

CHAPTER 1

1.1 Introduction:

The earliest recorded use of powered missiles in warfare was in 1232 at the military siege of Kaifeng, former capital of the Chinese province of Henan, in which rockets were used to set fire to tents and wicker-work fortifications. European technology developed these rockets into larger and longer-range weapons. In 1807, for example, Copenhagen and a large French fleet in its harbor were almost totally destroyed by a British naval attack using thousands of iron rockets. The national anthem of the United States reflects the common use of these weapons in naval battles in the 17th and 18th centuries, when Francis Scott Key saw the American flag "by the rocket's red glare."

The first true ballistic missile—one that has a brief period of powered flight, continues on a ballistic trajectory outside the atmosphere, then curves back to an impact point on earth—was developed at the end of World War II. Serious efforts to find a defense against ballistic missiles began shortly after the first German V-2 slammed into London, without success. Overall, the United States has spent more than \$100 billion (in current dollars) in the pursuit of missile defense since the mid-1950s (plus \$17 billion on the Patriot system, developed separately by the Army as an anti-aircraft system.) The United States remains the only nation devoting a significant portion of its national defense budget to missile defense.

Historically the first solid rockets were projectile launchers in war, based on gun powder comprising a mixture of potassium nitrate (oxidizer), charcoal and sulphur (fuel/binder). Tippu Sultan, the king of Mysore in the late 18th century, used indigenously developed rocket motors in his battle against the British first time in the world. The British became astonished after being

exposed to rocket motors near Seringapatam in 1799 and were forced to borrow them. These rocket motors were having the lacking in range, accuracy, safety and largely unreliable.

The next important development in combat rocket was the introduction of smokeless powder comprising nitrocellulose (NC) and nitroglycerine (NG) by A Nobel in 1890. This kind of propellant is known as double base propellant or homogeneous propellant exhibiting excellent mechanical properties. The homogeneous propellants are defect free and therefore more reliable. The propellant grains of double base propellant made through the extrusion technology and know as free standing grain and some time known as cartridge. The rocket motors made out this propellant are cartridge loaded rocket motors and extensively used in sounding rocket and as sustainer grain for missiles. But the limitation to produce the rocket motors of the size of 60 to 200 mm (outer diameter) and weighing the propellant of 5 to 200 kgs became the motivating factors to develop the technology suitable for large size of solid rocket motor.

The technology of making large size propellant grains emerged along with the basic understanding of polymer science. The solid composite propellant came into existence due to the significant advances made in developing the polymer casting technique very soon after World War II. The path breaking scientific idea of chemists to develop the functionally terminated polymer which will be use in both way for high energetic material as well as binder to accommodate all the powders and additives into its matrix. It was thought of that the pre viscous polymers were mixed with solid powder composition to form slurry that could be cured insitu after casting in suitable moulds.

1.2 Rocket and Missile Propellants:

The propellants are currently used to maintain the required performance of weapon systems, in military rockets and missiles require environmentally harmful substances, such as ammonium perchlorate and lead compounds. Projects aim to develop and demonstrate new propellant formulations that do not contain perchlorates, lead compounds, RDX, or other environmentally objectionable materials.

1.3 Explosives:

Explosives are used in munitions as the main charge in warheads and in the fuses, primers, and detonators used to initiate the main charge. The performance of explosive materials is often tied to environmentally objectionable materials such as lead and RDX. In addition, the synthesis processes for explosive compounds such as trinitrotoluene (TNT) and triaminotrinitrobenzene (TATB) generate significant amounts of hazardous waste or require environmentally harmful precursor materials. Projects are focused on developing explosives made with environmentally friendly synthesis processes and materials while not sacrificing performance.

1.4 Ammunition and Projectiles:

Potential environmental hazards are associated with nearly all the components of a round of ammunition typically used by the military. Primer formulations use harmful lead compounds. Propellants contain nitrocellulose and significant amounts of hazardous waste are generated during their production. Projectiles are made of harmful materials such as lead and depleted uranium. Projects focus on the development and demonstration of alternatives that do not contain harmful materials or generate hazardous waste in production.

