CHAPTER 4

GENERAL DISCUSSION
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4.1 General

Conventional gun propellants have reached to their saturation level in terms of energy output. Single base propellants, which are based on nitrocellulose give force constant up to 1050 J/g. Double base propellants based on nitrocellulose and nitroglycerine exhibit the force constant up to 1200 J/g with higher flame temperature (2600-3600 K), linear burning rate coefficient and pressure index. Pressure index is an important parameter of gun propellant, which determines the combustion behaviour of the propellant and hence the suitability for gun ammunition. Therefore, the value of pressure index should be below 1.0 for safety of the gun. Triple base propellants, which are based on nitrocellulose, nitroglycerine and nitroguanidine, extensively used in tank gun ammunition give force constant up to 1100 J/g with the advantages of lower flame temperature (2700 K) and acceptable limits of burning rate characteristics. The muzzle velocity in the range of 1200-1700 m/s can be obtained with the existing conventional gun propellants depending on the formulations. However, there is an increasing demand for energetic propellants for advanced systems with improved performance in terms of density, energy, mechanical properties, extended shelf life and reduced sensitivity.

The main requirements for an extrudable gun propellant are that it should possess a high specific energy and fulfil the needs of modern high performance ammunition for artillery and battle tank gun in particular. Also, it
should be processable into the desired propellant shape. The primary requirement of gun propellant is the force constant of the cured propellant which should be at least 1100 J/g. The force constant can be expressed as follows:

\[ F = n \cdot R \cdot T_0 \]

where, 
\[ n = \text{No. of moles of propellant gas products per kg of propellant} \]
\[ R = \text{Gas Constant} \]
\[ T_0 = \text{Adiabatic flame temperature} \]

Literature survey reveals that efforts are being made all over the globe to improve the performance of gun propellants, i.e., increase the force constant of gun propellants. Attempts have been made in realizing energetic compounds as propellant ingredients to improve the energy output. Therefore, thrust of the recent research has been in the area of newer and novel energetic binders, energetic plasticizers and oxidizers, which could enhance the force constant of the propellant. The use of energetic additives, mainly binder and plasticizers containing chemical groups such as nitro, nitrato, etc. having more nitrogen, oxygen and fluorine in the structure is considered to be one of the practical ways to improve the energy level and other technical performances of solid propellants. These compounds have high explosive properties, good thermal stability and low melting points.

Another way of improving energy level of gun propellants is by increasing the enthalpy release and increasing the average molecular weight of combustion gases per unit mass of the propellant. Use of ingredients with low bond energies i.e. large positive heat of formation could enhance force
constant. In order to achieve this, the propellant should have sufficient oxygen to maximise the energy release. This is possible when the molecules contain bonds between the 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. The main constituents of the propellant combustion gases are hydrogen, carbon monoxide, carbon dioxide, nitrogen, water, ammonia and methane. To have higher energy, the propellant should give low molecular combustion gases like hydrogen, carbon monoxide and nitrogen rather than carbon dioxide. Nitrogen is preferred over carbon monoxide though the molecular weight of nitrogen (N₂) is same as that of carbon monoxide (Mw =28). Hence, amount of carbon should be minimized to avoid the formation of C (solid), CO and CO₂. The other factors for selection of energetic ingredients are heat of formation, density, oxygen balance, ratio of specific heat of gases, sonic velocity which are required to have higher performance of gun propellants. The plasticizers selected for study are azido and nitramine compounds containing first row elements. They have C — NO₂, N — NO₂, N ≡ N bonds in their molecular structures and give low molecular weight combustion gases thus contributing to the energy of the propellant system.

4.1.1 Heat of formation

The heat of formation depends on the bond energies between the atoms of the various ingredients used in propellant formulations. In order to get a high combustion temperature, one must select reactants with large positive heats of formation and products with strongly negative heats of formation. The maximum energy output is possible from an energetic reactant
molecule when it contains bonds with as small bond energies as possible and the products with as high bond energies as possible. Heat of formation is given by-

\[ \Delta H_f = \Delta H_{f \text{ products}} - \Delta H_{f \text{ reactants}} \]

The plasticizers studied under the present research work contain C–C, O–NO₂, N–NO₂, C–H bonds in their molecular structures, which have small bond energies and on decomposition give combustion gas products CO₂, H₂O, N₂ with high bond energies. Thus, these plasticizers have high heats of formation. Therefore, they are useful in enhancing the energy of the propellant systems when used as energetic plasticizers. Bond energies of some atoms are given in Table 4.1.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond energy (kJ/mol)</th>
<th>Bond</th>
<th>Bond energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-H</td>
<td>411</td>
<td>O-H</td>
<td>465</td>
</tr>
<tr>
<td>C-C</td>
<td>358</td>
<td>O-O</td>
<td>138</td>
</tr>
<tr>
<td>C=O</td>
<td>599</td>
<td>N-H</td>
<td>368</td>
</tr>
<tr>
<td>C≡C</td>
<td>812</td>
<td>N-O</td>
<td>255</td>
</tr>
<tr>
<td>C-O</td>
<td>350</td>
<td>N=O</td>
<td>601</td>
</tr>
<tr>
<td>C=O</td>
<td>740</td>
<td>N=N</td>
<td>163</td>
</tr>
<tr>
<td>C≡N</td>
<td>883</td>
<td>N≡N</td>
<td>443</td>
</tr>
<tr>
<td>H-H</td>
<td>435</td>
<td></td>
<td>947</td>
</tr>
</tbody>
</table>

