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Studies on some Nitramine-based Low-vulnerability Ammunition Propellants with Cellulose Acetate as a Binder

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ABSTRACT

Several formulations of propellants based on RDX as an energetic solid ingredient and cellulose acetate (CA) as a binder were processed, using either dioctyl phthalate (DOP) or triacetin (TA) as plasticizer and a small amount of nitrocellulose (NC). The performance of these propellants was evaluated on the basis of closed vessel firing data. The vulnerability aspects of these formulations were compared with those of conventional picrite propellant, NQ, on the basis of their ignition temperatures and sensitivity to friction and impact. Triacetin was found to be better plasticizer than DOP for CA binder. Some RDX/CA/TA/NC-based propellants were found to have energy levels comparable with NQ propellant and had less sensitivity to heat, impact and friction, and therefore have the potential for being used as low-vulnerability ammunition propellants for gun applications.

1. INTRODUCTION

The conventional/normal nitrocellulose (NC)-nitro glycerine (NG) based gun propellants are highly prone to accidental initiation as a result of external stimuli, such as fire, shock wave and impact. The range of threats to gun ammunition depends upon the system in which it is placed. Such threats may be due to the shaped charge jets, kinetic energy penetrators or hot spall. In fact, NC-NG based propellant charges are found to be more sensitive than the high explosive warheads, especially when they are stored inside the battle tank or any other fighting vehicle. Due to the sensitive nature of the conventional gun propellants, there is always a risk of accidental loss of not only the stored ammunition but also of the crew and vehicle. To reduce this risk factor the development of low-vulnerability ammunition (LOVA) propellant is a possible alternative for conventional nitrate-ester-based propellants[1-4]. Generally, in the preparation of LOVA formulations emphasis has been laid on the employment of an inert binder/plasticizer system in which fine crystals of nitramine (RDX/HMX) are uniformly dispersed. Such formulations have higher ignition threshold and reduced burning rates at low pressures. Therefore, these formulations offer significant reduction in vulnerability to ignition and impact[5].

In recent years efforts have also been directed towards the use of energetic binders[6-8] in place of inert binders for LOVA formulations. Such formulations have superior ballistic properties than the currently available LOVA and nitrate-ester based formulations; at the same time they have low-vulnerability to heat and shock. However, energetic binders which have been used in such LOVA formulations are not yet easily available in the open market and if available, their cost is enormous. Additionally, these energetic binders need special plasticizing and curing conditions. Therefore, LOVA formulations based on such energetic binders are not economical at present. On the other hand, a binder like cellulose acetate (CA) is easily available and cheaper also.

In the present work, our aim was to prepare various LOVA formulations having performance comparable with conventional picrite gun propellant, NQ. Several RDX/CA-based LOVA compositions

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were processed for this purpose. The plasticizer used was either dioctyl phthalate (DOP) or triacetin (TA). The merits and demerits of the various LOVA formulations processed have also been discussed on the basis of their closed vessel (CV) firing test results, computed data, mechanical properties and vulnerability aspects.

2. EXPERIMENTAL DETAILS & DATA

The percentages by weight of each ingredient added in various propellant formulations processed for the present studies are given in Table 1.

Table 1. Composition of LOVA formulations (Values are in weight per cent)

Ingredient	Formulation No. 1	2	3	4	5	6	
CA	13	13	13	13	12**	12	12
NC (N_2 : 12.2 %)	4	4	4	4	4	4	-
RDX	77*	77	77*	77	78	78	80
DOP	6	6	-	-	-	-	-
TA	-	-	6	6	6	6	5
DNT	-	-	-	-	-	-	3

*RDX particle size 5μm and 20 μm with 9 : 1 ratio
**CA cross-linked with TDI
+ The values reported against each ingredient are the actual quantity weighed and not the analytical result.

Table 2. Theoretical thermodynamic data of LOVA propellants

	Formulation No							
		2	3	4	5	6	7	NQ*
Force constant (J/g)	1063	1063	1081	1081	1100	1100	1113	1063
Adiabatic flame temperature (K)	2640	2640	2812	2812	2877	2877	2897	2800
Co-volume (cc/g)	1.0355	1.0355	0.9992	0.9992	0.995	0.995	1.0013	0.975
Specific heat ratio (γ)	1.2783	1.2783	1.2631	1.2631	1.2621	1.2621	1.2645	1.250
Moles of product gas per gram (n) (mol/g)	0.04845	0.04845	0.4626	0.04626	0.04599	0.04599	0.04622	0.0440
P_{max} ** (MPa)		268	268	270	270	275	275	278

