic and is now the most commonly used oxidizer in composite propellants. AP - hydroxyl-terminated-polybutadiene (HTPB) composite mixtures containing Al powder are the most frequently used in solid rocket propellants world-wide. AP is the work-horse oxidizer for composite solid propellants. It is a white crystalline solid, usually in powdery form. The crystals are orthorhombic in structure at room temperature, with a crystal phase transition to cubic structure at 240°C. AP is oxidizer rich and can sustain self-deflagration above at 20bar. This does not imply that it is of the explosive class, it is usually very safe to handle and even grindable. For the purpose of using in propellants it is desirable to use AP particles that are more or less spherical in shape, and special efforts may have to be taken to spheridise AP particles by the supplier. Propellants with fine AP burn faster in general, than those with coarse AP; so significant burning rate tailoring is effected by the choice of suitable distribution of particle size of AP in the propellant. The greatest advantage with AP is the immense experience and vast information on AP-based propellants available over several decades, which imparted growing confidence in that oxidizer. Ammonium nitrate was considered early as an environment-friendly alternative to AP, because of its low cost, low sensitivity and absence of chlorine. But its multiple crystal phase transition at low temperatures and poor performance preclude its use. At 32.1°C it undergoes phase change, which is accompanied by a large volume change. Hence AN is used only in its phase stabilised form (PSAN, phase stabilised AN) with its phase transition at 32.1°C either suppressed or shifted to higher temperatures.

The binder used in propellant formulations should have good mechanical properties and good adhesion between the oxidizer and metal additives. In the early mid-forties the binder used was asphalt, which was later replaced by polyurethanes and polyvinylchlorides. In the 70's hydroxy terminated polybutadiene (HTPB) was developed as a standard binder for composite solid propellants, because of its excellent mechanical properties

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and very good adhesion with aluminium and ammonium perchlorate (AP), which are all the standard ingredients in the present-day composite solid propellants. In order to achieve higher performance an entirely new system of binder- oxidizer combination is necessary. Use of binders and oxidizers with low bond energies i.e. large positive heats of formation (ΔH_f) could enhance I_{sp}. To achieve large specific impulse values energetic groups like nitro, nitrato, nitramino, dinitramino, azido, difluoramino groups etc. are incorporated in advanced high energy binders. Table 1.2 lists typical properties of conventional binders used in composite propellants

Table 1.2: Properties of conventional binders

Binder	Oxygen Balance (%)	Density (g/cm^3)	ΔH_f (kJ/mol)
HTPB	-323.8	0.916	-51.9
CTPB	-315.7	0.916	-9.17
PBAN	-273.3	0.980	203.34

From Table 1.2 it is seen that all the binders have negative oxygen balance with densities less than one. PBAN has positive heat of formation, while HTPB and CTPB have negative heat of formation.

1.7. New High-energy Oxidizers and Binders

Over the years, high performance, insensitive munitions, and pollution prevention issues in relation to solid rocket propellants have grown in importance [16-18]. In the past, a number of ingredients that increase performance suffered from instability problems as well as incompatibility with binders. Still others, especially oxidizers, were hygroscopic and became strongly acidic on absorbing moisture. In addition, many compounds were hazardous because of their extreme sensitivity.

Most of the current operational solid propellants make use of AP as oxidizer. The most perceptible disadvantage of AP is its chlorinated exhaust products that are detrimental to the environment and produce a distinct smoke signature behind missiles that can be easily detected. During the burning of large boosters, enormous quantities of HCl are released to the atmosphere. 503 tonnes propellant liberates about 100 tonnes of HCl and other chlorine containing compounds during its burning thereby polluting the atmosphere and hence could cause "ozone depletion" in the stratosphere. The large amount of HCl emission could cause "acid rain". These aspects have become a matter of serious concern for environmentalists all over the world. Hence there is a need for development alternate materials, which are both environment-friendly as well as more energetic to meet future space missions. The growing environmental awareness in recent years has generated interest in search for new performance high-energy oxidizers [19-21]. The main considerations in the new propellant development are 1) a quantum jump in specific impulse (15–20 sec.) and 2) an environment-friendly propellant system. Factors such as safe handling and manufacturing, environmental safety, low cost, and chemical compatibility with oxidizer and other propellant ingredients, are also essential for newly developed propellants.

AP evolves hydrogen chloride (HCl), which acts to increase average molecular weight, and because AP has a relatively high (-602 cal/g) negative heat of formation, it is only moderately energetic. Thus, in the 1960's there was an effort to enhance propellant performance by incorporating more energetic oxidizers with oxygen content similar to that of AP but with a lower negative heat of formation. Energetic oxidizers were investigated, including those containing a hydrazinium diperchlorate (HP2) as shown in Table 1.3.

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Table 1.3: Properties of conventional oxidizers

Oxidizer	Oxygen Balance (%)	Density (g/cm^3)	ΔH_f (kJ/mol)
AN	20.0	1.73	-365.04
AP	34.0	1.95	-296.00
HP2	41.0	2.20	-293.30
HP	24.0	1.94	-177.80
RDX '	-21.6	1.82	70.63
HMX	-21.6	1.96	74.88

Table 1.3 lists some of the elementary characteristics of oxidizers including AP and AN. It shows that HMX has the highest heat of formation but it has a negative oxygen balance. AN, AP, hydrazinium perchlorate (HP) and hydrazinium diperchlorate (HP2) have negative heat of formation with a positive oxygen balance. A detailed performance calculation, in combination with a binder is required before establishing the suitable combination of oxidizer and binder.

The oxidizers exhibited lower heats of formation than AP, produced energetic propellants that were detonable in addition to being friction and impact sensitive. In addition, many had undesirable combustion characteristics.

In order to improve the solid-rocket propulsion the worldwide research is focused on new energetic ingredients such as hexanitro-hexazaisowurtzitane (CL-20), ammonium dinitramide (ADN), hydrazinium nitroformate (HNF), trinitroazetidine (TNAZ), 3-nitro-1,2,4-triazole-5-one (NTO), octanitrocubane (ONC) structures of which are given in Table 1.4.

Table 1.4: Energetic oxidizers developed in the past years

Energetic Oxidizers	
Hexanitrohexazaisowurtzitane (CL–20)	O_2N-N, O_2N-N, $N-NO_2$, $N-NO_2$, O_2N-N, $N-NO_2$
Hydrazinium nitroformate (HNF)	$N_2H_5\ C(NO_2)_3$
Trinitroazetidine (TNAZ)	O_2N-N, NO, NO_2
Ammonium dinitramide (ADN)	$NH_4N(NO_2)_2$
3-nitro-1,2,4-triazole 5-one (NTO)	N, HN, NO_2, NH, O
Octanitro cubane (ONC)	O_2N, NO_2, O_2N, NO_2, O_2N, NO_2, O_2N, NO_2
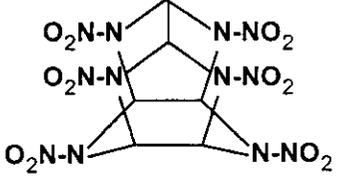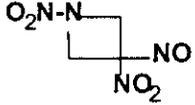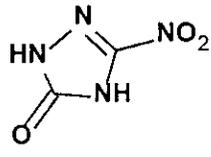
The main characteristics in demand for new oxidizers are high density, high oxygen balance and also no chlorine content.

Cl–20 is a high energetic dense caged nitramine [22,23]. It is superior to HMX with respect to density, enthalpy of formation and oxygen balance. The salt of nitroform and hydrazine ie., HNF is being studied for use with fuel binders [24] like HTPB, glycidyl azide polymer (GAP) etc., which is expected to give 8% higher performance than the current propellant combination [25]. TNAZ is of interest to the military as a melt castable explosive [26] and is advantageous over HMX and RDX in terms of higher energy content. ADN is a chlorine free oxidizer. It has positive oxygen

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balance and an enthalpy of formation superior to those of AP and AN. NTO is a less sensitive explosive and has a higher crystal density [27]. Its detonation velocity and pressure are equivalent those of RDX and HMX. ONC is a C-nitro compound in which the nitro groups are attached by way of nitrogen to carbon [28]. ONC is a highly nitrated cubane molecule and the most powerful known non-nuclear explosive [29]. Table 1.5 gives some elementary properties of new oxidizers.

Table 1.5: Properties of new oxidizers

Oxidizer	Melting point (°C)	Oxygen Balance (%)	Density (g/cm^3)	ΔH_f (kJ/mol)
ADN	92	25.80	1.82	-150.60
HNF	122	13.10	1.87	-72.00
CL-20	167-170	-10.95	2.04	381.20
TNAZ	101	-16.66	1.84	33.64
NTO	270	-24.60	1.93	-111.84
ONC	275	0	2.10	413.80

Table 1.5 shows that ADN and HNF have positive oxygen balance, while CL-20, TNAZ and NTO have negative oxygen balance. Both Cl-20 and ONC have high positive heat of formation; hence they are potential ingredients in high performance explosives. The density of ADN, HNF and TNAZ are closer. ADN and HNF are lower melting solids, while others are high melting solids. The heat of formation of HNF is more positive than ADN. The consideration of oxygen balance, density and heat of formation may serve as a good guidance to select potential oxidizers for use in propellants or explosives.

Out of the different types of new binders synthesized and characterized the following binders are promising candidates with regard to above factors. They are glycidyl azide polymer (GAP), poly-3,3–bis

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(azidomethyl) oxetane (BAMO), *Poly glycidyl nitrate* (PGN), poly-3–nitrato-methoxy-3–methyl oxetane (NIMMO) and their copolymers, and nitrated HTPB [30]. Energetic binders used in composite solid propellants and their *structures are given in* Table 1.6. GAP and poly BAMO are unique energetic materials containing azide groups in the polymer chain [31]. The presence of highly endothermic azide bond structure makes GAP and Poly BAMO highly energetic. Hydroxyl terminated GAP, Poly BAMO, or Poly NIMMO and their copoly-mers make use of the terminal hydroxyl groups for curing with isocyanates to form a polyurethane network structure [32].

Table 1.6: Energetic binders developed in the past years

Energetic Binders	Structure
GAP	$HO-[CH_2-CH-O-]_n H$ with side chain CH_2N_3
Poly NIMMO	$HO-[C(ONO_2)(CH_3)-O-]_n H$
PGN	$HO,\ [C(CH_2-O-)(CH_2-ONO_2)]_n$
Poly BAMO	$-[H_2C-C(CH_2N_3)_2-CH_2-O-]_n$
Nitrated HTPB	$HO-[CH_2\cdot CH=CH-CH_2-]_x[CH_2-CH(O_2NO)-CH(ONO_2)-CH_2-]_y OH$

Table 1.7 : Properties of some energetic binders for propellants

Property	PNIMMO	PGN	GAP	Nitrated HTPB	BAMO
Heat of formation (kJ/kg)	-309	-284.5	+957	-442	+2460
Glass transition temperature T_g (°C)	-25	-35	-50	-58	-39
Oxygen balance (%)	-114.3	-60.5	-121.2	--	-123.8
Density (g/cm^3)	1.26	1.39-1.45	1.30	1.20	1.30

Table 1.7 shows the comparative properties of new energetic binders. It is seen from the table, positive heat of formation was obtained for the azide based binders GAP and BAMO. The density of PNIMMO, PGN, GAP and BAMO is higher than that of nitrated HTPB. PGN has oxygen value higher than that of other polymers. The glass transition temperature of nitrated HTPB is much lower than that of the other polymers. The oxygen balance is higher for the polymers other than HTPB.