4.1.2 Oxygen balance

Oxygen balance is important for the propellant or explosive characteristics. It is expressed as the excess weight % of oxygen present in the molecule after complete conversion of the fuel elements to $\text{CO}_2$, $\text{H}_2\text{O}$, etc. If the amount of oxygen bound in the explosive is insufficient for the complete oxidation reaction, the material is said to possess a negative oxygen balance and if it possess sufficient oxygen, it is said to have a positive oxygen balance. Explosives such as nitrate esters, nitro compounds and nitramines contain only elements carbon, hydrogen, oxygen and nitrogen and are called CHNO explosives having the general formula $\text{C}_a\text{H}_b\text{N}_c\text{O}_d$.

Oxygen balance is given by the following equation

$$OB,\% = \frac{(d \cdot 2a \cdot b) \times 1600}{2M}$$

Where, $M$ is the relative molecular mass of the explosive

Gun propellants are formulated with negative oxygen balance in the range of -50 to -20 percent. The single base propellants have oxygen balance near to -50 percent, double base propellant -20 percent and triple base propellant have oxygen balance around -30 percent. The force constant can be improved by choosing fuel rich energetic ingredients which can produce low mean molecular weight gaseous products. High oxygen balance of this propellant leads to formation of large molecular weight combustion products due to complete combustion of ingredients. The energy of the propellant system can be enhanced by using ingredients with higher oxygen balance. The plasticizers selected for the present research study have high oxygen balance and therefore they can replace the non energetic plasticizer
in the propellant compositions thus enhancing the energy of the propellant systems. Oxygen balance and enthalpy of formation of some plasticizers are given in Table 4.2.

Table 4.2: Oxygen balance and Enthalpy of Formation of some Plasticizers

<table>
<thead>
<tr>
<th>Plasticizer</th>
<th>Oxygen balance (%)</th>
<th>Enthalpy of Formation (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diethyl phthalate</td>
<td>-194.4</td>
<td>-768</td>
</tr>
<tr>
<td>Dibutyl phthalate</td>
<td>-224.2</td>
<td>-843</td>
</tr>
<tr>
<td>Dioctyl phthalate</td>
<td>-258.1</td>
<td>-1122</td>
</tr>
<tr>
<td>Triacetin</td>
<td>-139.3</td>
<td>-1331</td>
</tr>
<tr>
<td>Ethyl centralite</td>
<td>-256.4</td>
<td>-105</td>
</tr>
<tr>
<td>BDNPA</td>
<td>-63.7</td>
<td>-154</td>
</tr>
<tr>
<td>BDNPF</td>
<td>-51.0</td>
<td>-142</td>
</tr>
<tr>
<td>DANPE</td>
<td>-79.9</td>
<td>554</td>
</tr>
<tr>
<td>EGBAA</td>
<td>-84.2</td>
<td>-167.4</td>
</tr>
<tr>
<td>DAPOL</td>
<td>-90.1</td>
<td>410</td>
</tr>
<tr>
<td>Me-NENA</td>
<td>-43.6</td>
<td>1113</td>
</tr>
<tr>
<td>Et-NENA</td>
<td>-67.0</td>
<td>784</td>
</tr>
<tr>
<td>Bu-NENA</td>
<td>-104.3</td>
<td>259</td>
</tr>
<tr>
<td>NG</td>
<td>+3.5</td>
<td>-349</td>
</tr>
</tbody>
</table>

DANPE: 1,5-Diazido -3-nitrazapentane  DAPOL: 1,3-Diazido propane-2-ol
EGBAA: Ethylene glycol bis azido acetae  NG: Nitroglycerine
Me-NENA: Methyl NENA  Et-NENA: Ethyl NENA
Bu-NENA: Butyl NENA  BDNPA/F: Bis (2,2-dinitropropyl) -acetal/formal

Plasticizer is a key ingredient of solid gun propellant and plays a vital role in controlling the mechanical properties. It imparts the homogeneity and plasticity to the propellant dough and hence facilitates the processing of the propellant. Plasticizers used in gun propellants are high boiling liquids, usually organic high molecular weight esters compatible with nitrocellulose and nitroglycerine.