1.5 Solid Composite Propellant:

Solid composite propellant is the simplest and most reliable source of energy for modern rocketry, space launch vehicles, gas generators for air bag system and ballistic missiles. The rocket motor consists of solid composite propellant as the energy source called solid rocket motor, simplest form of all rocket designs. They are configured into the stages and normally consist of three stages. The stages segments are made of specific steel and carbon reinforced composite materials. These stages are filled with the solid composite propellant (SCP) to form the solid rocket motor. These SCPs are the vital and most reliable energy source in the modern rocketry. Solid rocket motors (SRMs) and space vehicles derive energy through hydroxyl terminated polybutadiene (HTPB) / aluminium powder (AL) / ammonium perchlorate (AP) based SCPs. The main advantages of AP based propellants are good specific impulses, high reliability, and a relatively simple manufacturing process. Holmes *et al.* 1989 ; Shutton 2001 ; Mahilal *et al.* 2012 have reported that there are at least ten different ingredients used in producing a solid propellant. But, mainly four typical ingredients namely HTPB (a polymeric binder, 10-15 %), toluene di-isocyanate (TDI) (a curing agent as an additive 1-3.5 %), ammonium perchlorate (AP) (oxidizer 65-70 %) and aluminium powder (AIP) (metal fuel 15-20 %).

1.5.1 Hydroxyl Terminated Polybutadiene (HTPB):

The HTPB is an oligomer of butadiene terminated at each end with hydroxyl group. These attached hydroxyl groups are responsible for reaction with isocyanates to form polyurethane polymers. HTPB provides the structural integrity to the propellant via polyurethane reaction with toluene di-isocyanate and cross linking agents, in which solid loadings of oxidizer, metallic fuel, burn rate modifier and other additives are held. The HTPB binder is being used in composite solid propellants for rockets and missile applications [Mahanta *et al.* 2007 ; K. Bina *et*

al. 2004]. Figure 1.1 shows the basic reaction for the polymerization of 1,3 butadiene, the monomer used to obtain polybutadiene.

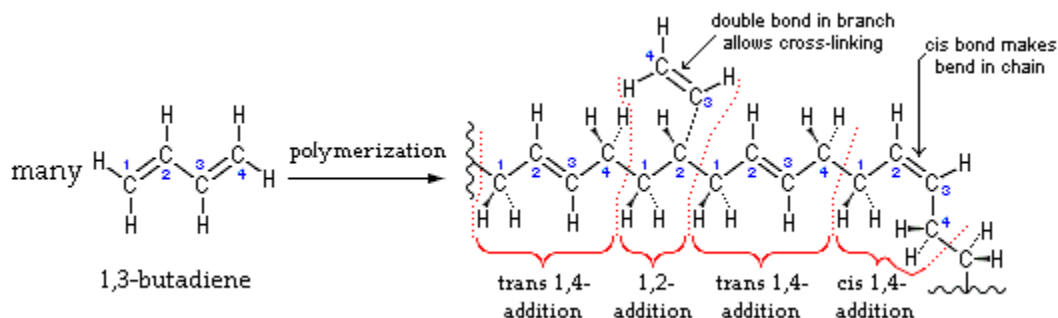


Fig 1.1: Oligomer of Butadiene

1.5.2 Aluminum (Al):

The second most important ingredient of solid composite propellant is the metallic fuel. Metal fuel is added in composite propellants to enhance the performance by increasing the combustion temperature. In addition to Al(P), beryllium, zirconium, boron and magnesium have also been tried into the propellant system, but could not succeed due to their inherent constraints. Compared to Al, beryllium (Be) has a highly toxic oxide that can cause fatal effects, whereas, demerit of zirconium (Zr) is its poorer combustion Activity and lower energy than Al. Boron is too expensive relative to Al, and Magnesium (Mg) tends to decrease the specific impulse of SCPs [Meyer *et al.* 1984]. Thus, compared to others, Al is the best metal fuel because of its high heat of combustion, low cost, ready commercial availability, low degree of toxicity, and relatively high combustion Activity. Figure1.2 compares the mass and volumetric heats of combustion of various metals.