1.8. Development of Dinitramide Based Energetic Materials

In 1989, Schmitt and Bottaro reported their synthesis of an unusually powerful energetic material. The synthesis of this new compound ammonium dinitramide or ADN, developed from efforts to make potent explosives that were also stable and safe to handle. Such materials could be processed on a large scale for use as rocket fuel. The simplest class of nitramine is the nitro derivative of ammonia [33-35] i.e. nitramide (NH_2NO_2). The alkyl derivatives of dinitramide (R-N(NO$_2$)$_2$) have low stability. The

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The alkyl derivatives of dinitramide (R-N(NO$_2$)$_2$) have low stability. The previously synthesized dinitramide salts were known to be good explosives, but were not practical to use since they tend to be highly sensitive and unstable. Schmitt and Bottaro surmised that deprotonation of the dinitramide to form its anion (-N(NO$_2$)$_2^-$), the dinitramide, might lend extra stability. Using counter ions such as ammonium, they hoped, might help maintain high packing density, an important factor in detonation power and efficiency. ADN was indeed found to possess enhanced stability and insensitivity yet also proved to be a powerful explosive. It was discovered that ADN had been synthesized some 20 years earlier by chemists in the former Soviet Union, but due to its potential uses in weapons of destruction, knowledge of its creation had been kept top secret. ADN possessed the following formula:

$$\left[\begin{array}{c} O \quad\quad O \\ \| \quad\quad \| \\ O^- \;\; N \!\cdot\!\cdot\! N \; N \!\cdot\! O \\ \backslash N \diagup \\ \cdot\cdot \end{array} \right]^- \quad NH_4^+$$
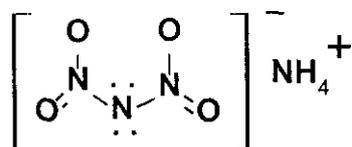
It is stable to moderate shock, pressure, and heat, and does not detonate in small quantities. Usually, only extremes of temperature or pressure will cause it to explode.

Figure 1.3 shows the calculated specific impulse of propellants with an energetic binder and Al for different oxidizers. As it is seen from Figure 1.3, the I_{sp} is higher for HNF based propellants and is lower for ADN and AP based propellants. As the oxidizer percentage increases, all the systems show a different trend. For AP based propellants, the I_{sp} value starts decreasing after 15% of oxidizer, while for HNF based propellants an increase in I_{sp} followed by gradual increase after 25% of oxidizer content. In the case of ADN based formulations a maximum I_{sp} of 272 sec. was obtained for a 10-15% oxidizer content and show a gradual decrease in I_{sp} as the oxidizer content is increased further.
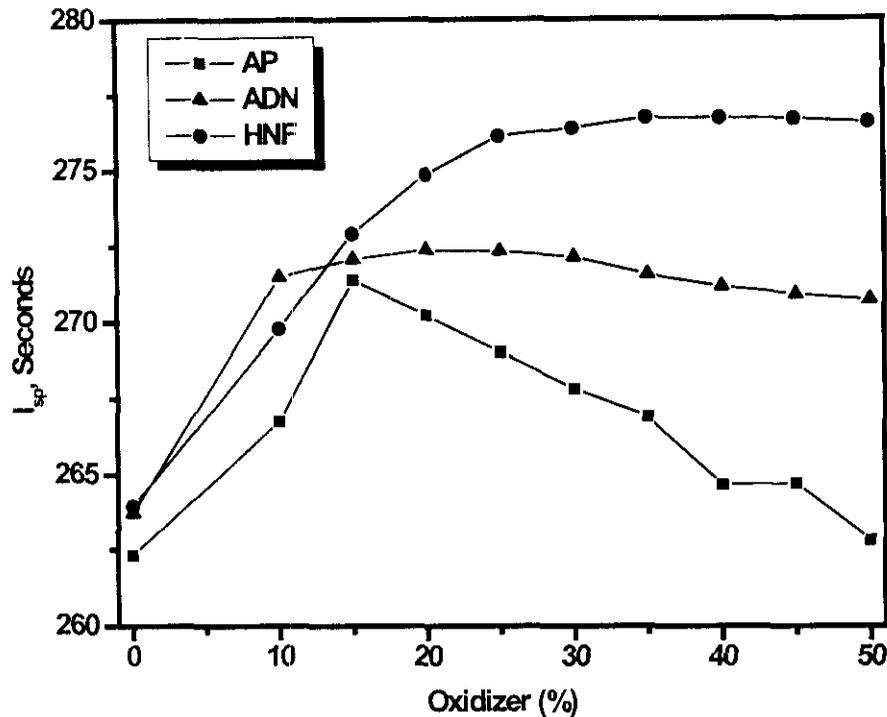
Figure 1.3: Specific impulse of propellants containing an energetic binder, Al and various oxidizers

As such ADN is designated as "Class C" or minimum hazard material [36]. By comparison, lead azide or nitroglycerine, compounds extremely sensitive to minor spark or shock, are considered as "Class A". ADN exhibits a fairly broad melting range of about 90-95°C, with decomposition occurring at 150-160°C. Pyrolysis and spectroscopic studies [37] indicate that decomposition yields mostly ammonia, water, N_2O and NO_2. One of the major photochemical decomposition products of ADN is AN. Experiments have shown that exposure to ambient light leads to a large increase in AN in 24 hours (0.1 to 3 wt%), and after 120 hours, about half the ADN decomposes to AN. Some of this decomposition may also have been aided by ambient moisture since crystals were left in open dishes. Table 1.8 lists the properties of ADN in comparison with AP.

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Table 1.8: Comparative properties of ADN and AP

Property	ADN	AP
Melting point (°C)	92-94	300-350
Yield of gas (moles/100g)	4.03	3.58
Stability/Compatibility	Adequate stability	Superior stability
Crystal shape	Needles/leaflets with ability to form prills	Spherical shape as received
Sensitivity	Sensitivity greater than AP	Sensitivity less than ADN
Contribution to I_{sp}	3-5s higher than AP	Less than ADN

As it is seen from Table 1.8, ADN has a more favourable heat of formation i.e., -298 as compared with −602 cal/g for AP. This condition is due to the relatively weak N-N and N-O bonds in ADN as compared with the stabilized Cl-O bonds in AP. The lower heat of formation and the greater volume of gas generated cause ADN formulations to have a higher I_{sp} than corresponding AP compositions.

Because of the combined explosive properties and unusual stability of ADN, it is an attractive candidate for use in a variety of military and scientific projects. These include using ADN as an oxidizer in ballistic missiles and in space shuttle booster rockets. Currently the propellant most commonly used in the space shuttle boosters is a mixture of ammonium perchlorate (AP) and powdered aluminium all held together with a hydrocarbon binder. Sometimes, the binder also acts as a fuel, and efforts are underway to develop energetic polymers (discussed earlier) for use as binders. As a propellant, ADN has the added benefit of being both an oxidizer and a fuel. Additionally, ADN is calculated to have an eight percent better lift capacity than AP, which means more mass could be accommodated per shuttle or missile flight. ADN is envisaged as a suitable successor to AP. The use of ADN in composite solid propellants eliminates
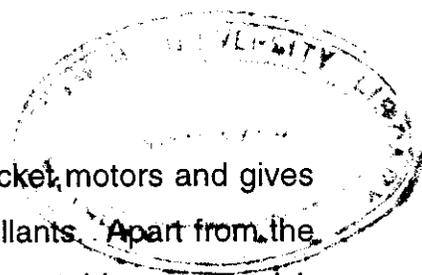
the emission of chlorinated exhaust products from rocket motors and gives 5-10 sec more I_{sp} than conventional AP based propellants. Apart from the ammonium salt of dinitramide (ADN), many different stable oxygen rich salts with a variety of cations are possible, which could provide a new class of energetic materials.

1.9. Formulations of New Generation Solid Propellants

The main propellant characteristics with regard to performance are specific impulse, density, availability, safe use, ease of handling and manufacturing. Ingredients with a high heat of formation, high oxygen balance and a high density must be selected for realizing best performing propellant. Based on the gained experience, it is possible to formulate and develop new solid propellants. One important point in the formulation of these new propellants is the introduction of an energetic binder. The behaviour of these new energetic polymers with plasticizers requires complete study including rheology, casting and its mechanical properties. In Table 1.9 a set of theoretical performance data with these new classes of energetic oxidizers [38] and binders are given.

Table 1.9: Theoretical performance of advanced propellants made with new energetic oxidizers

Composition	I_{sp} (s)	I_{vol}(s g/cm^3)	HCl (%)
HTPB 14/AP 68/Al 18	264.5	465.2	21.0
PNIMMO/AP 58/Al 20	263.5	484.1	17.6
GAP/AP 58/Al 20	266.0	491.9	17.5
PNIMMO 25/AP/NaNO$_3$/Al 20	254.6	474.8	8.08
GAP 22/AP 56/(Al/Mg 70/30)	260.3	471.3	10.7
GAP/ADN 55/Al 20	276.5	479.3	Nil
GAP/CL-20 55/Al 20	267.1	505.8	Nil
GAP/HNF 60 /Al 15	277.2	486.4	Nil

Table 1.9 gives the calculated performance characteristics of few propellant combinations utilizing conventional and as well as new energetic oxidizer and binders. For a conventional propellant based on HTPB, maximum specific impulse obtained is 264 seconds, while for a new oxidizer binder system such as GAP-ADN or GAP-HNF, the specific impulse obtained is around 276 to 277seconds. This clearly indicates the improved performance for a new oxidizer-binder system. Regarding the environmental pollution, the conventional AP based formulations release as much as 7-20% HCl, while those utilize new oxidizers release zero HCl emissions. It can be seen from the Table 1.9 for formulations utilizing novel ingredients; the specific impulse has been totally recovered and enhanced, eliminating the HCl emissions.

1.10. Preparation of Energetic Nitro Compounds by Nitration

A great emphasis of research is directed towards the synthesis of new nitro compounds, which would be useful as potential ingredients in propellants. Nitration has been an active area of industrial chemistry for over a century [39,40]. The continued interest is a testimony to the importance of nitration. The most common industrial nitration is the sulfuric acid catalyzed reaction with nitric acid [41]. This process is used for the production of many industrial chemicals such as nitrobenzene, which is used as solvent and in the manufacture of aniline. Dinitrobenzene, nitrotoluenes are used as intermediates to dyes, pharmaceuticals and perfumes. Acid catalyzed nitrations are also used in the manufacture of high explosives such as TNT, RDX, HMX and related nitramines. Historically, nitro derivatives played a special role as the most commonly used compounds. Energetic nitro compounds viz., C-nitro derivatives, O-nitro compounds or N-nitro compounds are the building blocks for energetic materials [42]. The nitro functionality is introduced into precursor or substrate molecules by a process called nitration. Nitration is the reaction between an organic compound and a nitrating agent (generally HNO_3 or its

derivatives) to introduce a nitro group on to a carbon atom (C-nitration) or to produce nitrates (O-nitration) or nitramines (N-nitration). The nitro group most frequently substitutes a hydrogen atom, however, other atoms or groups can also be substituted. New and improved nitration processes have also been developed that minimizes production costs and promise reduced safety hazards [43].

