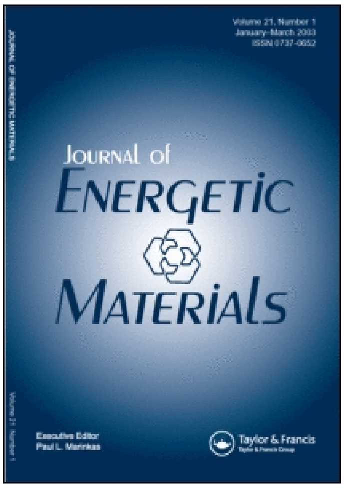

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Studies on Triple Base Gun Propellant Based on Two Energetic Azido Esters

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Triple base propellant is the workhorse propellant because it possesses several advantages like reduced flash, flame temperature, and erosion of the barrel as compared to double and single base propellant. Hence, efforts are going on worldwide to increase its performance by increasing its energy using energetic plasticizers and binders. In the present article, nonenergetic plasticizer dibutyl phthalate (DBP) is replaced by two energetic azido ester plasticizers, tris(azido acetoxy methyl) propane (TAAMP) and bis(azido acetoxy) bis(azido methyl) propane (BABAMP), in triple base composition and their different properties are studied.

Experimental closed vessel (CV) results (loading density 0.2 g/cm^3) clearly indicate that the triple base composition with 2% DBP has force constant 1018 J/g, which is increased to 1026 and 1030 J/g on replacement of DBP by 1 and 2% TAAMP, respectively. Mechanical properties of propellant compositions containing 1 and 2% TAAMP (compression strength 279 and 291 kg$_f$/cm^2, percentage compression 11.2 and 10.5, respectively) are also better than those of composition containing DBP (compression strength 275 kg$_f$/cm^2 and 10.3% compression). Similarly, 1 and 2% replacement of DBP by BABAMP shows further

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rise in energy (1032 J/g, 1038 J/g respectively) than that of compositions containing 1 and 2% TAAMP. These two compositions also exhibit better mechanical properties (compression strength 311.2 and 312.3 kg_f/cm^2*, % compression 11.0 and 10.5, respectively) than compositions containing 1 and 2% TAAMP. The differential thermal analysis (DTA) results brought out the fact that the compositions containing energetic plasticizers revealed maximum decomposition temperature in the range of 172–174°C which is close to DBP plasticized triple base gun propellants (174°C). The energetic plasticized propellant compositions of both (TAAMP and BABAMP) showed sensitivity data in the range of (*H_{50} *19 to 22 cm, F of I 25 to 29 and friction insensitivity 19.2 kg) acceptable limit for gun propellant.*

Keywords: BABAMP, DBP, mechanical properties, TAAMP, triple base propellant

Introduction

The utilization of propellant compositions for gun, rockets, and missiles has led to large research efforts in an attempt to improve their performance characteristics. The solid rocket and gun propellants are composed of oxidizers, binders, plasticizers, and sometimes a fuel. Generally, triple base propellants are used for tank and field gun ammunitions. Dibutyl phthalate or triacetin is generally used as inert plasticizers in combination with resinous binder material. The performance of triple base propellants with respect to energy level and mechanical properties can be enhanced by means of incorporating energetic plasticizers in place of inert plasticizers.

The fracture of propellant grains during the combustion is a major factor responsible for producing sudden high chamber pressure which is due to inferior mechanical properties [1]. It has been reported that the plasticizer in combination with binder helps in processing of propellant by achieving optimum viscosity of propellant dough and improving the mechanical properties of triple base propellant [2,3].

Energetic groups like nitro, nitroso, fluro, fluronitro, azido, and azidoesters have enough potential to modify the energetics and mechanical properties of a plasticizer. Hence, these plasticizers have an important role in rocket and gun propellants. During the present work, evaluation of two new potential energetic azido esters [TAAMP (I), BABAMP (II)] as energetic plasticizers in triple base composition has been studied.

Azido ester plasticizers have been reported to have better thermal and chemical stability, excellent mechanical properties, high energy content, and good compatibility with binders like glycidyl azide polymer (GAP), poly 3-nitratomethyl-3-methyl oxetane (poly NIMMO), etc., compared to nitrate esters plasticizers like trimethylol ethane tri nitrate (TMETN), butane-1,2,4-triol trinitrate (BTTN), etc. [4]. Azido esters, which are high nitrogen compounds, are useful ingredients for gun propellant because their combustion product contains more nitrogen. They are also extremely stable and show little tendency to react even at high temperatures that exist in gun barrels while offering no interference to missile guidance systems, which use infrared radiations that are transparent to the infrared region [4].

