ABSTRACT
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Gun is a device in which chemical energy of the propellant is converted into kinetic energy. Generally solid propellants are used in guns, which due to their regularity of burning produce high pressures in the gun barrel enabling the projectile to be propelled with the required velocity. The solid gun propellants mainly include single base, double base and triple base propellants. Conventional gun propellants have reached to the saturation point in terms of energy output. Plasticizer is one of the key ingredients of gun propellant formulations, which plays an important role in ease of processing and enhancement of mechanical properties.

The performance of gun propellant is measured in terms of force constant (FC), which primarily depends on the energy content of the propellant and mean molecular weight of the combustion products. The solid gun propellants with non-energetic plasticizer offer force constant upto 1070J/g, which do not satisfy the need of enhanced demand of modern guns needing force constant higher than 1200J/g. Liquid plasticizers like diethyl phthalate (DEP), dioctyl phthalate (DOP), dibutyl phthalate (DBP), triacetin, and solid plasticizers like camphor, dinitrotoluene, etc., are extensively used in conventional gun propellants. The use of energetic plasticizer is considered to be one of the practical ways to improve the energy level and performance of solid gun propellants. Energetic plasticizers, viz., 1,5-diazido-3-nitrazapentane (DANPE), ethylene glycol bis azido acetate (EGBAA), 1,3-diazido-2-propanol (DAPOL), N-n-butyl -N-(2-nitroxy ethyl)-nitramine (Bu-NENA) and other alkyl NENAs have taken over the twin role of increasing the
energy as well as plasticization to impart better mechanical properties. However, very little technical information is available in open literature on evaluation of these plasticizers in gun propellant formulations. Hence, keeping in view the present need of research, these plasticizers were selected for the present study. A systematic and exhaustive research work was undertaken to evaluate the above selected plasticizers in gun propellant formulations to study their effect on ballistic parameters and the findings are reported in the present thesis covering their ballistic performance, mechanical properties, sensitivity and stability.

Literature survey shows that a number of energetic plasticizers are being synthesized in global research programmes for their use in futuristic solid gun propellant formulations. Energetic groups like nitro, nitroso, fluoro, fluoronitro, azido and azido esters have enough potential to modify the energetics of plasticizer and also the mechanical properties of propellant formulations. Azido esters have been reported to possess better thermal and chemical stability, excellent mechanical properties, high energy content and good compatibility with binders. Azido esters, which are high nitrogen compounds, are useful ingredients for gun propellant because their combustion products contain more nitrogen. They are extremely stable and show little tendency to react even at high temperatures that exist in the gun barrel. The azido group contributes a positive heat of about 85 kCal / azido group, which is substantially high and capable to add energy to the propellant system. They also reduce the amount of flame in the exhaust gases.
Low temperature sensitivity of gun propellant is one aspect on which, very little work has been carried out worldwide. Nitratoethyl nitramines, known as NENA compounds, have recently been discovered to be potentially very useful ingredients in gun propellants due to increasing demand of less sensitive propellant compositions. In the recent past, special interest has been shown to N-n-butyl-N-(2-nitroxy ethyl) nitramine (Bu-NENA). Bu-NENA has been found to have the potential of substituting nitroglycerine in propellant and explosive compositions. It has also improved thermochemical properties and in addition it is found to be a good plasticizer for nitrocellulose (NC).

In the present study, energetic plasticizers namely 1,5-diazido-3-nitrazapentane (DANPE), ethylene glycol bis azido acetate (EGBAA), 1,3-diazido-2-propanol (DAPOL), N-n-butyl-n-(2-nitroxy ethyl)-nitramine (Bu-NENA) and a few selected other alkyl NENA compounds have been extensively evaluated in gun propellant formulations as a plasticizer. The findings with respect to their ballistic performance coupled with thermal stability, mechanical properties and sensitivity data have been generated, exhaustively.