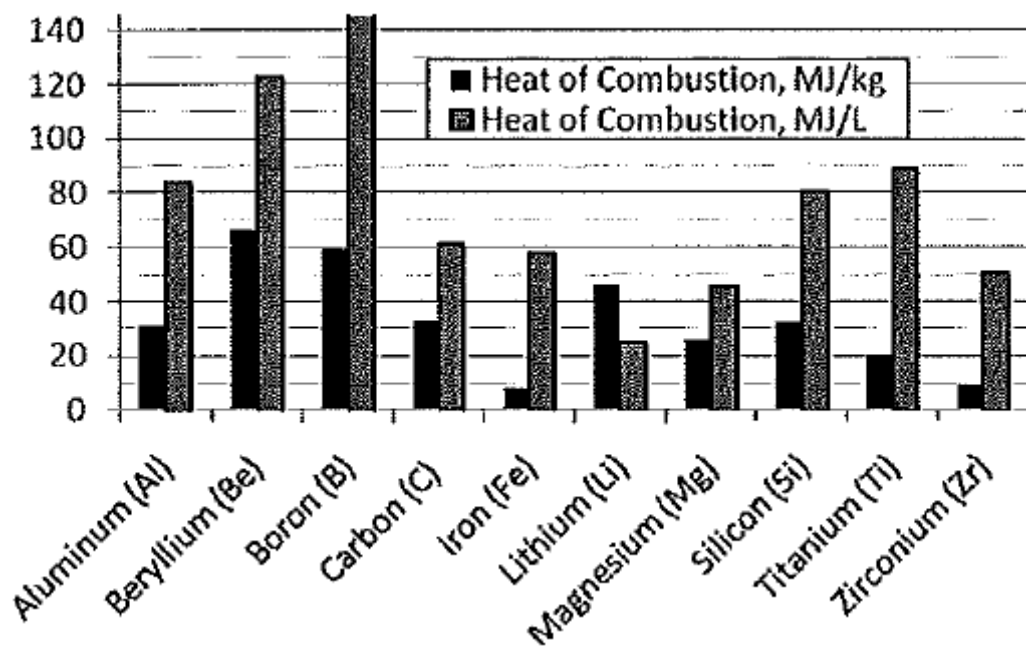


Fig.1.2: Theoretical Energy Release of Thermite, Intermetallic and Combustible Metals

1.5.3 Ammonium perchlorate (AP):

Ammonium perchlorate is a workhorse inorganic oxidizer, which is being exploited in the SCPs worldwide since late 1940's [Hunley *et al.* 1999]. The function of AP is to provide the required oxygen during the combustion of propellants [Douglass, 1971]. Some other nitrate and perchlorate of lithium, potassium and sodium are also being used in rocket, depending upon the specific requirement. The inherent properties of AP (i.e. thermal and mechanical stability) and its ability to control the propellant's burning rate made ammonium perchlorate the best choice of each scientific community of aerospace research. The researchers of propulsion systems have reported an increase in burning rate with a decrease in the particle size of AP. However, particle sizes below 40 micrometres are considered hazardous, because of easy ignitability and sometimes detonation [Jones, (2003)]. Ammonium perchlorate (AP) is a white crystalline solid inorganic compound with the formula NH_4ClO_4 . It is the salt of perchloric acid and ammonia.

The powerful oxidizer is used in the manufacturing of rocket propellant, explosives and pyrotechnics, as an etching and engraving agents and also being used in analytical chemistry.

The important physical properties of ammonium perchlorate are given in Table 1.1.

Table.1.1: Physical Properties of Ammonium Perchlorate

Chemical formula	NH_4ClO_4
Molar Mass	117.49 g/mol
Appearance	White Crystalline
Density	1.95 g/cm ³
Melting point	Exothermic decomposition before melting at >200°C
Solubility in water	11.56 g/100 mL (0°C) 20.85 g/100 mL (20°C) 57.01 g/100 mL (100°C)
Solubility	Soluble in Methanol Partially soluble in Acetone Insoluble in Ether
Crystal Structure	Orthorhombic (< 240°C) Cubic (>240°C)

1.6 Structure of Ammonium Perchlorate:

Ammonium perchlorate is orthorhombic in nature at room temperature. The unit cell of the orthorhombic modification contains four molecules. The unit cell parameters are: $a = 0.9202$, $b = 0.5816$ and $c = 0.7449$ nm. Four oxygen atoms form a tetrahedron around the chlorine atom. The distance between chlorine and oxygen is 0.143 nm. Each ammonium ion is surrounded by 12 no. of oxygen atoms; eight of them are at a distance of 0.294–0.308 nm and four at a distance of 0.325–0.352 nm. Figure 1.3 shows the graphical representation view of ammonium perchlorate and Figure 1.4 shows the chemical of the said inorganic oxidizer.