Table 1.10: Electrophilic Nitrating Agents

NO_2^+ Carrier	Acid Catalyst	NO_2^+ Carrier	Acid Catalyst
HNO_3	H_2SO_4 $H_2SO_4:SO_3$	$RC(O)ONO_2$	None
	H_3PO_4 $HClO_4$ HF	NO_2F	BF_3, PF_5, AsF_5, SbF_5
	$HF-BF_3$ BF_3	NO_2Cl	HF, $AlCl_3$, $TiCl_4$
	CH_3SO_3H CF_3SO_3H	N_2O_3	BF_3
	FSO_3H Solid acids	N_2O_4	H_2SO_4, $AlCl_3$, $FeCl_3$, BF_3
$AgNO_3$, $NaNO_3$, KNO_3, NH_4NO_3	$FeCl_3$, BF_3, $AlCl_3$, CF_3COOH	N_2O_5	BF_3
$RONO_2$	H_2SO_4, BF_3	NO_2BF_4, NO_2PF_6 and other salts	None

The nitronium ion, NO_2^+ is the reactive nitrating agent in electrophilic nitrations. Table 1.10 summarizes the most frequently used electrophilic nitrating agents. The activity of nitrating agent is believed to be directly dependent on the concentration of nitronium ion, and the nitrating potential of a selection of few systems commonly used in the laboratory and in production is summarized [44] in Table 1.11.

Table 1.11: Selected nitration media and their properties

System	By-Products	Features
Pure HNO_3	Dilute HNO_3, acyl nitrates	Low nitrating strength, limited substrate choice, disposal/ recycling problems.
HNO_3-H_2SO_4	Dilute mixed acid, acyl nitrates	High nitrating strength, wide substrate choice, severe disposal problems
NO_2BF_4	HBF_4, acyl tetrafluoborate	Very high nitrating strength, limited substrate choice, high expense & very corrosive by-products
HNO_3-Ac_2O	Acetyl nitrate, acetic acid	Moderate nitrating strength, limited substrate choice, highly hazardous
N_2O_5	Potentially None	High nitrating strength, wide substrate choice, no by-products.

A brief account of various nitrating agents being used in the synthesis of energetic nitro compounds is given in the following sections.

1.10.1. Dinitrogen Pentoxide

Since its first reported synthesis in 1849 from chlorine and silver nitrate [45], N_2O_5 has been extensively used by organic chemists for the nitration of variety of substrates. N_2O_5 has proven to be quite useful in the nitration of aromatics, alkanes, alcohols, amines, amides and hydroxyl containing polymers [46].

The easiest and most widely used method for the preparation [47] of N_2O_5 is the dehydration of HNO_3 by P_2O_5. Pure N_2O_5 is sublimed from this mixture and collected in a cold trap at -78°C as shown in Equation 1.7.

$$6HNO_3 + P_2O_5 \longrightarrow 3N_2O_5 + 2H_3PO_4$$

$$\ldots\ldots\ldots(1.7)$$
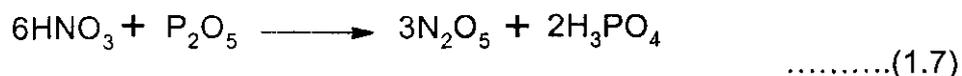
Direct ozonolysis of N_2O_4 produces N_2O_5 as well [48]. This reaction is instantaneous as noted by the immediate disappearance of the red gaseous N_2O_4. Pure N_2O_5 is collected as white crystals at -20°C. The reaction is shown in Equation 1.8.

$$N_2O_4 + O_3 \longrightarrow N_2O_5 + O_2$$

..........(1.8)
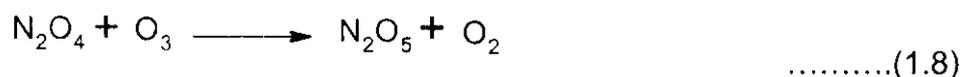
Anodic oxidation of N_2O_4 in 100% HNO_3 using controlled potential technique [49] yields solutions of N_2O_5/HNO_3. The reaction is given in Equation 1.9.

$$N_2O_4 + 2NO_3^- \longrightarrow 2N_2O_5 + 2e^-$$

..........(1.9)
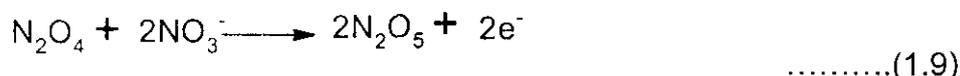
A voltage of +1.85V versus the standard calomel electrode (SCE) is required for the desired electrochemical oxidation.

1.10.2. Nitronium Salts

Although a wide category of nitronium salts are known at present, the most frequently used nitronium salt for nitrating aromatics is NO_2BF_4 [50]. A simple and efficient preparation of the same was achieved by Olah et al. [51-53] letting a 2 mole excess of BF_3 react with an equimolar mixture of HNO_3 and anhydrous HF. The reaction is given in Equation 1.10.

$$HNO_3 + HF + nBF_3 \longrightarrow NO_2^+BF_4^- + H_2O. (n-1) BF_3$$

..........(1.10)
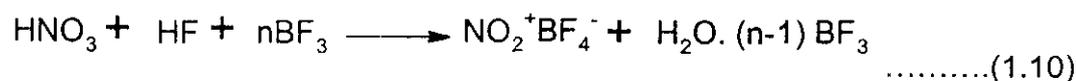
Water formed as by-product in the reaction is bound by BF_3 as a stable hydrate from which BF_3 can be easily regenerated by distilling with H_2SO_4 or oleum.

NO_2BF_4 is a versatile nitrating agent capable of nitrating much number of organic and inorganic compounds. It can be safely used with a wide variety of solvent medium. Examples of other nitronium salts include $NO_2HS_2O_7$, NO_2SbF_4, NO_2AsF_6 etc.,

1.10.3. Nitration with HNO_3 - H_2SO_4

By far the nitration with nitric acid in the presence of strong protic acids such as H_2SO_4, FSO_3H and CF_3SO_3H or other Lewis acids has been practiced by chemists throughout the world [54]. The nitration using HNO_3 and H_2SO_4 is most widely practiced. The mixture of nitric acid and sulfuric acid is an excellent nitrating agent for many of the aromatic and aliphatic compounds. The formation of nitronium ion NO_2^+, the active nitrating species is given by Equation 1.11.

$$HNO_3 + 2H_2SO_4 \longrightarrow NO_2^+ + 2HSO_4^- + H_3O^+$$

$$\ldots\ldots\ldots(1.11)$$
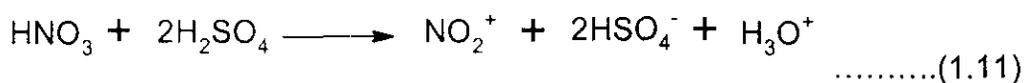
H_2SO_4 aids the ionization of HNO_3 to the nitronium ion, the de facto nitrating agent, and also binds the water formed in the reaction. A convenient way of altering the nitrating activity is by changing the concentration of H_2SO_4 and HNO_3. The use of mixed acids has many advantages and disadvantages. Advantages include low cost of materials and ease of handling. Nitration can be carried out at low and high temperatures and does not require a solvent. The disadvantages include, the recycling of spent acids left after the reaction, highly corrosive nature of acids to the reactor and other systems, poor regioselectivity for many of the aromatics, problems in disposal and neutralization of spent acids etc.,

For preparing high-energy oxidizers based on dinitramide salts, a suitable nitration technique is to be adopted. The methodology should invoke a favourable nitration method, better safety, high yield etc., in the nitration of deactivated amines. In order to provide an in-sight into the

synthetic methodologies adopted in preparing these dinitramide based energetic materials, the part-II of this chapter attempts to consolidate the available methods of synthesis of ammonium dinitramide with a summary of the methods and properties of other dinitramide salts.

PART-II

1.11. An Overview on the Synthetic Routes and Properties of Ammonium Dinitramide (ADN) and other Dinitramide Salts

In recent years, there has been a considerable interest in the design of new high performance propellants for space applications. Ammonium salt of dinitramide (ADN, $NH_4N(NO_2)_2$) attracts wide interest as a potentially useful energetic material. There are a number of methods reported for the synthesis of dinitramide salts. This part of the chapter reviews the general synthetic methods used for the synthesis of inorganic, organic and metal dinitramide salts and their properties with a special emphasis on ammonium dinitramide because of its importance as a high-energy oxidizer in composite solid propellants. The salient features with reference to the extent of conversion and ease of separation of the products on the various synthetic methodologies are also addressed.

1.12. Dinitramidic Acid and its Salts

Dinitramidic acid (DNA) is a very strong mineral acid [55,56] having pKa value of −5.6 and is thermally labile. It forms stable salts with almost all bases, ammonia, metals, tertiary amines, melamine, cubane tetraamine, dinitro azetidine etc., The dinitramide salts are more stable than the related covalently bound N,N-dinitro derivatives such as alkyl dinitramines. The higher stability of ionic dinitramide salts is due to the presence of the overall negative charge that is distributed by resonance over the entire molecular system, thereby imparting a higher N-N bond order [57] as shown in Figure 1.4 (a-c).