The selected plasticizers were synthesized in the laboratory by methods reported in the literature and characterized as per standard procedures/methods. They were incorporated in the gun propellant formulations by using standard solvent method of processing. The dough formed in the sigma blade mixer was extruded in a hydraulic press in heptatubular configuration. One blank batch (without energetic plasticizer)
was also processed. The grains were dried to the desired moisture level and evaluated for ballistic properties, thermal stability, mechanical properties and sensitivity data. The ballistic evaluation was carried out in a closed vessel of 700cm³ at a loading density of 0.2/0.15g/cm³. Theoretical calculations were carried out using in-house ‘THERM’ program.

DANPE was evaluated in double base composition. The results obtained from closed vessel firings for the propellant compositions studied under the present work show that with the replacement of DEP with DANPE (7% by weight) increases the force constant by ~54 units. This is due to the higher positive heat of formation of DANPE (+554 kJ/mol) and low molecular weight of the combustion products of DANPE based propellant formulations. The oxygen balance of DANPE (-79%) is higher than that of DEP (-194%). This increases the calorimetric value of the propellant composition by ~ 5%. This in turn increases the flame temperature (~ 5.23%) of DANPE based composition. The burn rate coefficient ($\beta_1$) increased from 0.136 to 0.189 cm/ s/MPa. The pressure index ($\alpha$) slightly increased from 0.80 to 0.81. When nitroglycerine (NG) was replaced by DANPE, (5% by weight) the force constant slightly decreased by 5 J/g. The burning rate coefficient also slightly increased from 0.178 to 0.189 cm/s/MPa. Similarly when nitrocellulose was replaced by DANPE, calorimetric value decreased by 71 units and flame temperature decreased by 173 K. The force constant values determined from closed vessel testing were found to be close to the theoretical values and the burning rate coefficient and pressure index were found to be in acceptable limits of the gun propellant and they were comparable to DEP based gun propellant formulations. The propellant compositions when tested for
sensitivity showed that DANPE based propellants are slightly more sensitive to impact. This is attributed to the higher oxygen balance of DANPE (-79%) than DEP (-194%). Secondly, the heat of formation of DANPE is +554 kJ/mol as against DEP (-768.48 kJ/mol). The chemical energy that is stored in the molecular structure of DANPE gets released as thermal energy under the influence of impact. DEP has negative heat of formation (-768.48 kJ/mol) and hence offers lower impact sensitivity. Secondly, the presence of azide linkage (C-N₃) in DANPE molecule makes it more sensitive as the bond is highly polarized to undergo breakage, when subjected to impact. The friction sensitivity results indicate that DANPE based propellant compositions exhibit higher sensitivity (19.2 kgf) than that of DEP based compositions (28.8 kgf). The factors like molecular symmetry, friction shear and thermal behaviour are responsible for the propellant sensitivity. The sensitivity figures also show that DANPE based compositions are safe for processing and applications. The decomposition temperature for DANPE based propellants is in the range of 200-206°C as against 175-180°C for DEP based formulations. The calorimetric values are found to be higher for DANPE based propellants than DEP based propellants. This is due to the higher oxygen balance of DANPE. The results of thermal stability show that DANPE based propellant formulations are thermally stable without evolution of brown fumes. The level of thermal stability of DANPE based formulations is comparable to that of DEP based propellant formulations. The tensile strength increases (120.2 kg/cm²) and % elongation decreases of DANPE based propellant compositions (13.3%) than that of DEP based compositions, (TS:112.4 kg/cm² and % E:16.8% ) when NC and NG percentage is unaltered. This can
be attributed to the probable hydrogen bonding taking place in between nitro (NO₂) group of DANPE and hydroxyl (OH) group of nitrocellulose, dipole-dipole interactions between DANPE and polymer matrix as well as due to Van der Waals forces acting between the molecules. This effect is prominently seen in composition with 7% DANPE. The composition in which nitroglycerine and nitrocellulose are replaced by DANPE, the tensile strength decreases due to lower NC:NG ratio and how increased percentage elongation due to higher plasticizer content.