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 operational phase of gun, missile, and rocket propellants [5]. An excessive amount of flame is extremely undesirable in the exhaust gases since this provides data that pinpoint the sites from which the gun, missiles, or rockets are being fired. So, azido esters could be employed as energetic plasticizers in the formation of reduced flame temperature in gun propellant systems.

In this respect, two potential azido ester plasticizers (TAAMP and BABAMP), synthesized in HEMRL (Pune), were selected to replace the non energetic plasticizer (DBP) in triple base gun propellant [6]. Different compositions with 1 or 2% replacement of DBP were also processed with the aim of augmenting the ballistics and mechanical properties.

Experimental

Five triple base gun propellant formulations were prepared containing different nonenergetic/energetic plasticizers. The basic (control) composition 1 contains 30% NC (12.2% N) along with 25% NG, 40% picrite, 2% K_2SO_4, 1% N,N-diethyl diphenyl urea (carbamite), and 2% DBP. Further, compositions were prepared by replacing DBP by 1 and 2% of plasticizers TAAMP and BABAMP. The processing of these formulations was carried out in a horizontal sigma mixer using acetone:alcohol (80:20) as a solvent (20%). The batch size of compositions was 500 g.

Details of processing of propellant manufacture is described elsewhere by Pillai et al. [7]. The propellant dough was made in a sigma blade incorporator by solvent method. Propellant strands were extruded in a heptatubular rosette-shaped configuration using a suitable die/pin assembly (11.6/6.0/0.8/0.8) in a vertical hydraulic press of 40 T capacity. Extruded strands were predried (about 15 min) and then cut to grains of suitable length (21.5 ± 0.3 mm) using a rotary cutting machine. The propellant grains were subjected to various tests. The evaluation of different propellant formulations was carried out by closed vessel (CV) firing at 0.2 g/cm^3 loading density in a 700 cm^3 vessel. All samples were conditioned at 27°C for 24 h before firing. Force constant (F), pressure exponent (α), linear burning rate coefficient (β_1), etc., were also evaluated. The theoretical thermochemical predictions were obtained by using the Thermo program [8].

For mechanical properties, heptatubular rosette-shaped grains were prepared by maintaining length/diameter (L/D) ratio 2.04 ± 0.01 to get consistent results. The samples were subjected to mechanical properties testing to determine % compression (%C) and compression strength (CS) using a Hounsfield H25 KS materials testing machine (maximum capacity 25 KN). An average of five readings was taken for CS and %C. The compression rate of 10 mm/min was maintained.

The sensitivity to impact was determined by the Fallhammer method using a 2-kg drop weight. The results are reported in terms of height for 50% probability of explosion (H_{50}) of the sample. The friction sensitivity of the compositions was measured on a Julius Peter's apparatus until there was no explosion/ignition in five consecutive test samples at that weight.

A thermal characterization study was also carried out using a differential thermal analysis (DTA) technique, Electroceremics model no. 9503 differential thermal analyzer for all the compositions at the heating rate of 10°C/min.

Results and Discussion

Structural formulae of energetic plasticizers are given in Table 1. Thermal, physical, and sensitivity properties of two azido esters, synthesized in HEMRL earlier, are given in Table 2 [6]. The details given in Table 2 show that these esters may produce high energy output as their enthalpy of formation and oxygen balance values are quite high. On basis of this, these plasticizers are used in different gun propellant compositions

Table 1
Structural formulas, IUPAC, and common names of azido esters

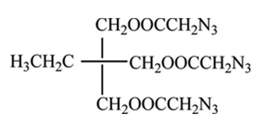
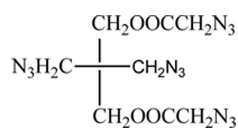
Properties	I	II
Structural formula		
IUPAC name	1,3-Bis (azido acetoxy)-2-azido acetoxy methyl-2-ethyl propane	1,3-Bis (azido acetoxy)-2,2-bis(azido methyl) propane
Common name	Tris (azido acetoxy methyl) propane	Bis (azido acetoxy) bis (azido methyl) propane
Abbreviation	TAAMP	BABAMP

Table 2
Thermal, physical and sensitivity properties of the azido esters

Properties	TAAMP	BABAMP
DSC Tmax (°C)	254.5	245.8
Oxygen balance (%)	−110.6	−90.8
Heat of formation (kJ/mol)	−157.5	605.6
Impact sensitivity H_{50} (cm)	>170	>170
Friction sensitivity (kg)	36	36

with varying percentages. Detailed compositions are given in Table 3. The theoretical thermochemical calculations (Table 4) show significant changes in energy levels of new plasticized compositions with TAAMP and BABAMP. The energy level was found to increase from 1033 to 1037 and 1040 J/g on replacement of nonenergetic plasticizer DBP with TAAMP (in compositions 2 and 3) by 1 and 2%, respectively. The increase in energy level is due to the presence of three energetic azido groups in TAAMP as one azido group contributes 85 kCal toward the positive heat of formation [4]. The energy level was further found to increase from 1033 to 1045 and 1057 J/g