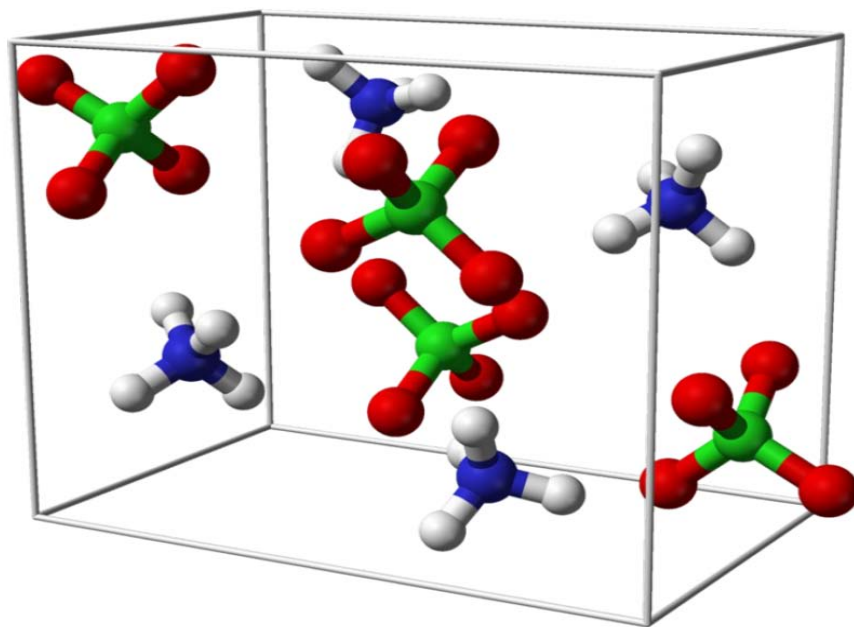


Fig.1.3: Diagram of Ammonium Perchlorate

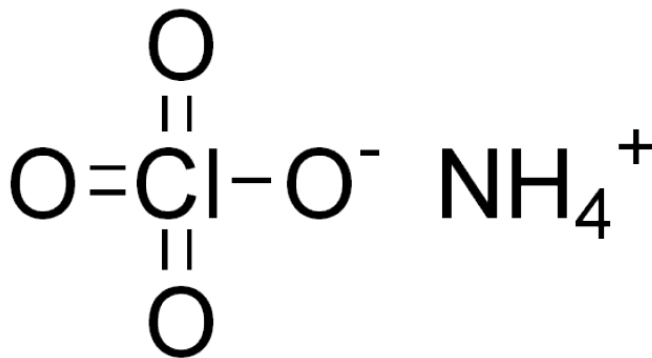


Fig1.4. Chemical Formula of Ammonium Perchlorate

1.7 Thermal Decomposition of Ammonium Perchlorate:

Ammonium per-chlorate, the workhorse oxidizer, is an inorganic crystalline material also known as monopropellant. Two most important crystal modifications of ammonium per-chlorate are: orthorhombic (Region of existence: $T < 240^\circ\text{C}$) and cubic one, which is stable at temperatures $T > 240^\circ\text{C}$. Heat of phase transition of ammonium per-chlorate from orthorhombic to cubic modification is 11.3 kJ/mol. Thermal decomposition of AP has been intensively used in the period of 1960s. The AP decomposition mechanism has been explained using the concept of electron and proton exchange at the elevated temperatures as reported by Boldyrev *et al.* (2006). They studied the governing mechanism of thermal decomposition of AP and proposed electron and proton transfer processes. AP is decomposed in two stages; low temperature decomposition governed by the electron transfer process and high temperature decomposition initiated by the proton transfer process. The solid composite propellants with high burn rate and thereby reduced ignition delay and operational time is the need of modern space vehicles. The thermal decomposition supported theories i.e electron transfer theory and proton transfer theory, depending upon the temperature level, has been accepted very well among the researchers.

1.7.1 Electron Transfer Theory:



Since electron transfer occurs locally, the probability of its realization is the higher, when the distance between the ions is small. Because of this, an efficient acceptor of electrons is considered to be not any ammonium ion, but only that located in interstices. Further electron transfer occurs not in the bulk but on the surface, where the conditions for its realization are better due to the presence of local surface energies. After having captured an electron, the ammonium radical decomposes into ammonia and hydrogen atom:



Hydrogen migrates over the lattice. Electron migrates exactly in the same manner over the anion sublattice:



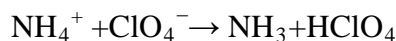
As a result of the interaction between ClO_4 radical and H, HClO_4 is formed. It may continue interacting with H:



The ClO_3 radical is a trap for electrons. Having trapped an electron, it is transformed into ClO_3^- ion. After that, chlorite ion and ClO_4 radical can decompose; interact with NH_4^+ ions, etc. As a result of this interaction, secondary products are formed. Among them, the major ones are chlorine, nitrogen hemi oxide and water.