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(a)   (b)   (c)
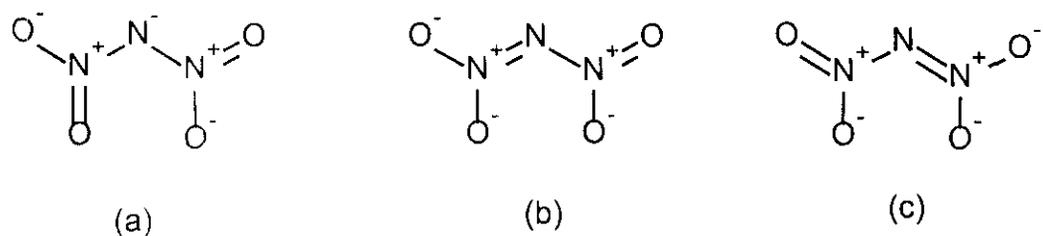
Figure 1.4 (a-c): Resonance structures of the dinitramide anion

The dinitramidic acid as such is unstable due to self-protonation and is rather stable in very dilute aqueous solutions. It exists in the ionized state in polar solvents including water and strong acids. In less polar solvents it exists in the covalent state [58]. The structure shown in Figure 1.5. can be considered as a superposition of the aci-form with a strong hydrogen bond in which hydrogen is equally bonded to two oxygen atoms. The stability of dinitramide salts in solid state varies and is associated with the structural symmetry of the anion in the crystal lattice. The anion symmetry depends on the cation size, the smaller the cation the higher is the stability. Other factors such as nature of the impurity and its amount also affect the stability of the anion.
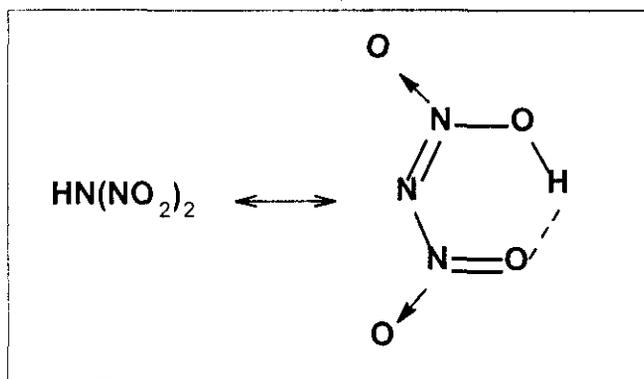
Figure 1.5: Aci form of dinitramidic acid

Aqueous solutions of the dinitramide anion show absorption bands at 212, 284 and a shoulder at 335nm in the UV spectrum [57]. The peak at 284nm is characteristic of the anion. The reported molar extinction

coefficient values are 5207 L mole^{-1} cm^{-1}, 5258[59] L mole^{-1} cm^{-1} and 5627[60] L mole^{-1} cm^{-1}. IR spectrum of NH$_4^+$ salt of dinitramidic acid [61,62] shows characteristic peaks at 1531 cm^{-1} (v asymmetric in phase of NO$_2$), 1344 cm^{-1} (v symmetric in phase of NO$_2$), 1174 and 1200 cm^{-1} (v symmetric out of phase of NO$_2$), 1020 cm^{-1} (v asymmetric of N$_3$), 951 cm^{-1} (v symmetric of N$_3$). Ammonium salt of dinitramidic acid shows the following characteristic frequencies in the Raman spectra [61-62] - 1505 cm^{-1} (v asymmetric in phase of NO$_2$), 1335 cm^{-1} (v symmetric in phase of NO$_2$), 1174 cm^{-1}(v symmetric out of phase of NO$_2$), 1025 cm^{-1} (v asymmetric of N$_3$) and 955 cm^{-1} (v symmetric of N$_3$). Dinitramide anion is stable to pH between 7-14 and slowly decomposes in concentrated acids at room temperature. Dinitramide salts are normally readily soluble in water, alcohol, nitro methane, methyl acetate, acetonitrile and other polar solvents, but insoluble in ether, benzene, hexane or methylene chloride.

1.13. Methods of Preparation of Dinitramide

The methods of preparation of dinitramides, can in general, be classified into four groups.

The first being formation of N,N-dinitro derivative RN(NO$_2$)$_2$ and subsequently the cleavage of R-N bond leading to dinitramide anion as shown in Equation 1.12.

$$R\text{---}N(NO_2)_2 \longrightarrow \text{-}N(NO_2)_2^-$$

......(1.12)
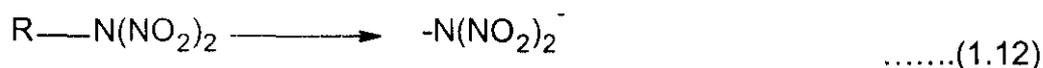
The second method of synthesis is based on inorganic synthetic routes involving direct nitration of NH$_3$ or NH$_2$NO$_2$ using either NO$_2$BF$_4$ or N$_2$O$_5$, followed by reaction with a base as shown in Equation. 1.13.

$$NH_3 \longrightarrow NH_2NO_2 \longrightarrow HN(NO_2)_2 \xrightarrow{NH_3} NH_4N(NO_2)_2$$

.....(1.13)

40
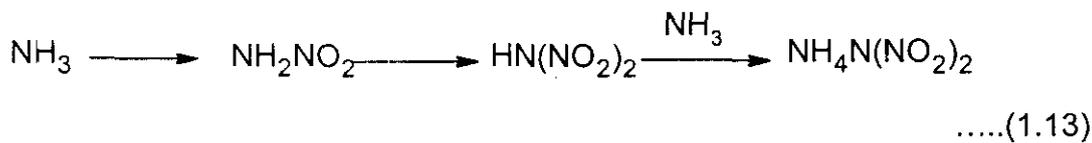
The third method involves nitration of deactivated amines such as NH_2NO_2, NH_2CONH_2 or NH_2COOCH_3 using strong nitrating agents such as NO_2BF_4 or N_2O_5 to give dinitramidic acid as shown in Equation. 1.14.

$$H_2N-X \xrightarrow{N_2O_5 \text{ or } NO_2BF_4} HN(NO_2)_2 \qquad \text{......(1.14)}$$
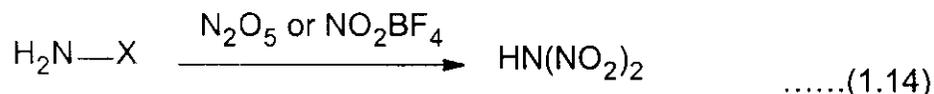
where,

X is $-NO_2$, $-CONH_2$, $-COOR$

The fourth method consists of double decomposition reaction of the already synthesised dinitramide salts with respective metal salts as shown in Equation. 1.15.

$$MN(NO_2)_2 \xrightarrow[-MX]{M'X} M'N(NO_2)_2$$

where,
X is $-OH$, Cl, $-SO_4$

$$\text{......(1.15)}$$
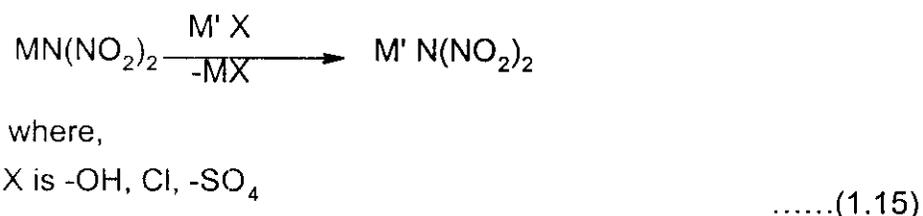
The established method of preparation of alkyl dinitramine practiced earlier [63] is via N-nitromethylcarbamate, which is prepared from alkyl monoisocyanates, followed by nitration with nitronium ion as shown in Scheme 1.1.
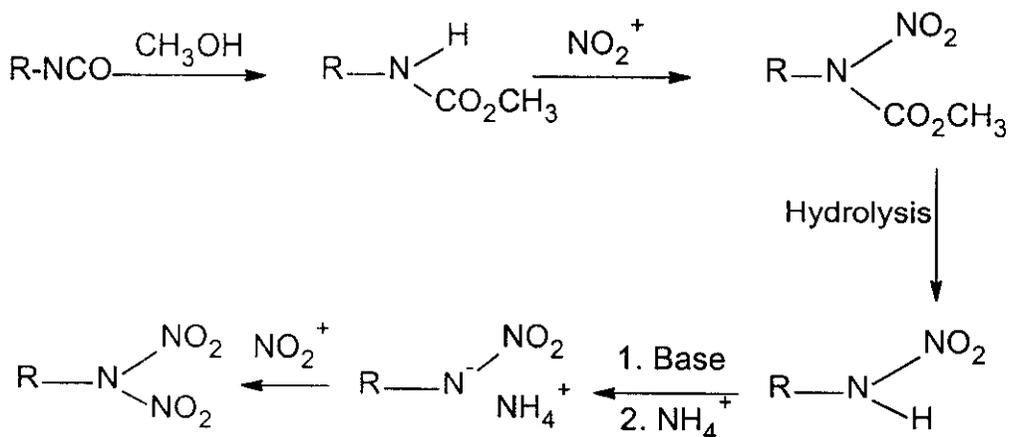
Scheme 1.1: Formation of alkyl dinitramines from isocyanates

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The four step method shown in Scheme 1.1, was later modified by a one step synthesis by nitration of aliphatic isocyanates[64] using stoichiometric quantities of NO_2BF_4 and HNO_3 in acetonitrile. The reaction is shown in Equation 1.16.

$$R-NCO \xrightarrow[CH_3CN]{NO_2BF_4/HNO_3} R-N\Big\langle \begin{array}{c} NO_2 \\ NO_2 \end{array}$$

$$......(1.16)$$
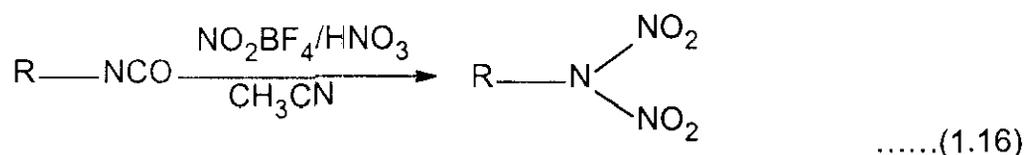
This route differs from Scheme 1.1, as it involves only one step and requires the use of nitric acid and high quality NO_2BF_4.

In the following sections, the methods for the synthesis of ammonium dinitramide and other dinitramide salts reported in the literature are described:

Bottaro et al., disclosed a method of preparation of dinitramide salts [65], in which the alkyl dinitramine precursor may be formed directly from an aliphatic isocyanate using stoichiometric quantities of nitronium tetrafluoborate and nitric acid in acetonitrile as shown in Equation 1.16. The yield varied from 1 % to 35 % depending on the alkyl substituent present in the isocyanate (Table 1.12). Instead of monoisocyanates, alkyl diisocyanates were used to make the corresponding bis(N,N-dinitramino alkanes). Examples are hexamethylenediisocyanate and ethane1,2-diisocyanate. When the latter compound was nitrated by the procedure in Equation.1.16, no dinitramide was formed. Different substrates investigated using this method and the product obtained along with the yield are given in Table 1.12.