The utilization of azido plasticizers has become a reality during the last several years due to their high heats of formation. Generally, inert plasticizers used in conventional gun propellants are diethyl phthalate (DEP), dibutyl phthalate (DBP), dioctyl phthalate (DOP), dioctyl adipate (DOA), etc. These plasticizers do not contribute significantly to the energy of the propellant system. In contrast, energetic plasticizers contain explosophoric groups such as nitro, nitrato, fluoronitro, fluoroamino, azido, etc., and contribute to the energy of the system due to their high heats of formation. Literature survey reveals that large number of energetic plasticizers have been synthesized and characterized all over the world. However, very limited technical information is available in open literature on the evaluation of energetic plasticizers in solid gun propellant formulations.

Azido ester plasticizers have been reported to have better thermal and chemical stability, excellent mechanical properties, high energy content and good compatibility with binders as compared to nitrate esters plasticizers like trimethylol ethane trinitrate (TMETN), butane 1,2,4 - triol trinitrate (BTTN) etc. Organic azido esters, which are high nitrogen compounds are useful ingredients for gun propellant because their main combustion product is
Nitrogen is an extremely stable molecule and shows little tendency to react even at high temperatures that exist in gun barrels and rocket engines. Additionally, nitrogen is completely transparent in the infrared region and contributes no interference to missile guidance systems, which use infrared radiations.

The azido group contributes a positive heat of formation of about 85 kcal/azido group, which is substantially high and contributes to the energy content of the system. Azido esters can also be used as a means of reducing the amount of flame in the exhaust gases generated during the gun, missile and rocket propulsion. An excessive amount of flame is extremely undesirable in the exhaust gases since this provides data that pinpoint the sites from which the gun, missile and rockets are fired. Therefore, azido esters could be employed as energetic plasticizers in the formation of reduced flame in gun propellant systems.

Nitramines are of interest for gun applications because they are energetic source of smokeless combustion products. Nitratoethyl nitramines, known as NENA compounds, have recently been discovered to be potentially very useful ingredients in gun propellants due to increasing demand for developing less sensitive propellant compositions. It has been reported by Mullay et al\textsuperscript{10} that NENA compounds can replace the less safe energetic molecules such as nitroglycerine (NG) or butane triol trinitrate (BTTN). In addition they can also replace less energetic materials such as commonly used mixtures of bis dinitropropyl acetal/ formal (BDNPA/F). When used as plasticizers, NENA compounds offer advantages of increased energy and plasticization over other plasticizers, as well as decreased vulnerability as
compared to nitrate ester plasticizers. In the recent past, special interest has been paid to Bu-NENA. Bu-NENA can be used as a substitute for nitroglycerine in propellant and explosive compositions. It has improved thermo chemical properties and in addition to this, it is particularly a good nitrocellulose plasticizer.

4.2 Special features of the present research

The starting materials for synthesis of the azido and nitramine plasticizers selected in the present study are easily available and at a low cost. Synthesis of the plasticizers is simple, quite safe, practicable and favourable for high yields with maximum purity. The instrumental techniques applied for characterization of the energetic plasticizers are found to be highly reliable and accurate. The synthesis of the energetic plasticizers can be carried out without difficulty or time consuming purification process. Synthesis can be easily scaled up for production of bulk quantity. Methods can be extended for synthesis of other novel energetic materials. The azido and nitramine plasticizers readily plasticize nitrocellulose and other cellulosic binders. They are compatible with RDX. These plasticizers have high heats of formation and generate low molecular weight combustion gases, thus increase the energy of the propellant system in which they are used. These plasticizers can replace non-energetic plasticizers in the double base propellant systems and thus make them use in tank gun applications.

These plasticizers are less sensitive to impact than conventional nitrate esters. Thus, they reduce the hazard potential associated with the conventionally used nitrate ester plasticizers. Nitramines, i.e., alkyl NENAs
exhibit superior low temperature sensitivity characteristics, give smokeless products and can be used in gun propellant needed for advanced futuristic munitions.

### 4.2.1 Comparison of performance of energetic plasticizers under study

Normally double base propellants exhibit high flame temperatures due to higher energy content. High flame temperature is an important factor influencing erosion effects in gun barrels. The erosion of gun barrels leads to reduced gun performance. Flame temperatures should therefore be kept below certain limit. The present study was carried out keeping in view the need to formulate the double base compositions based on energetic plasticizers which can exhibit flame temperature $<3200$ K coupled with higher force constant and thus may be used in futuristic tank gun applications.

Hence in order to get a comparative study of the performance of the propellant compositions based on the energetic plasticizers undertaken in the present study, a graph was plotted on flame temperature (theoretical calculated) Vs force constant (experimentally determined from closed vessel tests) of the propellant compositions, based on the energetic plasticizers (DANPE, EGBAA, DAPOL and Bu-NENA). The graph is shown in Fig. 4.1.
Legends:
- Compositions based on NC/NG/Carbamite/DEP/DANPE
- Compositions based on NC/RDX/Cellulose Acetate/Triacetin/EGBAA
- Composition based on NC/NG/Carbamite/DEP/DAPOL
- Composition based on NC/NG/Carbamite/DEP/Bu-NENA