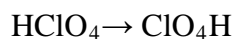
1.7.2 Proton Transfer Theory:

1. Proton transfer from cation to anion.



1.5

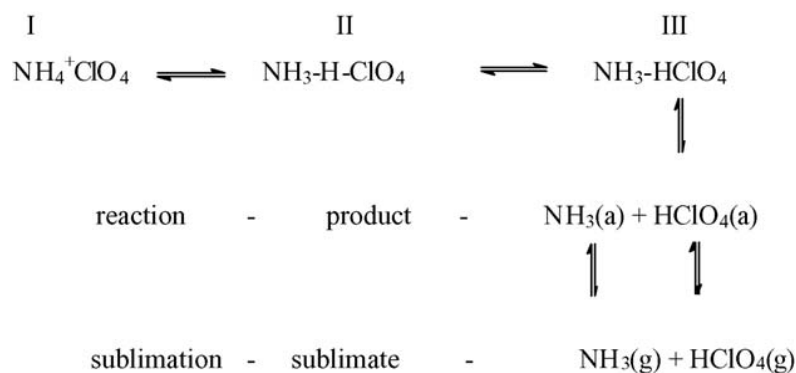
2. Reorientation of the protonated anion.



1.6

3. Proton jump from one anion to another.

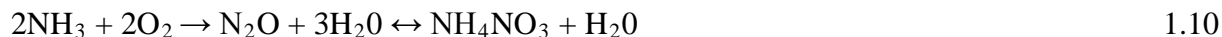
Stages 2 and 3 correspond to transfer of the carrier along the lattice.



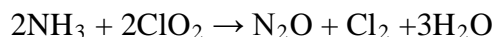
At low temperature, the products of thermal decomposition of pure AP are NH_3 , H_2O and a small amount of N_2O and O_2 . However, HCl , H_2O , N_2O , NH_3 , Cl_2 , NO , O_2 , NO_2 and a small amount of ClO_2 are formed during the high temperature stage of AP's decomposition. Based on this mechanism, the following proton transfer route for the decomposition of AP was proposed:

Low Temperature:

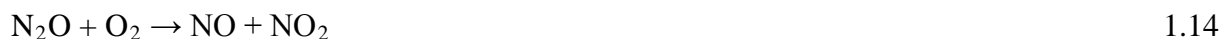




High Temperature:



1.13



Thermal decomposition of AP is highly affected by transition metals, transition metal oxides and their mixtures. Transition metals and metal oxides are used as catalysts to enhance the rate of thermal decomposition of AP, which eventually modifies the burn rate. Transition metals / metal oxides / mixture of metal oxides have been reported to be the most effective burn rate modifiers due to their greater selectivity, thermal resistance and mechanical strength. The electronic configuration of transition metals and metal oxides is helpful in enhancing the decomposition of AP. The thermal decomposition of AP is through the electron and proton transfer theory. The particle size and shape of the catalyst play the greater role in tailoring the burn rate. With reduction in the particle size, the specific surface area increases, this provides the surface for the chemical reaction.

1.8 Specific Impulse of Solid Composite Propellant (SCP):

Specific impulse (Isp) is another important factor to qualify the total propulsion system as it specifies the energy of a propellant. Higher the specific impulse, higher the performance of the propulsion system, is the ultimate requirement of the mission and is always being the center of research of aerospace researchers and scientists. It is defined as the impulse (Thrust X Time) per

unit weight of propellant. The equations relating to the Isp with chemical parameters are given below.

$$I_{sp} = F \times T / W \quad 1.15$$

$$I_{sp} \propto (\Delta H)^{1/2} \quad 1.16$$

$$I_{sp} \propto (T_c / M_c)^{1/2} \quad 1.17$$

Where, F = thrust, T = time, W = weight, ΔH = heat release (heat of combustion) per unit weight of propellant, T_c = chamber temperature, and M_c = average molecular weight of combustion products.