The base composition containing non-energetic plasticizer triacetin (TA) exhibited a force constant of 1136 J/g. The replacement of triacetin by EGBAA in parts of 2 %, 4% and 6% showed an increase in force constant by maximum 56 J/g. The burning rate coefficient was also found to increase marginally (from 0.107 to 0.125 cm/s/MPa). This can be attributed to the high heat of formation (-167 kJ/mol) of EGBAA in comparison to heat of formation of triacetin (-1331kJ/mol). It is encouraging to notice that there is no rise in the pressure index (0.80). In addition, EGBAA was found to possess very good plasticization ability. This is shown by the considerable increase in compressive strength (CS) ranging from 363 to 420 kgf/cm² and increase in percentage compression from 13.0 to 14.0 %. The low glass transition temperature of EGBAA (-70.8°C) resulted in superior low temperature strain capability of the propellant formulations. The thermal stability results show that the propellant formulations incorporating EGBAA are thermally stable. The vulnerability characteristics results show superior value, i.e., friction insensitivity up to 36 kgf and impact sensitivity (h₅₀) of the order of 43-50 cm with an ignition temperature of 350°C.
Four propellant compositions were formulated using DAPOL as the energetic plasticizer by incremental replacement of diethyl phthalate (DEP) with DAPOL in the tune of 2, 4 and 6%. Theoretical calculations carried out using in-house ‘THERM’ program with DAPOL based propellant compositions showed significant increase in force constant. The ballistic evaluation carried out in closed vessel (700 cm$^3$) showed that diethyl phthalate when replaced by DAPOL, the force constant increased from 855 to 1021 J/g with decrease in pressure index values. The impact sensitivity results indicate that DAPOL based propellant compositions exhibit marginally higher sensitivity ($h_{50}: 30-33$ cm) than DEP based compositions ($h_{50}: 35$ cm). This is attributed to parameters like molecular symmetry, friction shear and thermal behaviour along with oxygen balance. The friction sensitivity is 36kgf. However, the sensitivity figures are within acceptable limits and show that DAPOL based compositions are safe for processing and applications. The thermal stability test results show that DAPOL based compositions is comparable to DEP based compositions and are thermally stable. Mechanical properties results showed 15.9% increase in compression strength and 11.5% increase in percentage compression of DAPOL based compositions than that of DEP based propellant (CS: 290 kg/cm$^2$ & % Compression: 48.5%).

Studies were conducted with nitroglycerine as plasticizer in base composition and in other compositions, nitroglycerine was replaced by NENA compounds and mixtures of NENA compounds and the findings on ballistic performance and sensitivity data are reported in the thesis. Theoretically, the basic formulation, which does not contain alkyl NENAs shows maximum force constant (FC), maximum calorimetric value (cal-val) and highest specific heat
ratio (ϒ) (FC: 1037 J/g, cal-val: 881 cal/g and ϒ:1.2508). The flame temperature (To) is found to be highest in this composition (To: 2800 K). As we move from lower to higher alkyl NENAs (from Methyl NENA, Ethyl NENA to Butyl NENA), the force constant and flame temperature decreases. The factors contributing to the force constant can be viewed by the equation, 

\[ F = nRT_o \]

The effect of lowering of flame temperature exceedingly outweighs the effect of increase in the number of moles of combustion gases, lowering of average molecular weight of combustion gases and increase in gas volume in the formulations, responsible for increase in force constant. Nitroglycerine has a positive oxygen balance +3.52% as against -43.6 % for Methyl NENA, -67.0% for Ethyl NENA and -104.0% for Butyl NENA. Oxygen balance is the factor responsible for conversion of carbon monoxide to carbon dioxide during propellant combustion and related exothermicity of the reaction is manifested in the higher flame temperature, calorimetric value and finally force constant for basic composition based on nitroglycerine as compared to other compositions containing alkyl NENAs.