Fig. 4.1: Plot of Force Constant Vs Flame Temperature of Energetic Plasticizers

From Fig. 4.1 it is seen that the propellant compositions based on (NC/NG/Carb/DEP/DANPE) where percentage of DANPE is 7 ((replacing DEP), 12 (replacing NG) and 17 (replacing NC and NG) exhibit force constant 1100 J/g. The propellant composition based on DANPE (7%) exhibits higher flame temperature (>3200K). The LOVA propellant composition based on NC/RDX/Cellulose Acetate/Triacetin/EGBAA) exhibit force constant more than 1100 J/g. LOVA gun propellants with percentage of EGBAA (4 & 6%) and flame temperature >3200K. Propellant composition based on Bu-NENA
(replacing total 16% DEP) exhibits force constant >1100 J/g and flame temperature 3200 K. Gun propellant systems needing force constant to the tune of 1100 J/g and flame temperature <3200 K may make use of the formulations developed under present study. However, it is recommended to carry out dynamic firings prior to the adaptation.

4.3 Applications of plasticizers selected in the present research

Conventional triple base gun propellants based on nitrocellulose, nitroglycerine and nitroguanidine have been extensively used for tank gun ammunition. The ballistic requirements for tank gun ammunition are higher force constant to achieve the maximum possible muzzle velocity, lower flame temperature (<3273 K) to minimize the gun barrel erosion, lower burn rate characteristics ($\alpha < 1.0$) to ensure safety of gun and ($\beta_1 < 0.15 \text{ cm/s/MPa}$) to achieve loadability, ease of manufacture and consistent performance of propellant. In addition impact sensitivity ($h_{50} > 25 \text{ cm}$), friction sensitivity ($>20 \text{ kgf}$), thermal stability (Abel heat test $>10 \text{ min}$, Methyl violet test $>40 \text{ cm}$, B & J test $<5 \text{ ml /5 g}$) and mechanical properties (tensile strength $>100 \text{ kgf /cm}^2$ and percent compression $>10\%$) are important parameters to assess the suitability of propellant for tank gun ammunition. Typically these parameters should satisfy the values indicated as above. The conventional gun propellants fulfill requirements of flame temperature and burning rate characteristics, but their energy output in terms of force constant is limited to 1100 J/g. Hence to propel the advanced projectiles with high velocity, propellants exhibiting higher force constant are required to be developed. The
azido and nitramine plasticizers studied in the present research fulfill the above mentioned requirements (sensitivity, mechanical properties, force constant and stability) to some extent. Hence the propellant formulations containing energetic plasticizers (azido and nitramine) may be used in futuristic tank gun applications e.g. 120 mm tank gun ammunition.

Conventional triple base gun propellants used in artillery including 120 mm tank ammunition and particularly those that are poly-based, use a matrix component, usually nitrocellulose (NC), in combination with nitroglycerine (NG), which also acts as a high energy plasticizer for the NC, together with an amount of an energy adjusting component such as an energetic solid exemplified by cyclo trimethylene trinitramine (RDX), cyclo tetramethylene tetranitramine (HMX), ethylene di-nitramine (EDNA), and others. Diethylene glycol dinitrate (DEGDN) and triethylene glycol dinitrate (TEGDN) are also employed as conventional primary high energy adjustment components. However, the use of these materials in propellant formulations is discouraged because, while these materials enable a propellant to obtain and maintain a high energy level, they, at the same time, impose serious safety limitations as these materials may easily be set off or initiated by heat, impact and/or shock. Generally, efforts directed to reduce one or more of these sensitivities have also resulted in reducing the energetic output of the propellant. Heat sensitivity has proved to be somewhat less of a problem to overcome than impact or shock.

In the past, several approaches have been used in an effort to reduce the risks associated with sensitive materials while attempting to minimize the
associated reduction in energetic output of the overall composition. One such approach has involved the elimination or very limited use of shock-sensitive high energy compounds such as RDX and HMX. In this manner, these compounds have been replaced with various other known high energy plasticizers for nitrocellulose (NC), for example, including nitroglycerine (NG), acetyl triethyl citrate (ATEC) and a variety of nitrated acetals and others with some success.

However, RDX is a low cost primary high energy compound with particularly desirable attributes. These include the ability to increase overall propellant impetus or performance and also to increase the density of the propellant grains, which allows for greater bulk loading density in the cartridge case as compared to conventional propellants in similar geometries. Thus, if the sensitivity of the RDX-containing formulations could be decreased without reducing or eliminating the RDX, compositions with superior performance could be achieved.

RDX has been added to JA-2, conventional tank and artillery propellant in the past to achieve advanced ballistic performance. However, it has been reported that researchers at Army Research Laboratory (ARL) found RDX crystals on the surface of the JA-X propellant during aging. These researchers theorized that the RDX, partially dissolved in the DEGDN fraction, was carried to the surface of the granules as the DEGDN began to leach out at higher temperatures. This crystalline growth on the surface was a significant sensitivity hazard, and greatly increased the likelihood of initiation due to unplanned mechanical stimuli. For this and other reasons, including the
inherent sensitive nature of RDX, the use of RDX in artillery propellant compositions, has been generally discouraged.\textsuperscript{12}

It would present an advantage if a significant amount of the low cost high energetic propellant ingredient RDX could be utilized to increase the propellant impetus and loading density in a manner which does not cause the propellant composition to be more sensitive to heat, impact and/or shock. This is especially true with respect to munitions for tank guns.