Equation (1.17) states that the high chamber temperature and low molecular weight products are the basic requirements for achieving the higher Isp. Heat of combustion is depends upon the heat of formation of the ingredients of propellant system, should have large positive or less negative heat of formation value. It also clear that the molecules consisting the less molecular weight also enhance the Isp. This why hydrogen is not only good fuel but also desired exhaust products. Specific impulse greatly depends upon the energy and combustion behavior of contained propellant. Achieving high energy propellant along with the improved burn rate and combustion behavior with less sensitivity of friction, impact, temperature, pressure and long service life is the futuristic need for the ballistic missiles and space applications. To achieve it, there is a need for replacement of inert modifier, flow and processing aids with energetic materials in the solid composite propellant. These energetic materials are composite materials of ultra fine size which are specifically synthesized to fulfill both the objectives i.e. enhancement in burn rate as well as imparting additional energy to the propellant.

1.9 Burn Rate of SCPs:

The burn rate, the performance measuring parameter of solid composite propellant, the rate at which propellant is consumed and chemical energy is released. This chemical energy is converted to kinetic energy (by means of nozzle), which provides a thrust to the solid rocket motors of space vehicles and missiles. The burn rate of the SCPs is a function of stoichiometry of the propellant ingredients. It strongly depends on thermal decomposition of AP, a major ingredient of the SCPs. Thermal decomposition of AP is greatly dependent on particle size and shape and catalyst concentration. Higher burn rate with lower pressure exponent is the desirable requirement in space vehicles or missiles. According to the Shutton and Biblarz (2001), burn rate is conveniently described by the Vieille-St. Robert Law, which is given as below:

$$r = aP^n \quad (1.18)$$

Where, r = burn rate in mm/sec, a = function of initial temperature, P = combustion pressure in MPa and n = pressure index.

1.9.1 Temperature Sensitivity of Burning Rate:

The burn rate of a solid propellant is dependent on pressure index based on above mentioned equation. However it is also dependent on the initial temperature of the propellant T_i , even when the pressure is kept constant. The parameter “ a ” is not a true constant, since it can be expressed as a function of initial temperature T_i and temperature sensitivity σ_p .

$$a = a_{ref} e^{\sigma_p(T_i - T_{i,ref})} \quad 1.19$$

1.9.2. Pressure Index (n):

The ‘ n ’ value is of great importance as the burn rate depends on the combustion pressure and n is the exponent to the pressure. A slight variation in the ‘ n ’ value may lead to the unstable burning of the propellant. Hence, for stable and safe combustion process, the value of ‘ n ’ should be minimum and for HTPB based propellant, it is of the order of 0.4-0.44.

1.10 Factors Affecting the Burn Rate of SCPs:

The burn rate is one of the important parameters in the solid rocket motor design and development. It depends mainly upon the following, (1) propellant composition, (2) particle size and distribution of the oxidizer, (3) burn rate modifier, (4) particle size and distribution of burn rate modifier, (5) internal combustion pressure of the rocket motor, (6) initial temperature of the propellant, (7) thermal decomposition of oxidizer, (8) size and shape of the propellant grain and (9) flame Temperature. The burn rate of solid composite propellant is sensitive to propellant composition. A small change in propellant composition greatly influences the burn rate behaviour and its combustion index. The main ingredient responsible for controlling the burn rate is ammonium perchlorate (AP), an oxidizer. AP is used in one size or combination of two or more and known as monomodal, bimodal and so on.

1.10.1 Effect of Particle Size of Ammonium Perchlorate on Burn Rate of SCPs:

The burn rate of solid composite propellant consisting of smaller particle size of AP exhibit the higher burn rate against the larger particle size of AP. But one must take care while designing the propellant composition with the smaller particle size of AP as the AP below 40 micron leads to the agglomerations of the particles and moreover it turns in explosive nature. Jeppson *et al.* 1998 has demonstrated the relationship between burn rate on particle size of AP and shown in Fig.1.5. The burn rate reduces as the particle size of AP increases. This may be due to the filling of voids created among the particles leading to close and dense packing of particles in HTPB based polymer matrix. The use of ammonium per-chlorate of drastically reduced particle size in polymer matrix of propellant exhibits the higher viscosity of propellant slurry

which reduces the process-ability and the propellant grain becomes prone to the crack development.