Table 3
Compositions of propellant formulations

	Compositions				
Ingredients (% by wt.)	1	2	3	4	5
Nitrocellulose (12.2% N)	30	30	30	30	30
Nitroglycerine	25	25	25	25	25
Picrite	40	40	40	40	40
Carbamite	1	1	1	1	1
K_2SO_4	2	2	2	2	2
Graphite (parts)	0.05	0.05	0.05	0.05	0.05
DBP	2	1	–	1	–
TAAMP	–	1	2	–	–
BABAMP	–	–	–	1	2

Table 4
Theoretical thermo chemical data of different compositions.

Parameter	Compositions 1	2	3	4	5
Flame temp. (K)	2937	2995	3052	2978	3008
Force const. (J/g)	1033	1037	1040	1045	1057
Pmax (MPa)	254	257	259	254	255
Co volume	0.9299	0.9271	0.9245	0.9266	0.9235
Gamma	1.242	1.240	1.239	1.240	1.239
n value (mol/g)	0.0423	0.0420	0.0417	0.0419	0.0416
Specific energy (J/g)	4208	4275	4309	4300	4342

on replacement of nonenergetic plasticizer DBP with BABAMP (in compositions 4 and 5) by 1 and 2%, respectively. The reason for further increase of force constant is due to the presence of four azido groups in BABAMP as compared to the three azido groups in TAAMP.

A similar trend was also found in actual CV firing results (Table 5) at a loading density of 0.2 g/cm^3. Compositions containing BABAMP (compositions 4 and 5) show higher force constant values (1032 and 1038 J/g) compared to compositions

Table 5
CV firing results (loading density 0.2 g/cm^3)

Parameters	Compositions 1	2	3	4	5
Force const. (J/g)	1018	1026	1030	1032	1038
Pmax (MPa)	245	247	247	248	249
Rise time (ms)	12.3	11.8	11.1	11.4	10.2
dPmax (MPa/ms)	31.4	32.4	35.3	33.7	35.6
Pressure exp. (α)	0.69	0.72	0.69	0.71	0.68
β_1 (cm/s/MPa)	0.1265	0.1323	0.1580	0.1370	0.1461
Cal val (Cal/g)	937.6	955.2	966.2	982.2	999.4

containing TAAMP (1026 and 1030 J/g) in comparison to compositions containing DBP (1018 J/g). The higher force constant of BABAMP-based compositions compared to TAAMP-based compositions may be attributed due to the presence of one more azido group in BABAMP molecule.

Further, the flame temperatures (theoretical) of energetic plasticized compositions show a marginal rise (2995–3052 K) as compared to nonenergetic DBP plasticized composition (2937 K) but are still within the desirable limits for gun propellants.

The values of the rate of pressure rise with respect to time (dP_{max}) for compositions containing energetic plasticizers were found similar to that of DBP-based formulations (31.4–35.6 MPa/ms). The Pmax values of formulations containing energetic plasticizer were marginally increased compared to compositions containing conventional plasticizer. Composition 1 gave Pmax = 245 MPa compared to compositions 2 and 3, which gave Pmax = 247 MPa. Similarly, compositions 4 and 5 realized Pmax = 248 and 249 MPa, respectively. The compositions containing energetic plasticizer showed higher linear burning rate coefficient, β_1, in the range of 0.1323–0.1580 cm/s/MPa compared to the composition containing DBP, which gave $\beta_1 = 0.1265$ cm/s/MPa. This may be due to the exothermic cleavage of the azide bond, leading to high energy released at burning surface during combustion as reported by the researchers in this field for another energetic plasticizer GAP [9]. The specific heat ratio values (gamma) obtained were reduced from 1.242 for compositions containing DBP to 1.239–1.240 for compositions containing energetic plasticizers. The specific energy (F/γ-1) increased from 4208 to 4289–4342 J/g on replacement of nonenergetic plasticizer by both energetic plasticizers in triple base gun propellants. The results of Cal Val (Table 5) also support the fact that compositions containing energetic plasticizer give higher energy output.