The use of nitratro ethyl nitramine (NENA) compounds in propellant formulations is known. US Patent by Urenovitch\textsuperscript{13} discloses low vulnerability (LOVA) propellant containing mixtures of alkyl nitrate ethyl nitramines (alkyl NENAs) and/or bis (2-nitroxy-ethyl) nitramine (DINA) with nitrocellulose (NC). A further US Patent by Zeigler,\textsuperscript{14} also discloses the use of alkyl nitrate ethyl nitramine in combination with nitrocellulose/nitroguanidine in double base propellants which may also contain cyclonite (RDX).

US Patent granted to Strauss et al\textsuperscript{15} incorporates a cyclic nitramine in the form of 2-nitroimino-5-nitro-hexahydro-1,3,5 triazine (NNHT) which may be combined with methyl and ethyl NENA, nitrocellulose and RDX. Dillehay et al\textsuperscript{16} also showed the possible use of alkyl NENA compounds in LOVA propellants which may contain RDX.

The plasticizers selected in the present research work have superior properties as energetic plasticizers and they can be used in double base propellants and nitrocellulose RDX based propellants. They are potential candidates for futuristic advanced gun ammunition. The requirement of high force constant of modern gun ammunition may be met with these azido
plasticizers which not only function as processing aids but also increase the specific energy of the system. Hence, they can be used in 120mm MBT tank gun for FSAPDS ammunition where velocity > 1700 m/s is needed.

4.4 Futuristic research in the field of gun propellants related to present study

4.4.1 Toxicity of plasticizers selected for the present research

Widely used gun propellant compositions contain various compounds that may be environmentally hazardous or even toxic including dinitro toluene (DNT), dibutyl phthalate (DBP), diphenyl amine (DPA). Significantly DPA is classified as a highly toxic material. DBP is suspected carcinogenic and according to a study carried out by the United States Department of Health and Human Services, exposure to DNT is associated with an increased frequency of liver, bile duct and gall bladder cancers.

Compounds such as adiponitrile, triacetin, dibutyl phthalate are very good plasticizers but are inert and actually lower the energy content of the propellant systems. On the other hand, compounds such as diethylene glycoldinitrate, 1,1,1-trimethylol ethane trinitrate, nitroisobutyl trinitrate and nitroglycerine contribute energy but have undesirable characteristics associated with nitrate esters; toxicity (headache potential), volatility, low thermal stability and shock sensitivity. The plasticizers studied in the present research include 1,5 diazido-3-nitraza pentane (DANPE), ethylene glycol bis azido acetate (EGBAA) and 1,3 diazido -2-propanol (DAPOL) are azido esters and may pose some toxic impact on environment. Secondly, nitramines (alkyl NENAs) may also be associated with toxicity effects. Literature survey hardly
reveals any work carried out on toxicity aspect of these plasticizers. Hence, a systematic study may be taken up in future on the toxicity aspects and associated hazard potential of these plasticizers.

4.4.2 Exudation of plasticizer

It is also known that some plasticizers have a tendency to oxidize or to migrate over time towards the surface of the propellant and sometimes even to sublimate. The plasticizer migration causes irregularities in combustion. Due to this, chemical changes occur in the propellant compositions during storage which in turn affect the propellant integrity. Alkyl NENAs or nitramines have a tendency to migrate over time towards the surface of the propellant. In view of this, detailed studies may be carried out with these plasticizers at various temperatures and use of stabilizers or additives which can prevent this exudation.

4.4.3 Dynamic Firings of gun propellant compositions

The propellant compositions containing the energetic plasticizers under present study were evaluated in closed vessel firings in order to study the ballistic parameters. The ballistic parameters data has given encouraging and promising results in terms of enhanced performance. However, actual gun firings using the propellant formulations studied under the present research work may be conducted to confirm the experimental results and thus exhaustive ballistic data can be generated.
4.4.4 Development of less erosive propellants

It is commonly known that hotter burning gun propellant is more erosive. However, it is not always true. A number of cases have been reported where erosion does not increase with flame temperature and chemical attack of bore of propellant gas species has been the primary determinant of erosivity. Most common LOVA propellant formulations are more erosive than equivalent conventional propellants. Many LOVA propellants contain RDX. Several investigators have found that RDX is highly chemically erosive.20