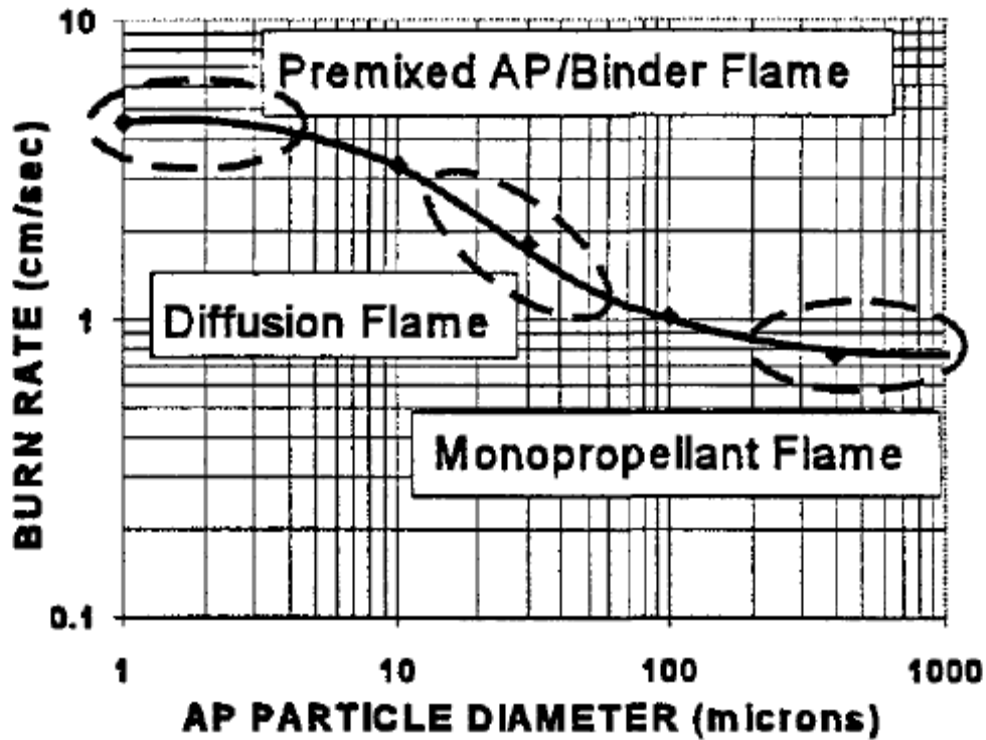


Fig.1.5: Combustion Regime and Effect of AP Particle Size on the Burning Rate of Monopropellant

1.10.2 Effect of AP Solid Loading on Flame Temperature:

The burn rate is a surface phenomenon and depends on the surface temperature. Higher the surface temperature the higher is the combustion flame and in turn higher the burn rate of solid composite propellant. The flame temperature is a function of propellant composition especially loading of ammonium perchlorate [Cruise, (1979)].

The solid loading of AP in SCPs alters the flame temperature to some extent and further AP loading decreases the flame temperature, consequently there is no effect on the burn rate

enhancement. Cruise, (1979) has established the relation between AP loading and flame temperature by modelling using the proPep software Fig.1.6.

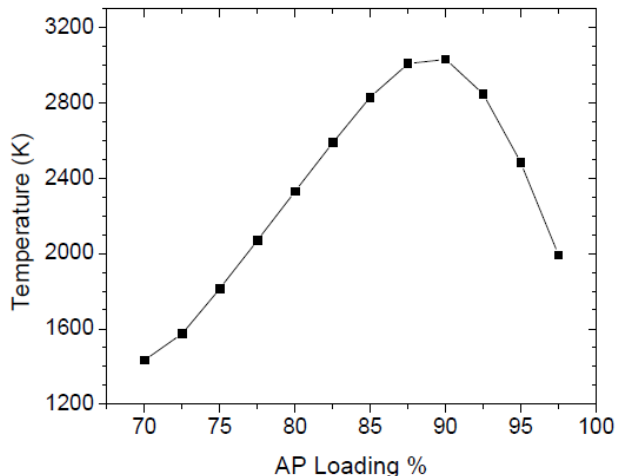


Fig.1.6: Flame Temperature of AP Based Solid Composite Propellant with Varying Loading of AP

1.11 Additives:

Meyer (1984) reported that small quantities of additives did not affect the performance (Isp) of the propellant but greatly influenced the burn rate of solid composite propellant. Mostly transition metal and metal oxides in the micro-scale size are used as a catalyst. The researchers have carried extensive studies on the application of nano-particles of transition metals and metal oxides due to their extremely high specific surface area. However, the exact mechanism for enhancing the burn rate of the propellant is under debate. The oxides of iron, manganese, copper, nickel and copper chromites are widely used. The transition metals, transition metal oxides, and composites of ternary materials such as MnO_2 , CuO , NiO , CoFe_2O_4 , Fe_2O_4 , and CuCr_2O_4 etc. are the common catalysts used to enhance the thermal decomposition of ammonium perchlorate.