The results of ballistic parameters obtained from closed vessel firings are in agreement with the theoretical ones. The results of ballistic evaluation carried out by closed vessel showed that Me-NENA based compositions are low temperature sensitive. Et-NENA based compositions and mixture of Me-NENA + Et-NENA based compositions show nil temperature sensitivity in the same temperature range. No effect of additives was observed in other compositions. This behaviour can be attributed to the low melting point moieties like Me-NENA (38-40°C) and Et-NENA (5°C). Me-NENA is solid at room temperature. The presence of solid particles in the propellant matrix can
render the propellant mechanically inferior at sub zero temperature. However, at higher temperature after melting, Me-NENA can function as an efficient plasticizer bringing down the burning rate coefficient values. At low temperatures the propellant with inferior mechanical properties can become brittle, which would result in higher burning rate sufficient to offset the effect of lowering of temperature on the burning rate. As a result, Me-NENA based propellant formulations maintain low temperature sensitivity at ambient and above ambient temperatures. This also agrees with the findings of other researchers. Low temperature sensitivity is also evident in case of ethyl NENA and Me-NENA + Et-NENA mixture based formulations at higher temperatures. Tailoring of mechanical properties in these compositions is not sufficient to cause lower temperature sensitivity at low temperature. Me-NENA + Bu-NENA based formulations do not exhibit temperature sensitivity for the same reason.

Four propellant formulations were processed based on diethyl phthalate and Butyl NENA as non energetic and energetic plasticizer, respectively. The basic composition contained DEP and in other compositions, gradual replacement of DEP with Bu-NENA to the tune of 5, 10 and 16% was done. From the thermo-chemical data of DEP and Bu-NENA based propellant formulations, it is seen that with increase in the percentage of Bu-NENA, gradual improvement in the force constant from 885 to 1116 J/g with a steady increase in flame temperature from 2469 K to 3198 K was observed as compared to base composition (FC: 920J/g and T₀: 2418 K). This can be attributed to the higher oxygen balance of Bu-NENA (-104.0 %) than that of DEP (-194.4%). This also increases the calorimetric value (from
801 to 1027 Cal/g) and lowers the specific heat ratio of the compositions. Thus, a reverse trend was observed in the specific heat ratio values ($\gamma$: from 1.2616 to 1.2421). The mean molecular weight of gases also showed increasing trend from base composition to Bu-NENA based compositions (21.84 to 23.30 g/mole). The experimental ballistic evaluation results obtained from closed vessel are in close agreement with theoretical ones. The linear burning rate coefficient and pressure index values were found to be in the acceptable limits of gun propellant. In case of sensitivity to impact, the Bu-NENA based compositions are found to be comparatively sensitive than DEP based compositions as they exhibit figure of insensitivity from 39 to 42. In case of sensitivity to friction, they are comparable to DEP based compositions. Both the compositions (Bu-NENA and DEP based) exhibited relatively lower sensitivity to friction (36 kgf). Thus Bu-NENA based propellants are found to be safe for processing and application in gun propellant formulations as the friction sensitivity values are higher. The thermal stability determined by Abel Heat test and Methyl Violet test also showed that Bu-NENA based propellant formulations are thermally stable. Mechanical properties results showed 39.3% increase in compression strength and 26.6% increase in percentage compression of Bu-NENA based compositions than that of DEP based propellant (CS: 290 kg/cm² & % Compression: 48.5%). Thus, they are superior in mechanical properties than DEP based formulations.

The plasticizers selected in the present research work have superior properties as energetic plasticizers and they are potential candidates for futuristic advanced gun ammunition. The requirement of high force constant
of modern gun ammunition can be met with these azido and nitramine plasticizers which not only function as processing aids but also increase the specific energy of the system. The low temperature sensitivity aspect of the gun propellants can be met by use of alkyl NENAs. Their synthesis and characterization methods are simple and easy. Hence, they can be used in 120mm MBT tank gun for FSAPDS ammunition where velocity > 1700 m/s is needed.