New experimental low erosivity LOVA propellants have been produced by reducing RDX content and introducing nitrogen rich energetic binder or filler compounds. The resulting combustion gases rich in nitrogen act to re-nitride bore surface during firing and inhibit erosive surface reactions. The result is increased bore hardness, increased resistance to melting and reduced chemical erosion. The lowered hydrogen concentration in the combustion gases of some propellant formulations in the present research work reduce hydrogen assisted cracking of bore surface. The propellants under study are nitrogen rich and have impetus and flame temperature lower than RDX. Hence a compromise between performance, sensitiveness and erosivity can be reached. The order for erosion is given below-

\[ \text{CO}_2 > \text{CO} > \text{H}_2\text{O} > \text{H}_2 > \text{O}_2 > \text{N}_2 \]
4.5 Other challenges for research in the field of gun propellants

4.5.1 Development of gun propellants with minimum flame

In solid propellants, a considerable amount of flame is often produced in the exhaust gases during their operational phase. Excessive amount of flame is extremely undesirable in the exhaust gases since this provides data which pinpoints the sites from which the guns, missiles or rockets are fired. The energetic plasticizers studied in the present research work have azido and nitro groups which give more amount of nitrogen in their combustion products. Hence these can be used to develop propellants which can produce minimum amount of flame. The research carried out by Witucki and Flanagan\textsuperscript{21} also showed that the use of energetic plasticizers such as Bis (2-azidoethoxyethyl) nitramine and 1,12-diazido-3,10-dioxa-5,8-dinitrazadodecane (1.5 - 4.0 parts) to about 1.0 parts of resinous binder such as HMX can provide a propellant system with minimum amount of flame in their exhaust gases.

4.5.2 Development of smokeless propellants

It can be noted that the plasticizers studied in present research work have multiplicity of azido and nitro group and such esters are highly effective as energetic plasticizers which particularly function to increase burn rate of minimum smoke solid propellants as they are rich in nitrogen content. Thus these plasticizers can be used to develop propellants with minimum amount of smoke in their exhaust gases. Thus a significant increase in energy coupled with minimum production of smoke can be achieved.
This is also in concurrence with research carried out by Frankel and Witucki on use of Azidonitro carbamates in propellant compositions to obtain smokeless propellants. Frankel and Witucki\textsuperscript{22} in their patent have comprised a propellant system in which 1,3-diazido-2-propyl-N-nitro-N-trinitropropyl carbamate (DANTC) was used in place of triacetin in 1.5-4.0 parts to about 1.0 parts of binder to give an impulse of 242 sec as compared to 211 sec. Thus this propellant exhibited significant increase in energy coupled with minimum amount of smoke.

4.5.3 Use of mixed plasticizer system for low temperature coefficient gun propellants

From the present research study it is seen that Me-NENA based propellant formulations maintain low temperature sensitivity at ambient and above ambient temperatures. Low temperature sensitivity is also evident in case of ethyl NENA and Me-NENA + Et-NENA mixture based formulations at higher temperatures. In the similar way, in order to develop low temperature sensitive gun propellants, a new system of mixed plasticizer which includes dinitro diaza alkanes (DNDA) has emerged for use in barrel type weapons. Dinitro diaza alkanes (DNDA -57) is a mixture of 2,4-dinitro-2,4-diaza pentane (DNDA-5), 2,4-dinitro-2,4-diazahexane (DNDA-6) and 2,4-dinitro-2,4-diazahaheptane (DNDA-7). It is used in propellant systems whose temperature coefficient as well as the temperature sensitivity is lowered by using these plasticizers. A graph of performance of low temperature coefficient propellants (LTC) and conventional propellants is shown in Fig. 4.2.
DNDA -5, DNDA-6 & DNDA-7 have been used by researchers\textsuperscript{23,24} in the proportion of 45:44:11 having density of 1.35 g/cm\textsuperscript{3} and a glass transition temperature of -48\textdegree C. It is highly insensitive towards impact (h\textsubscript{50} 170 cm) and friction (36 kg). When used in gun propellant formulations, the adiabatic flame temperature of these propellants is more than 500 K below the conventionally used JA2 propellant at the same or higher level of specific energy force. Furthermore, these propellants proved to be insensitive to shaped charge attack and to fast cook-off. When tested in 75 mm scale model gun, the propellant provided an increase in muzzle velocity compared to JA2 propellant. High specific energy at comparatively low adiabatic flame temperature and low molecular weights of reaction gases are the special features of these propellants which can be used for new generation of gun propellants. Such propellants can utilize maximum potential power of the system over a wide range of temperature (-50 to +70\textdegree C). Some of the properties of dinitro diaza alkanes are given in Table 4.3.
Table 4.3 : Some properties of Dinitro diaza alkanes

<table>
<thead>
<tr>
<th>Property</th>
<th>DNDA-5</th>
<th>DNDA-6</th>
<th>DNDA-7</th>
<th>DNDA-57</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight</td>
<td>164</td>
<td>178</td>
<td>192</td>
<td>Impact : 170cm</td>
</tr>
<tr>
<td>Oxygen balance,%</td>
<td>-58.5</td>
<td>-80.8</td>
<td>-99.9</td>
<td>Friction : 36 kgf</td>
</tr>
<tr>
<td>Density @ 25°C, g/cm³</td>
<td>1.34</td>
<td>1.34</td>
<td>1.34</td>
<td>T_g : -48°C</td>
</tr>
<tr>
<td>ΔH_f, kJ/mol</td>
<td>-51.6</td>
<td>-79.5</td>
<td>-135.1</td>
<td>Density: 1.35 g/cm³ @ 25°C</td>
</tr>
</tbody>
</table>