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Substrate	Product	Yield
n-butyl isocyanate	1-(N,N-dinitramino)butane	35%
methyl isocyanate	N,N-dinitramino-methane	30%
1-adamantyl isocyanate	1-(N,N-dinitramino)adamantane	<<1%
hexamethylene diisocyanate	1,6-bis(N,N-dinitramino)hexane	10%
ethane-1,2-diisocyanate	1,2-bis(N,N-dinitramino)ethane	-0-
2-(trimethylsilyl-ethyl)-1-isocyanate	1-(N,N-dinitramino)-2-trimethylsilyl-ethane	25%

Dinitramide salts were synthesized by β-elimination reaction of 1-(N,N-dinitramino)-2-trimethylsilylethane catalyzed by CsF [57,65]. The reaction is normally carried out below 0°C. The 1-(N,N-dinitramino)-2-(trimethylsilyl)ethane was synthesised by reaction of an isocyanate with a mixture of HNO_3 and NO_2BF_4 as shown in Scheme 1.2. The yield of the desired 2-(trimethylsilylethyl)-N,N-dinitramine precursor was about 25%.
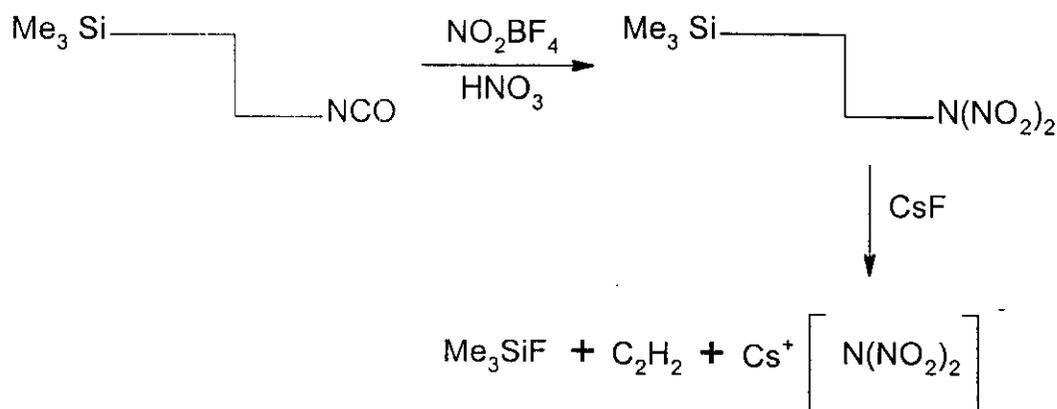
Scheme 1.2: Synthesis of cesium dinitramide from 1-(N,N-dinitramino) 2-trimethylsilylethane

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In Scheme 1.2, substitution of CsF by other metal fluoride salts in the β-elimination reaction results in other dinitramide salts. Dinitramide salts were also prepared by ion exchange reaction of cesium dinitramide using AMBERLYST 15 sulphonic acid resin charged with the appropriate cation, followed by elution with a suitable solvent.

Yet another method of preparing dinitramide salts makes use of nitramide (NH_2NO_2) as a starting material and NO_2BF_4 as a nitrating agent [65]. The reaction was carried out at $-20°C$ to form the free acid $HN(NO_2)_2$ as shown in Equation 1.17.

$$NH_2NO_2 + NO_2BF_4 \longrightarrow HN(NO_2)_2 + HBF_4$$

$$....(1.17)$$
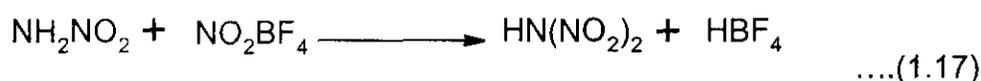
The free acid was then reacted with a corresponding base such as ammonia, hydrazine or metal hydroxides (MOH), where M is the desired metal cation, to form the desired dinitramide salt. The product yield was about 60%.

The reaction of an ionic nitronium salt such as NO_2BF_4 or N_2O_5 with ammonium carbamate $NH_2CO_2^- NH_4^+$, yields the intermediate dinitramidic acid [66]. The reaction was carried out in the temperature range of $-30 °C$ to $-40°C$ followed by neutralization either with ammonia, hydrazine, primary and secondary amine, or salt of the formula AX where A is mono, di or trivalent metal cation, to give the corresponding dinitramide salt. The product yield was 15%. The reaction is shown in Equation 1.18.

$$NH_4^+NH_2CO_2^- + NO_2BF_4 \xrightarrow[CH_3CN]{-30°C} HN(NO_2)_2 + NH_4^+BF_4^- + CO_2$$

$$.......(1.18)$$
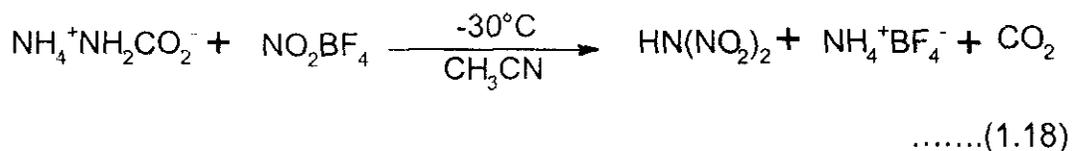
Schmitt et al., reported a method for forming dinitramide salt by reaction of NH_3 with a nitronium containing compound such as NO_2BF_4 or

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N_2O_5 [67]. The reaction was carried out at $-78°C$ in CH_2Cl_2 medium and is believed to proceed via the formation of covalently bonded NH_2NO_2, which further reacts with the nitronium-containing reagent to give dinitramidic acid and on subsequent neutralization with ammonia forms ammonium dinitramide. The reaction Scheme is shown in Equation. 1.19.

$$NH_3 + \xrightarrow[\text{Excess } NH_3]{NO_2\text{-}X} NH_2NO_2 \xrightarrow{NO_2\text{-}X} HN(NO_2)_2$$

$$\downarrow NH_3$$

where,

$$NH_4N(NO_2)$$

X is NO_3^-, BF_4^- or $HS_2O_7^-$

$$\dots\dots(1.19)$$
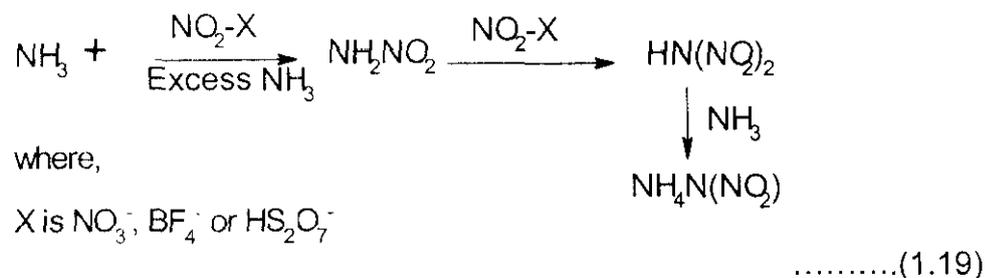
When the reaction was performed using NO_2BF_4, N_2O_5 or $NO_2HS_2O_7$ an yield of 21%, 5% and 20% is obtained respectively.

Hatano *et al.*, disclosed a clean and safe method for formation of ammonium dinitramide [68,69] starting from urea involving the following steps.

    a. forming urea nitrate by reacting urea with dilute HNO_3.

    b. forming nitrourea by reacting urea nitrate with sulfuric acid.

    c. reacting nitrourea with a nitrating agent and then neutralising the formed dinitrourea with ammonia.

The reaction sequence follows the steps shown in Equation. 1.20 and 1.21.

$$NH_2CONHNO_2 + NO_2BF_4 \longrightarrow (NO_2)_2NCONH_2 + HBF_4$$

$$\dots\dots(1.20)$$

$$(NO_2)_2NCONH_2 + 2NH_3 \longrightarrow NH_4N(NO_2)_2 + NH_2CONH_2$$

$$\dots\dots(1.21)$$

The reaction was carried out at −40°C in acetonitrile medium. The yield of the reaction varied from 5% to 20% depending on the reaction temperature and reaction time.

Stern *et al.*, described a process for preparing ammonium dinitramide [70] in which ethyl or methyl carbamate was nitrated using Ac_2O/HNO_3 to the corresponding mononitro compound, followed by ammonia treatment under anhydrous conditions to produce the ammonium salt of ethyl or methyl N-nitrocarbamate. It was further nitrated using nitronium salts and then treated with ammonia to give ammonium dinitramide, thus regenerating the starting compound in the final step. The reaction sequence is shown in Scheme 1.3.

$$Z\text{—}NH_2 \xrightarrow[HNO_3]{(CH_3CO)_2O} Z\text{—}NHNO_2$$

$$Z\text{—}NHNO_2 + NH_3 \longrightarrow Z\text{—}NNO_2^-NH_4^+$$

$$Z\text{—}NNO_2^-NH_4^+ \xrightarrow[2.\ NH_3]{1.\ N_2O_5} NH_4N(NO_2)_2 + Z\text{—}NH_2 + NH_4NO_3$$

where,

$Z = \text{-COOCH}_2\text{CH}_3 \text{ or -COOCH}_3$

Scheme 1.3: Synthesis of ammonium dinitramide from ethyl or methyl carbamate

The first step of nitration was performed at 0°C, while the second step of nitration was performed in CH_2Cl_2 medium at −48°C using N_2O_5, an overall yield of 70% to 76% is obtained.

A method for forming dinitramide salts by the reaction of N-(alkoxycarbonyl)N-nitroamide and a nitronium containing compound, followed by contacting the reaction mass with a base to form the

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dinitramide salt[71] has been described. The N-(alkoxycarbonyl)N-nitroamide reactant may be made by mixing an alkyl carbamate with Ac_2O/HNO_3 at 0°C followed by treatment with NH_3 to from NH_4^+ salt of N-(alkoxycarbonyl)N-nitroamide (ammonium nitrourethane). Further nitration of ammonium nitrourethane with NO_2BF_4 gives dinitrourethane (DNU), which was then base treated with NH_3 to give ammonium dinitramide. The reaction sequence is shown in Scheme 1.4.

$$NH_2COOR + Ac_2O + HNO_3 \xrightarrow[- CH_3COOH]{0°C\ /\ CH_2Cl_2} ROOC-N\begin{smallmatrix}H\\NO_2\end{smallmatrix}$$

$$CH_3CO_2^-\ NH_4^+ \quad \Big|\quad - CH_3COOH$$

$$(O_2N)_2NCOOR \xleftarrow[- 20°C]{NO_2BF_4} NH_4^+(O_2NNCOOR)^-$$

$$\Big| \quad NH_3\ excess$$

$$NH_4N(NO_2)_2 + NH_2COOR + NH_4BF_4$$

where

$R = -CH_2CH_3$
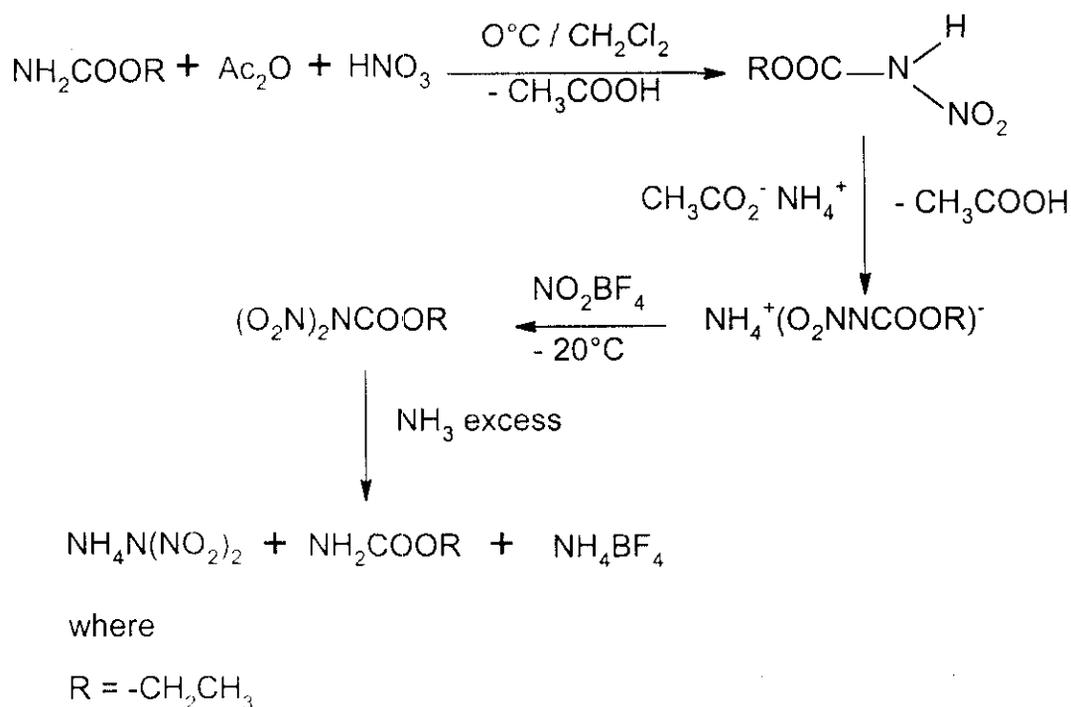
Scheme 1.4: Synthesis of ammonium dinitramide from alkyl carbamates

The reaction was carried out in the temperature range of –60°C to –20°C and the yield of ammonium dinitramide ranged from 50% to 60%.