The mechanical properties results are given in (Table 6). DBP-based control composition 1 exhibits compression strength 257 kg_f/cm^2 and 10.3% compression corresponding to 208 kg_f maximum force. Compositions 2 and 3 containing TAAMP gave higher compression strength (279 and 291 kg_f/cm^2),%

Table 6
Mechanical properties results

Compositions	Compression strength (kg_f/cm^2)	% Compression at maximum	Max. force (kg_f)
1	257	10.3	208.0
2	279	11.0	226.0
3	291	10.5	236.0
4	311	11.0	252.0
5	312	10.5	253.0

compression (11.2, 10.5) with higher maximum force (226 and 236 kg_f) as compared to composition 1. This may be as a result of better compatibility of Azido ester plasticizers with binders [10]. The increase in mechanical properties of compositions containing BABAMP (compositions 4 and 5) shows compression strength in the range of 311 and 312 kg_f/cm^2, while % compression values are 11.0, 10.5 at 252 and 253 kg_f maximum force, respectively. BABAMP gives better compression strength than TAAMP and 2% complete replacement of DBP by BABAMP (in composition 5) gives further high compression strength (312 kg_1/cm^2) compared to compositions 1–4. This may be due to the better plasticizing effect of azido ester plasticizers.

The impact and friction sensitivities data (Table 7) show that compositions containing TAAMP (compositions 2 and 3;

Table 7
Impact and friction sensitivity data

Compositions	Impact test H_{50} (cm)	Friction test F of I	Friction test Insensitive to friction (kg)
1	23	30	24.0
2	19	25	19.2
3	22	29	19.2
4	22	25	19.2
5	22	29	19.2

Table 8
Differential thermal analysis (DTA)

Compositions	Inception temperature (°C)	Peak temperature (°C)
1	158.0	174.4
2	161.0	173.0
3	166.0	174.0
4	160.6	172.0
5	162.0	173.0

H_{50} 19 and 22 cm, respectively; F of I 25 and 29, respectively; and friction insensitivity 19.2 kg for both) and compositions containing BABAMP (compositions 4 and 5; H_{50} 22 cm for both; F of I 25 and 29, respectively; friction insensitivity 19.2 kg for both) are comparable with DBP plasticized control composition (H_{50} 23 cm, F of I 30, and friction insensitivity 24 kg).

The differential thermal analysis (DTA) studies (Table 8) show peak decomposition temperature (174.4°C) for control composition 1. The formulations containing both energetic plasticizers exhibit more or less similar peak decomposition temperature (173–174°C) to those obtained for control composition.

Conclusion

Incorporation of energetic azido esters, 1,3-bis (azido acetoxy)-2-azido acetoxy methyl-2-ethyl propane (TAAMP) and 1,3-bis (azido acetoxy)-2,2 bis azido methyl propane (BABAMP), in triple base propellant formulations resulted in increase in energy level with marginal rise in flame temperature as well as better mechanical properties. Composition 5 containing 2% BABAMP has given better compression strength and higher force constant. Compared to composition 1, composition 5 shows comparable thermal stability and insensitivity toward impact and friction. The present study reveals that the composition containing energetic plasticizers TAAMP and BABAMP have better performance compared to DBP-containing compositions. However, BABAMP appears to be a more promising as an energetic plasticizer in triple base propellants compared to TAAMP.

References

[1] Horst, A. W. and L. Stiefel. 1988. Pressure wave phenomena in large-calibre gun. Gun propulsion technology. *Progress in Astronautics and Aeronautics*, 109.

[2] Agrawal, J. P. 1993. An overview on plasticizers for rocket propellants and explosives. *Industrial Product Finder*, 617–619.

[3] Simmons, R. L. 1996. Effect of plasticizer on performance of XM-39 LOVA. 27th Proceedings of Fraunhofer-Institute fur Chemische Technologie (ICT).

[4] Frankel Milton, B., E. R. Wilson, and J. E. Flanagan. 1983. Tetraazido polyesters and methods of preparation. U.S. Patent 4,406,718.

[5] Witucki, E. F. and J. E. Flanagan. 1983. Azido esters. U.S. Patent 4,419,286.

[6] Shekher, P. C., W. R. Moreshwar, N. J. Kamalesh, G. G. Mukund, and V. Sethuramasharma. 2006. Synthesis and characterization of two potential energetic azido esters. *Propellants, Explosives, Pyrotechnics*, 31: 477–481.

[7] Pillai, A. G. S., R. R. Sanghavi, V. H. Khire, P. D. Bombe, and J. S. Karir. 2000. Process technology development of LOVA gun propellant. *Indian Journal of Chemical Technology*, 7: 100–104.

[8] Karir, J. S. 2001. Calculation of thermo chemical constants of propellants by computer programme "Thermo." 28th International Pyrotecnics Seminar. 4–9 November 2001, Adelaide, South Australia.

[9] Sanghavi, R. R., P. J. Kamale, M. A. R. Shaikh, T. K. Chakraborthy, and S. Amarjit. 2006. Glycidyl azide polymer based enhanced energy LOVA gun propellants. *Defence Science Journal*, 56(3): 407–416.

[10] Detlef, D., D. Loffel, A. Messmer, and K. Schmid. 1999. Synthesis and characterization of azido plasticizer. *Propellants, Explosives, Pyrotechnics*, 24: 159–162.