Recent developments in the area of carbon based materials such as carbon nanotubes (CNT), graphene oxide (GO) and reduced graphene oxide (rGO) promised better catalysts and catalyst support due to their high specific surface area and high thermal and electrical conductivity. Dispersion difficulty of CNT leads to its restricted applications, whereas hydrophilic nature of GO/rGO and ease of its synthesis make it a potential precursor material for synthesis of graphene. Graphene is a two dimensional sheet of carbon owing the honeycomb structure, which provides the high specific surface area with superior electrical and thermal conductivity [Hummers *et al.* 1958 ; Pei *et al.* 2012 ; Park *et al.* 2009]. The rGO has tremendous electron transfer properties. These inherent properties of graphene have created the tremendous scope for its potential application as catalytic especially for the thermal decomposition of AP.

Kubota (2001) has confirmed that the burn rate of solid composite propellant can be modified by addition of small quantities (< 3%) of burn rate modifiers. Kumar and Ramakrishna (2014) found that a higher pressure exponent (n) and burn rate of propellant were observed with addition of iron oxide as compared to copper chromite. Addition of iron (III) oxide (Fe_2O_3) and copper (II) oxide (CuO) to an AP based propellant has reduced the ignition delay Hedman, (2012). AP is the major weight stake (65-70% by weight) of the propellant hence, thermal decomposition of AP is the key factor to get desired burn rate of SCP. It acts as a control to play with the burn rate of solid composite propellant. Kshirsagar *et al.* (2013) has suggested that the addition of burn rate modifiers such as CuCr_2O_3 , Fe_2O_3 , Cr_2O_3 and CuO in the propellant composition enhanced the burn rate of propellant by lowering the decomposition temperature of ammonium perchlorate.

It is much interesting to exploit the catalytic properties of both transition metal oxide based materials and graphene based materials in a single system. Recently, graphene based transition metal oxides composites (Fe_2O_3 , TiO_2 , Co_3O_4 and MnO_2 etc.) have been prepared and their

effect on thermal decomposition of AP have been studied by many researcher. Li *et al.* (2012) synthesized the Ni/graphene based nanocomposites using the simple one-spot method and observed a single step decomposition of AP. The same group in 2013 has observed the negligible effect of pure graphene on modification in thermal decomposition of AP, whereas, nano particles of Mn_3O_4 dispersed on GO exhibit tremendous effect. Yuan *et al.* (2014) have studied the thermal decomposition of AP in presence of Fe_2O_3/GO and observed a single step decomposition of AP at much lower temperature with high energy release against the individual effects of Fe_2O_3 and GO.

The catalyst having the capability to increase the burn rate, controlled by the thermal decomposition rate of ammonium perchlorate (NH_4ClO_4) with the lowest possible pressure index value (n) of solid composite propellant is the utmost requirement of the aerospace industry. Thermal decomposition of AP is governed by the electrons and proton transfer processes. Catalyst permitting faster release of electron and protons simultaneously and having high specific surface area, compatibility with other propellant ingredient and longer service life are required. Copper chromite ($CuCr_2O_4$) is a globally employed catalyst in solid composite propellants to meet the requirement of burn rate but has its own limitations for increasing the burn beyond certain extent. The heterogeneous coupling of a high energy band gap material (e. g. $CuCr_2O_4$) with a low energy band gap material (e. g. TiO_2) overcomes these limitations of $CuCr_2O_4$ and produces faster burn rate with low pressure index value due to p-type conductivity. Firstly electron is released from the thermally excited Cu-Cr-O and injected into the conduction band of TiO_2 consequently excites the TiO_2 . The simultaneous act of Cu-Cr-O.n TiO_2 on thermal decomposition of AP enhances the thermal decomposition of AP and releases higher enthalpy.

The electron and proton transfer processes can be enhanced by the addition of rGO that also avoids the agglomeration of catalyst particles [Giovannetti. 2008]. The rGO, due to its excellent electrical, mechanical and opto-electrical properties, will enhance the electron and proton transfer rates and consequently the burn rate of solid composite propellant will increase through the faster thermal decomposition rate of AP

Use of such a coupled oxide system with and without r-GO has not been attempted till date in propellant formulations for controlling the burn rate. In the present work an effort has been made to fill in this gap in the existing knowledge on burn rate modifiers.