In a method by Kyoo-Hyun Chung et al., dinitramide salts were prepared [72] starting from diethyl 4-azaheptanedioate, nitration of the same using HNO_3-TFAA (trifluoroacetic anhydride)-Br_2 gave N-nitro-4-azaheptanedioate, which was then base treated in the retro-michael reaction to give 3-nitramino-propanoate. The nitramino compound was

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treated with NO_2BF_4 at below 0°C to give dinitramino compound and subsequently reacted with base to give dinitramide salts. The overall sequence of the reaction is shown in Scheme 1.5. The product yield was 30%. O.A. Luk'yanov et al., proposed a similar approach for the synthesis of dinitramide salts in Michael and retro-Michael-type reactions [73].

H-N(CH₂CH₂CO₂Et)(CH₂CH₂CO₂Et) →[TFAA-HNO₃ / Br₂] O₂N-N(CH₂CH₂CO₂Et)(CH₂CH₂CO₂Et)

KOH / EtOH

NO₂BF₄

EtO₂CCH₂CH₂-N(NO₂)(NO₂) →[MOH] M⁺ ⁻N(NO₂)(NO₂)
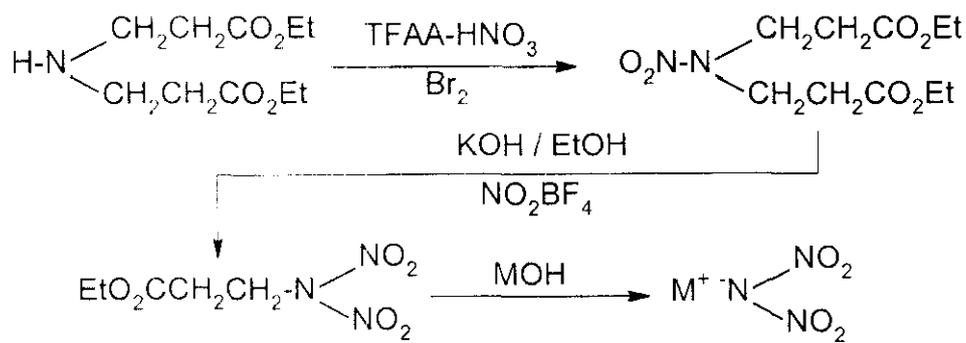
Scheme 1.5: Synthesis of dinitramide salts from diethyl 4-azaheptanedioate.

Kyoo-Hyun Chung also described another method of preparation of ammonium dinitramide [74] by nitration of bis(2-cyanoethyl)amine followed by decyanoethylation by a base and further nitration with NO_2BF_4. The reaction sequence is shown in Scheme 1.6. The reaction was carried out at −10°C. The product yield was 60%.

H-N(CH₂CH₂CN)(CH₂CH₂CN) →[HNO₃ / Ac₂O] O₂N-N(CH₂CH₂CN)(CH₂CH₂CN) →[OH⁻ / H⁺]

O₂N-N(CH₂CH₂CN)(N-H)

H₄N⁺ N⁻(NO₂)(NO₂) ←[NH₃] NCCH₂CH₂-N(NO₂)(NO₂) ←[NO₂BF₄]
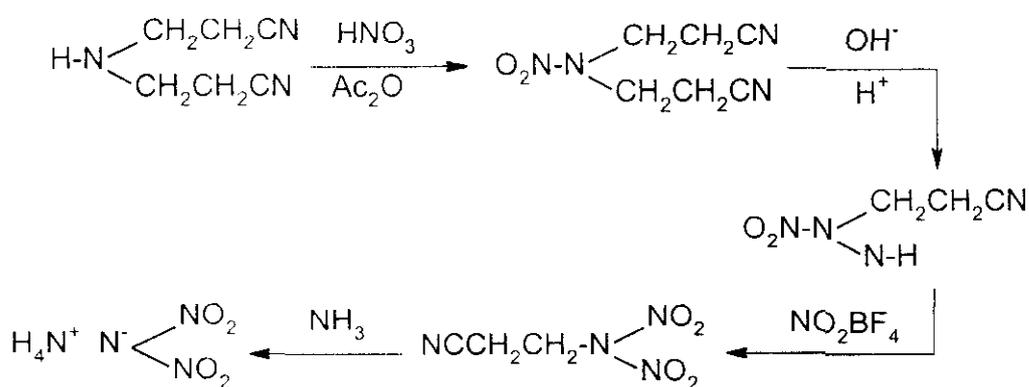
Scheme 1.6: Synthetic route to ammonium dinitramide from bis- (2-cyanoethyl)amine

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Langlet et al., described a method for producing dinitramide salts [75] from ammonia-sulfate derivatives such as $NH(SO_3H)_2$, $NH_2SO_3NH_4$, NH_2SO_3H, or $NH(SO_3NH_4)_2$ using mixed acid nitrating agents (HNO_3/H_2SO_4) as shown in Equation 1.22.

$$NH_2\text{-}SO_3NH_4 \xrightarrow[NH_3]{HNO_3/H_2SO_4} H_4N\text{---}N{\overset{NO_2}{\underset{NO_2}{<}}}$$

$$\dots\dots(1.22)$$
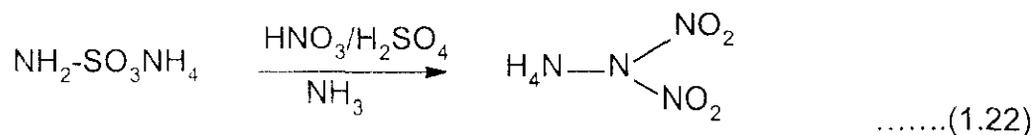
The reaction was carried out at -40°C using fuming HNO_3 (>90%) and con.H_2SO_4 (98%). Potassium salt of dinitramide is prepared the same way by employing potassium sulphamate as a starting material and neutralizing the dinitramidic acid with KOH. The overall yield of the product was about 60%. The above method also describes an easy adsorption-desorption purification technique for separation of dinitramide salts using different adsorbents.

1.14. Synthesis of alkyl dinitramines

Synthesis of alkyl dinitramines involves the direct nitration of the corresponding alkyl isocyanates with NO_2BF_4/HNO_3. The already synthesized dinitramide salts can also be converted into alkyl dinitramines. For eg., cesium dinitramide can be converted into the alkyl dinitramine [57] by reaction with the corresponding alkyl triflates (Equation. 1.23). The product yield was about 40%.

$$CsN(NO_2)_2 + CH_3OSO_2CF_3 \longrightarrow CH_3\text{-}N(NO_2)_2$$

$$\dots\dots\dots(1.23)$$

The reaction of dinitramidic acid with diazomethane [86] (Equation 1.24) in ether gives methyl dinitramine with 30% yield.

$$HN(NO_2)_2 + CH_2N_2 \longrightarrow CH_3N(NO_2)_2$$

$$\ldots\ldots(1.24)$$
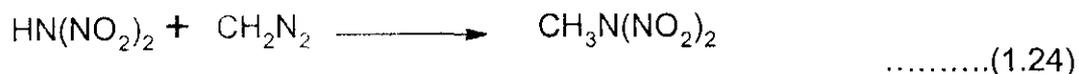
$AgN(NO_2)_2$ reacts with methyl or alkyl iodide to give corresponding alkyl N,N-dinitramines with 16-50% yield (Equation.1.25).

$$AgN(NO_2)_2 + RI \longrightarrow RN(NO_2)_2 + AgI$$

$$\ldots\ldots(1.25)$$
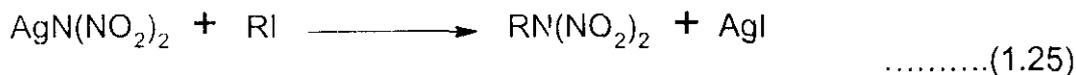
$KN(NO_2)_2$ reacts with triethyloxonium tetrafluoborate, giving a mixture of N and O-alkylated products (Equation.1.26).

$$KN(NO_2)_2 + Et_3O^+BF_4^- \longrightarrow EtN(NO_2)_2 + EtO-N=NNO_2$$
$$\downarrow$$
$$O$$

$$\ldots\ldots(1.26)$$
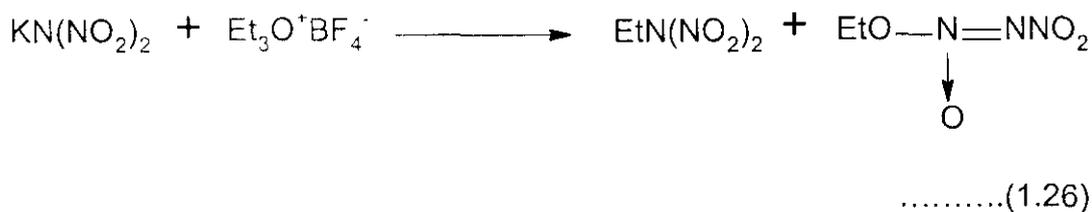
N and O-alkylated products are formed when mercury salt of dinitramide $Hg(N_3O_4)_2$ is mixed with an alkyl iodide in ether. The reaction is fast and is complete within 10-15min. The reaction is shown in Equation. 1.27.

$$Hg(N_3O_4)_2 + RI \longrightarrow RN(NO_2)_2 + RO-N=NNO_2$$
$$\downarrow$$
$$O$$

$$\ldots\ldots(1.27)$$
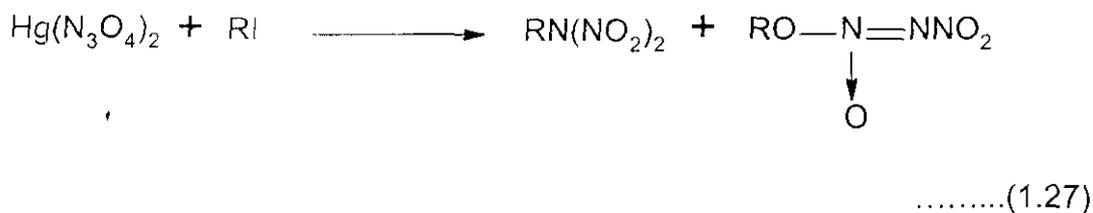
where.