4.5.4 Disposal of waste propellant

A large number of energetic materials are subjected to disposal either due expiry of their useful life or rejection in the manufacturing process. The environmental regulations do not favour the disposal of hazardous materials by open burning / detonation in view of the health hazard involved in these operations. The alternatives to open burning and open detonation are Thermal processes (Incineration and Molten Salt Oxidation), Hydrothermal Oxidation, Wet Air Oxidation, Biodegradation, Chemical treatment processes etc.

The disposal of propellants containing the energetic plasticizers studied in the present work has not been reported in the open literature. However, the disposal of the propellant formulations (single base & triple base) and combustible cartridge case (CCC) formulations have been reported by Pandey et al.\textsuperscript{25,26} using alkaline hydrolysis process with exhaustive evaluation.
of their hydrolysate as plant nutrients. The similar studies pertaining to the
disposal of the propellant compositions studied under the present work and
their evaluation as plant nutrient may be carried out. The impact of energetic
plasticizers (DANPE, DAPOL, EGBAA and Alkyl NENAs) may be ascertained
on hydrolysis process and the end product (hydrolysate) may be undertaken
as future research work.

4.6 Other applications of azido plasticizers

Inventors have found that combination of just a small quantity of
energetic plasticizer material into energetic crystalline material prior to
incorporation into the bulk plasticizer, binder and filler mixture of an explosive
or propellant composition has two unexpected and advantageous effects.\(^{27}\)
Firstly plasticizer addition leads to a reduction in friction sensitivity of energetic
crystalline material to equivalent or less than that of many commonly used
energetic fillers such as ammonium perchlorate. Secondly plasticizer addition
also results in reduced ferocity of response on stimulation. This novel
combination can more safely be used as starting material for the dry
mixing/blending/curing process. It can be more safely handled and
transported. The energetic plasticizer is preferably selected from the
compounds like butane triol trinitrate (BTTN), trimethylol ethane trinitrate
(TMETN), 1,5-diazido-3-nitrazapentane (DANPE), glycidyl azide polymer
(GAP), etc.

DANPE forms energetic azido eutectic mixtures with 1,5-dinitrato-3-
nitrazapentane (DINA) having freezing point -25°C. A propellant composition
comprising of DANPE, DINA, oxidiser RDX or HMX and ammonium
perchlorate and a polymer such as glycidyl azido polymer (GAP) with a fuel such as aluminium has been reported to exhibit enhanced performance characteristics at low temperature. 50% DINA + 29% DANPE gives freezing point -25°C and mixture of 29% DINA and 71% DANPE gives freezing point -55°C. 28

Generally hydrazine and aqueous hydrazine solutions are used in liquid propellants over the past two decades. Although they have been extensively utilised for propellant applications, concerns about the toxicity and carcinogenic nature of hydrazine have resulted in their limited use in the system. Additionally, hydrazine systems are decomposed by passing the liquid over an expensive metallic catalyst which must be replaced periodically. Flanagan J.E. 29 studied a new propellant system consisting of an admixture of 1,1,1-azidodinitroethane (AZDNE) and diluent such as methanol or ethanol, or 1-azidonitrobutanol, 1,3-diazo-2-propanol (DAPOL), 1,5-diazo-3-nitrazapentane (DANPE), 1,1,1-azidonitrobutanol, 1,4-diazo-1,1-dinitrobutane which can be substituted for hydrazine system without a loss in overall performance of the system. The specific impulse obtained from system consisting of AZDNE (90%) and DAPOL (10%) is 315.3 sec and from AZDNE (90%) and DANPE (10%) gave 318.2 sec as compared to hydrazine system which gave specific impulse of 241.1sec.

DAPOL can be used to synthesize tetra azido polyesters by esterification of aliphatic and aromatic diacid chlorides. Mixture of tetra azido polyesters and nitrocellulose when used in gun propellants serves to increase the impetus without increasing flame temperature due to the fact that this
composition produces more gas per unit weight on decomposition than a typical double base composition of nitrocellulose and nitroglycerine.\textsuperscript{29}

### 4.7 Other applications of NENA plasticizers

One promising approach for developing less sensitive gun propellants has involved the use of high energy nitramines such as alkyl nitrate nitramines as substitutes for sensitive esters such as nitroglycerine in multi based propellants. Zeigler\textsuperscript{14} has reported a propellant composition containing nitrocellulose (16.1%), nitroguanidine (26.5%), RDX (47.9%), ethyl centralite (0.4%), methyl NENA (4.6%) and ethyl NENA (3.4%) with carbon black and potassium nitrate. This system was found to be suitable for nitrocellulose/nitroguanidine type double base propellants. The study revealed that the tendency of nitramines to crystallize out of the propellant matrix can be avoided which in turn improves the storage stability of the propellants.

During the testing of NENA compounds it was found that they exhibited an incompatibility with ammonium perchlorate which is an important oxidizing agent used in rocket motors. This could restrict the usefulness of these compounds as plasticizers for ammonium perchlorate containing compositions. This in turn could greatly restrict the ability to utilize these compounds as plasticizers when attempting to produce safer munitions. Mullay J.J. et al\textsuperscript{30} demonstrated stabilized munitions comprising of ammonium perchlorate (95-45%), which were plasticized by NENA compounds (5-20%) and stabilized by including Lewis base compounds (0.5-5%). The preferred stabilizers used include urea, acetamide and nitroguanidine. These munitions provided improved safety and/or energetic properties over current munitions.
formulations. Some of the applications of non-energetic and energetic plasticizers are summarized in Table 4.4.

Table 4.4: Applications of some non energetic and energetic plasticizers

<table>
<thead>
<tr>
<th>Plasticizer</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Non- energetic</strong></td>
<td></td>
</tr>
<tr>
<td>Triacetin</td>
<td>Functions as plasticizers and desensitizer for nitroglycerine used in double base and composite modified double base propellants</td>
</tr>
<tr>
<td>Diethyl phthalate (DEP)</td>
<td></td>
</tr>
<tr>
<td>Dioctyl adipate (DOA)</td>
<td>Brings down the viscosity of HTPB and consequently increase solid loading which improve performance of propellants and plastic bonded explosives</td>
</tr>
<tr>
<td>Tricresyl phosphate (TCP)</td>
<td></td>
</tr>
<tr>
<td>Triethyl phosphate</td>
<td></td>
</tr>
<tr>
<td>Acetyl triethyl citrate (ATEC)</td>
<td>Excellent plasticizer for nitrocellulose and cellulose acetate butyrate based propellants. Imparts desirable non-vulnerability properties and used in XM-39 LOVA gun propellants</td>
</tr>
<tr>
<td><strong>Energetic</strong></td>
<td></td>
</tr>
<tr>
<td>Bis(2,2-dinitropropyl)-acetal/formal (BDNPA/F)</td>
<td>Energetic plasticizers for explosive /propellant formulations</td>
</tr>
<tr>
<td>Glycidyl azide polymer (GAP)</td>
<td>Energetic plasticizer for explosive /propellant formulations</td>
</tr>
<tr>
<td>(M&lt;sub&gt;n&lt;/sub&gt; : 400-500)</td>
<td></td>
</tr>
<tr>
<td>1,2,4-Butane triol trinitrate (BTTN)</td>
<td>Energetic plasticizer/co-plasticizer which minimizes loss in strain capability</td>
</tr>
<tr>
<td>Trimethylolethane trinitrate (TMETN)</td>
<td>Energetic plasticizer or co-plasticizer for high viscosity nitrocellulose and most preferred plasticizer for cyclodextrin nitrate polymers</td>
</tr>
<tr>
<td>Metriol trinitrate</td>
<td>Non-migrating plasticizer</td>
</tr>
<tr>
<td>Plasticizer</td>
<td>Applications</td>
</tr>
<tr>
<td>-------------------------------------------------</td>
<td>-----------------------------------------------------------------------------</td>
</tr>
<tr>
<td>6-Azidoheptyl-6-azidohexonate</td>
<td>Minimizes flame in the exhaust</td>
</tr>
<tr>
<td>Nitroglycerine</td>
<td></td>
</tr>
<tr>
<td>Ethylene glycol dinitrate</td>
<td>Energetic plasticizers for double base and composite modified double base propellants</td>
</tr>
<tr>
<td>Diethylene glycol dinitrate</td>
<td></td>
</tr>
<tr>
<td>Triethylene glycol dinitrate</td>
<td></td>
</tr>
<tr>
<td>Nitroisobutanetriol trinitrate</td>
<td>Nitrotrinitrate plasticizer for double base and composite double base propellants</td>
</tr>
<tr>
<td>2,2-Dinitro-1,3-propanediol diformate</td>
<td>Novel low sensitive, energetic plasticizer for composite and multi-base explosive and propellant formulations</td>
</tr>
<tr>
<td>1,5-Diazido-3-nitrazapentane</td>
<td>A potential energetic plasticizer for triple base gun propellants for improved ballistic performance</td>
</tr>
<tr>
<td>Ethylene glycol bis azido acetate</td>
<td>Can be used in LOVA propellants</td>
</tr>
<tr>
<td>1,3-Diazido propane -2-ol</td>
<td>Can be used in double base propellants</td>
</tr>
<tr>
<td>Alkyl NENAs</td>
<td>Can be used for low temperature sensitive propellants</td>
</tr>
</tbody>
</table>
REFERENCES