R = Et, Me, n-Pr, n-Bu, i-Pr

When the nitration is carried out using nitronium salts NO_2BF_4 or N_2O_5, the available NO_2^+ concentration in the reaction is very high and hence the yield of the product could also be very high. The yield of the

dinitramide salt depends on the anion present in the nitronium salt used for the nitration. For example when NH_3 is nitrated with NO_2BF_4 the yield of dinitramide salt is 25% whereas with N_2O_5 or $NO_2HS_2O_7$, the yield is 15% [57]. Similarly when NH_2NO_2 is nitrated with NO_2X much higher yields (>90%) are obtained when X is BF_4^- whereas the yields are much lower when X is NO_3 or $HS_2O_7^-$. The synthetic routes for the dinitramide salts are summarized in Table 1.13.

Table 1.13: Substrates and nitrating agents for the synthesis of dinitramide salts

Sl. No	Starting Material	Nitrating Agent	Reaction Temperature	Yield	Ref.
1	$Me_3Si(CH_2)_2NCO$	NO_2BF_4/HNO_3	< 0°C	25%	[57]
2	NH_2NO_2	a. NO_2BF_4 b. N_2O_5 c. $NO_2HS_2O_7$	-20°C -20°C -40°C	60% <1% 53%	[65] [65] [76]
3	NH_4COONH_2	NO_2BF_4	0°C	15%	[66]
4	NH_3	a. NO_2BF_4 b. N_2O_5 c. $NO_2HS_2O_7$	-78°C -78°C -78°C	25% 15% 15%	[67] [67] [67]
5	$NH_2CONHNO_2$	NO_2BF_4	-40°C	20%	[68,69]
6	$NH_2COOC_2H_5$	a. N_2O_5 b. NO_2BF_4	-48°C -60°C	70% 60%	[70] [71]
7	$HN(CH_2CH_2COOEt)_2$	NO_2BF_4	< 0°C	31%	[72]
8	$HN(CH_2CH_2CN)_2$	NO_2BF_4	-10°C	60%	[74]
9	$NH_2SO_3NH_4$	HNO_3/H_2SO_4	-45°C	60%	[75]

1.15. Chemical and Physical Properties of Dinitramide Salts

Dinitramide salts are stable to base but slowly decompose in concentrated acid at room temperature [77]. In 8M H_2SO_4, no loss is seen

after 8 hours but in 11M and above the decomposition is quite rapid. Similarly the decomposition in con. HNO_3 is found to be fast in 70% HNO_3 and above, and is slow in HNO_3 treated with urea. The oxides of nitrogen in the untreated HNO_3 catalyses the decomposition of dinitramide.

The decomposition occurs in acid medium via the protonation of dinitramide anion [57]. The protonation can occur either at the oxygen or the central nitrogen leading to the elimination of HNO_3, N_2O and H_2O. The protonation at oxygen is favourable.

Dinitramidic acid is most acidic among the known gas phase acids [78]. The gas phase acidity of dinitramidic acid was found to be $\Delta H°_{acid} < 310$ kcal/mol. Dinitramide anion is extremely unreactive in the gas phase and is a poor nucleophile. It does not react with O_2, CO_2, CS_2 or SO_2.

The bond angles and bond distances in the dinitramide anion are shown in Figure 1.5.
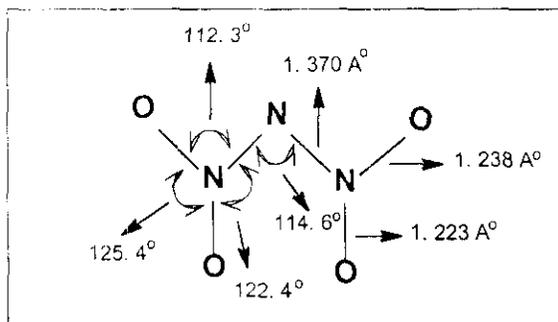
Figure 1.5: Bond angles and bond distances in dinitramide

Ammonium salt of dinitramidic acid has a melting point of 92°C followed by an onset of decomposition at 130-135°C, with a peak maximum at 180-190°C [79]. Thermogravimetric analysis shows single stage decomposition. The decomposition products are identified as NH_3, NO,

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N_2O, H_2O, NO_2, HONO and HNO_3 [80]. The physical properties reported in the literature for ADN are summarized in Table 1.14.

Table 1.14: Physical properties of ammonium dinitramide

Property		Ref
Melting point	92 °C	[57]
Density	1.8 – 1.84 g/cm^3	[81]
Decomposition temperature	127°C	[81]
Temperature of Ignition	142°C	[82]
Enthalpy of formation	-150.6 kJ/mol	[81]
Dissociation energy	255±12.5 kJ/mol	[81]
Friction sensitivity	72N	[81]
Impact sensitivity	5Nm	[81]
Electrostatic discharge	0.45 J	[82]
Figure of Insensitivity (Gas evolved, mL)	30(2.3)	[82]
Vacuum stability (80°C/40hr, mL/5g)	0.73	[82]
Yield of gas, moles/100g	4.03	[83]
UV absorption maxima in water	212 and 284nm	[84]
NMR peaks	^{14}N = -12.0 ppm (N$\underline{N}$O$_2^-$) -60.2 ppm ($\underline{N}$NO$_2^-$) -360.1ppm ($\underline{N}$H$_4^+$)	[85]
	^{15}N = -12.2 ppm (N$\underline{N}$O$_2^-$) -60.8 ppm ($\underline{N}$NO$_2^-$) -360.1 ppm ($\underline{N}$H$_4^+$)	[85]
	^{17}O = 496.6 ppm (NN$\underline{O}_2^-$)	[85]

The hygroscopic properties of dinitramide salts vary widely. The ammonium salt of dinitramidic acid is highly hygroscopic, while quaternary, aminoguanidine, and acetamidine salts are non-hygroscopic. All the dinitramide salts are photosensitive. The mechanical sensitivity of dinitramide salts also varies. Highly sensitive dinitramide salts are those of hydrazine and triaminoguanidine.

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1.16. Other Dinitramide Salts

Dinitramidic acid forms stable salts with mono and di-valent metals of group I,II, VII & VIII. They are crystalline substances with melting points in the range of 40-150°C. A number of organic and metal derivatives of dinitramides have also been synthesised and studied [84-86]. These compounds are considered to be model compositions of fuel-oxidizer system mixed at the molecular level. The general methods of preparation are given in Equations 1.28 to 1.35.

[a] By the interaction of metal hydroxides with β-substituted alkyl-N,N-dinitramines in organic solvents to give metallic dinitramide salt as shown in Equation 1.28.

$$X-CH_2-CH_2N(NO_2)_2 + MOH \xrightarrow{\text{-XCH=CH}_2} M-N(NO_2)_2$$

......(1.28)
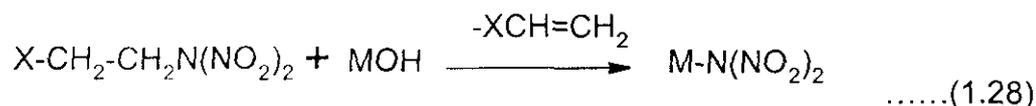
[b] Cation exchange reaction of Ag, K or Cs salt of dinitramide with the appropriate metal halide in water or organic solvents (Equation 1.29) gives the corresponding metal dinitramide salt.

$$M-N(NO_2)_2 + M'X_n \longrightarrow M'N(NO_2)_2 + n\ MX$$

......(1.29)
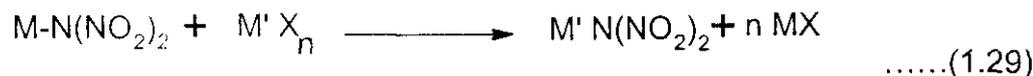
[c] The treatment of ammonium salt of dinitramide with solutions of strong bases or the reaction of aqueous and non-aqueous dinitramidic acid solutions with the appropriate metal hydroxide, oxide or carbonate will give the required dinitramide salt as shown in Equations.1.30 and 1.31.

$$NH_4N(NO_2)_2 + M(OH)_n \longrightarrow M(N(NO_2)_2)_n$$

......(1.30)

$$HN(NO_2)_2 \quad \cdots \cdots \boxed{\begin{array}{c} M(OH)_n \\ \hline M_2O_n \\ \hline M_2(CO_3)_n \end{array}} \longrightarrow M(N(NO_2)_2)_n$$

......(1.31)

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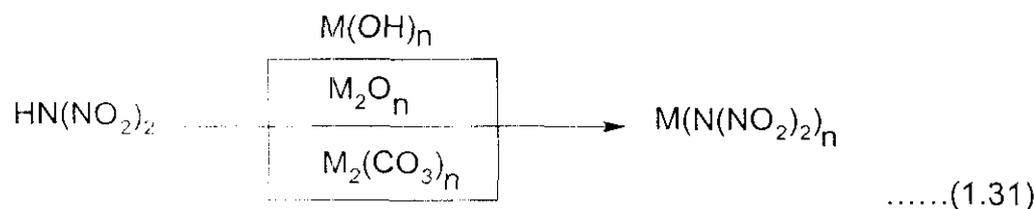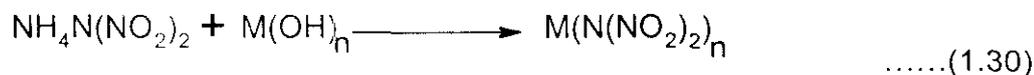
[d] The reaction of ADN with excess of organic amine either in bulk or in solvent, at 60°C for 4-5 hrs will give the desired dinitramide salt as shown in Equation.1.32.

$$RNH_2 + NH_4N(NO_2)_2 \longrightarrow R\text{-}N(NO_2)_2 + 2NH_3$$

.......(1.32)
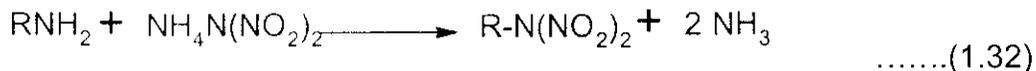
[e] By heating ADN with equimolar quantity of the carbonate salt of the amine in isopropanol or ethanol, till the evolution NH_3 or CO_2 is ceased. The dinitramide salt is then separated after evaporation of the solvent. The reaction is shown in Equation.1.33.

$$RNH_2.H_2CO_3 + NH_4N(NO_2)_2 \longrightarrow RNH_2.HN(NO_2)_2 + NH_3 + CO_2 + H_2O$$

......(1.33)
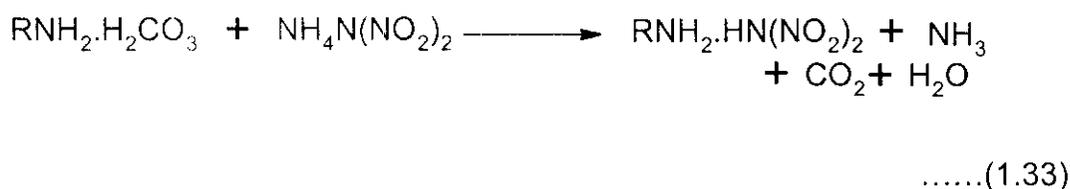
[f] The reaction of ADN with equimolar quantity of $Ba(OH)_2$ in aqueous medium gives barium dinitramide, which is reacted with a sulphate salt of the corresponding amine in ethanol to give the   corresponding amine dinitramide salts as shown in Equations.1.34 and 1.35.

$$Ba(OH)_2 + NH_4N(NO_2)_2 \longrightarrow Ba(N(NO_2)_2)_2 + NH_3 + H_2O$$

.......(1.34)

$$RNH_2.H_2SO_4 + Ba(N(NO_2)_2)_2 \longrightarrow RNH_2.HN(NO_2)_2 + BaSO_4$$

........(1.35)
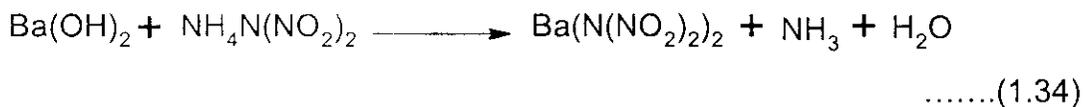
The X-ray evaluation of dinitramide salts [87] having organic, inorganic and metal cations reveals that these salts exist in different conformation depending on the cation present. The theoretical and structural studies of the dinitramide anion revealed that it is flexible and adopts different conformations depending on its environment. Ideal

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minimum energy conformation is of C_2 symmetry. However dinitramide salts show diversity of conformation with C_1, C_S and predicted C_2 symmetry. No two dinitramide salts give isostructural conformers. The conformation adopted by dinitramide anion is quite different with bent, twist and torsional angles. Table 1.15 and Table 1.16 summarize the different dinitramide salts, method of preparation and their melting point.

Table 1.15: Metal dinitramide salts

Dinitramide	Method of preparation	Melting point (°C)	Ref.
Li N(NO$_2$)$_2$	[b]	151	[88]
Na N(NO$_2$)$_2$	[b]	97	[88]
K N(NO$_2$)$_2$	[a, c]	128	[88,89]
Rb N(NO$_2$)$_2$	[a, c]	104	[88]
Cs N(NO$_2$)$_2$	[a, c]	82	[88]
Ag N(NO$_2$)$_2$	[a, c]	125-131	[84]
Pb N(NO$_2$)$_2$	[a, c]	102-106	[84]
Ba (N$_3$O$_4$)$_2$.H$_2$O	[f]	74-76	[84]
Ni (N$_3$O$_4$)$_2$.2H$_2$O	[b]	93-97	[84]
Ni (N$_3$O$_4$)$_2$.6H$_2$O	[b]	80-83	[84]
Mg (N$_3$O$_4$)$_2$.3H$_2$O	[b]	60-65	[84]
Mg (N$_3$O$_4$)$_2$.6H$_2$O	[b]	89-93	[84,90]
Cu (N$_3$O$_4$)$_2$.3H$_2$O	[b]	51-56	[84]
Fe (N$_3$O$_4$)$_2$.7H$_2$O	[b]	85	[84]
Co (N$_3$O$_4$)$_2$.6H$_2$O	[b]	82-86	[84]
Mn (N$_3$O$_4$)$_2$.8H$_2$O	[b]	41-63	[84,90]
Hg (N$_3$O$_4$)$_2$	[c]	93-103	[91]

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Table 1.16: Organic and Inorganic dinitramide salts

Dinitramide	Method of preparation	Melting point °C	Ref.
Guanidium dinitramide	[e]	146	[92]
Aminoguanidine dinitramide	[e]	87-88	[92]
5-aminotetrazole dinitramide	[f]	83-86	[92]
Aniline dinitramide	[f]	95-97	[92]
Benzylamine dinitramide	[d]	59-61	[92]
Diethanolamine dinitramide	[d]	75-78	[92]
Ethanolamine dinitramide	[d]	37-39	[92]
Methylamine dinitramide	[d]	43-45	[92]
Morpholine dinitramide	[d]	82-84	[92]
m-nitroaniline dinitramide	[f]	101-103	[92]
Piperazine bis-dinitramide	[d]	212-214	[92]
Tetramethylammonium dinitramide [b]	-	234-238	[92]
o-Toluidine dinitramide	[f]	70-71	[92]
3,5-dimethylpyridine dinitramide	[f]	70-73	[92]
Hexamethylenediamine bisdinitramide	[d]	89-90	[92]
Melaminium dinitramide	[d]	--	[93]
Cubane 1,4-bis (ammonium dinitramide) [a]	-	-	[77,93]
Cubane 1,2,4,7-tetrakis(ammonium dinitramide) [d]	-	-	[77,93]
3,3-dinitroazetidinium dinitramide	[c]	139	[94,95]
Triazidocarbenium dinitramide [c]	-	--	[96]
Butane,diammonium dinitramide	[d]	67-73	[97]
2-hydroxyethylhydrazinium dinitramide	[c]	--	[98]
$MeONH_2.HN_3O_4$	[e]	Oil	[99]
$H_2NCONH_2.HN_3O_4$	[e]	98-100	[99]
$H_2NC(=NH)NH_2.HN_3O_4$	-	55-58	[99]
$(C_5H_5NNO_2)N_3O_4$ [d]	[d]	67-69	[99]
$(NCCH_2CH_2)_2NH.N_3O_4$	[c]	115-117	[99]
$NH_2CH_2CH_2NH_2.2HN_3O_4$	[d]	125	[100]
$(O_2NOCH_2CH_2)NH.HN_3O_4$	[d]	114	[100]
$H_2NC(=NH)NHNH_2.HN_3O_4$	[d]	148	[100]
$NCCH_2CH_2NH_2.HN_3O_4$	[d]	94	[100]
Urotropinium dinitramide	[b]	121-124	[101]
Biguanidinium dinitramide	[f]	--	[102]
Biguanidinium bis-dinitramide	[f]	--	[102]
N-Guanylurea dinitramide	[f]	--	[103]
Ethane-1,2-diammonium dinitramide	[d]	--	[104]
$NH_2NH_2.HN_3O_4$	[c]	83	[99,105]
$H_2NOH.HN_3O_4$	[e]	18-23	[99,105]

[a] by ion exchange reaction of the corresponding perchlorate salts, [b] reaction of AND with tetramethylammonium hydroxide, [c] reaction of $C(N_3)_3^+$ BF_4^- and potassium dinitramide, [d] reaction of $(C_5H_5NNO_2)^+$ BF_4^- and potassium dinitramide

Apart from the practical application of dinitramide salts, few of these can be new reagents in organic synthesis [84,86]. Example is $Hg(N_3O_4)_2$. It is a covalent compound, where the Hg atom is bound to oxygen atoms of the nitro group. This salt can enter mercuration reaction and can add to olefins yielding mercury derivatives having dinitramide units as shown in Equation 1.36.

$$H_2C{=}CH_2 \ + \ Hg(N_3O_4)_2 \longrightarrow (O_2N)_2NCH_2CH_2HgN_3O_4$$

$$MeOH \qquad\qquad\qquad H_2O$$

$$MeOCH_2CH_2HgN_3O_4 \qquad\qquad HOCH_2CH_2HgN_3O_4$$

$$\dots\dots(1.36)$$
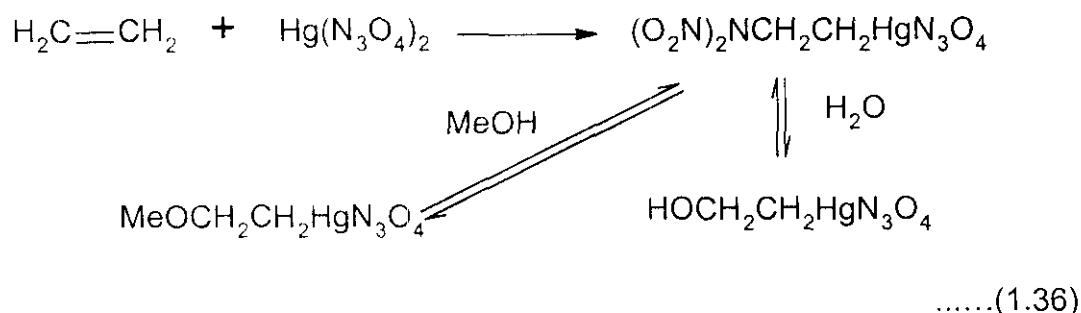
The salts derived from aliphatic amines decompose at 120-140°C, while quarternary ammonium and hydrazonium salts have higher melting and decomposition points. Dinitramide salts of hydroxylamine or methoxyamine are readily soluble in non polar solvents [99].

Azetidine based explosives are expected to have excellent performance because of the associated high strain energy with the four membered ring [94]. For example, the 3,3-dinitroazetidinium cation has a high oxygen balance and is useful as an energy rich substitute for the conventional cations, such as ammonium, guanidine, hydrazine etc., and these can be useful as propellant ingredients.

The alkali metal dinitramide derivatives are synthesized for use in pyrotechnic flare compositions. These metal dinitramide salts, apart from providing energy for the composition, provide pyrotechnic effects and increase the density of formulation. The amine salts of dinitramide are considered as explosives or components of energetic mixtures because of their good thermal stability and low susceptibility to hydrolysis [88]. Apart

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from the thermal stability, these amine salts have better unhygroscopicity and positive oxygen balance, and may find applications in new high-energetic compositions.

N-guanylurea dinitramide has low sensitivity and is a good candidate for insensitive munitions [103]. It is neither soluble in water nor hygroscopic. Its thermal stability is comparable to RDX and superior to that of ADN. The substitution of an organic cation for ammonium in dinitramide will result in change of combustion temperature and reactivity of the fuel.

The cubane and azetidine salts of dinitramide are of great interest because of the high strain energy and density of the cubane molecule and may have potential application in advanced propellants.

1.17. Conclusions

Energetic materials are the main source of energy for various military and space applications. The nitro containing energetic materials play an important role as key ingredients in most of the propellant and explosive combinations. Ingredients containing light chemical elements such as H, Al, Be, B, C, N, O and F are the most desirable for high-energy propellant compositions. These elements enhance enthalpy release per unit weight while reducing the average molecular weight of gases. Oxidizers such as ADN, CL-20 and HNF have been identified as the most energetic ingredients for achieving high-performance propellants.

The synthetic methods for the preparation of dinitramide salts are reviewed and the salient aspects of the reactions with respect to the product yield, purity and separation methods are discussed. The methods for the synthesis of dinitramidic acid involves dinitration of primary amines that are made weakly basic by suitable substituents using nitrating agents such as NO_2BF_4, N_2O_5, $NO_2HS_2O_7$ or 100% HNO_3 in presence of acid

catalysts. The product yield varies from 5 to 70% depending on the nitrating agent and the reactant. An account on the preparation of numerous salts of dinitramide consisting of metal, organic and inorganic derivatives is also given.

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