** At loading density of 0.2 g/cc
* Values for NQ are taken from Ref. 9.
(Composition of NQ:NC:20.8 %; NG:20.6 %; picrite, 55.0 % and carbamite: 3.6 %)

The processing of all LOVA formulations was carried out with existing setup used for processing conventional gun propellants. The binder CA and NC, along with the plasticizer (DOP or TA), was gelatinized with the help of suitable solvent in a Sigma blade incorporator (5·1 capacity). The desensitized fine RDX (unimodal or bimodal) was then added to the gelatinized binder and mixed into a homogenous dough. The dough was then extruded into heptatubular strands with the help of a vertical hydraulic press using a suitable die-pin assembly. Extruded strands were pre-dried and then made into grains of suitable length, using a rotary cutting machine. The propellant grains were dried at elevated temperature (40 °C) by blowing hot air, and then subjected to various tests.

The theoretically obtained thermodynamic data using computer software (THERM)[9] developed by the High Energy Materials Research Laboratory (HEMRL), Pune, for all LOVA formulations are presented in Table 2. The closed vessel firings of all the LOVA propellant samples, were carried out in a 700 cc CV at 0.2 g/cc density of loading. The closed vessel firing test results are presented in Table 3. The data for comparison of all the LOVA batches along with the data on picrite propellant NQ available from literature[9], are presented in Table 3.

Table 3. Results of closed vessel firing of LOVA propellants at 0.20 g/cc loading density

	Formulation No.							
		2	3	4	5	6		NQ
Force constant (J/g)	1027	1051	1050	1047	1120	1127	1134	1063
Linear burning rate co-efficient (β1) (cm/s/MPa)	0.214	0.10	0.0882	0.0601	0.0937	0.114	0.121	0.123
Pressure exponent (α)	1.255	0.988	0.844	0.740	0.853	0.990	0.989	0.75
Cal. val (cal/g)	795	812	881	887	899	941	903	880

The ignition temperature of propellant batches was determined by Julius Peters apparatus using 40 mg sample at a heating rate of 5 degree per minute. The impact sensitivity was determined on a sample of 20 mg and 2 kg falling weight by Bruceton Staircase method. Friction sensitivity was determined by Julius

Peters apparatus. For all these three tests, propellant sample passing 300 micron sieve and retained on 150 micron sieve was used. The data on these tests are given in Table 4.

Table 4. Comparison of vulnerability aspects for various LOVA propellants with those of NQ propellant

	Formulation No.							
		2	3	4	5	6	7	NQ
Impact sensitivity (ht for 50 % explosion (cm) (2 kg falling wt)	50	55	43	53	65	52	61	29
Friction sensitivity (insensitive up to) (kg)	36	36	36	36	32.4	36	36	16
Ignition temperature (^{0}C)	216	216	210	210	230	235	235	175

Compression strength, determined by INSTRON universal testing machine, Model-1185 using cylindrical propellant samples of *L/D* ratio 1, and density determined by Bianchi densimeter, are presented in Table 5.

3. RESULTS & DISCUSSION

3.1 Choice of Ingredients

The choice and quantities of the ingredients (i.e. oxidizer, binder and plasticizer) for the various LOVA formulations in the present study were based on the requirement of thermochemical properties.

Among the numerous energetic compounds reported to be suitable for LOVA propellants, the nitramines are available readily at a reasonable cost. RDX was therefore selected as an energetic ingredient in all the formulations processed for this work.

RDX content of 77-80 per cent in propellant gave the required force constant (> 1063 J/g) as seen from data in Tables 2 and 3. Fine particle size (5 μm) RDX substantially brings down the sensitivity, thereby improving typical LOVA characteristics[10]. Hence, 5 μm RDX was preferred in the present studies.

Desensitization of RDX is essential for its safe handling during processing, transportation and storage. This is generally done by coating fine crystals of RDX with inert material[11]. In the present work RDX was coated with DOP or TA and then used for further processing.

Cellulose acetate (CA) used for all the LOVA formulations processed in the present work was secondary acetate manufactured and supplied by Mysore Acetate & Chemicals Co. Ltd, Bangalore. The molecular weight of CA as determined by viscosity method was found to be of the order of 67,000. Acetyl value as combined acetic acid was in the range of 54 to 55.5.

The two plasticizers tried with CA were TA and DOP. Triacetin was selected to represent aliphatic inert plasticizers and DOP to represent aromatic inert type. Both are readily available from the trade.

It is known[12] that addition of small amount of NC enhances overall energy of propellant, increases burning rate, improves mechanical properties and processability. It serves as an energetic binder too. It was observed that addition of NC up to 4 per cent had no drastic effects on ignition temperature as well

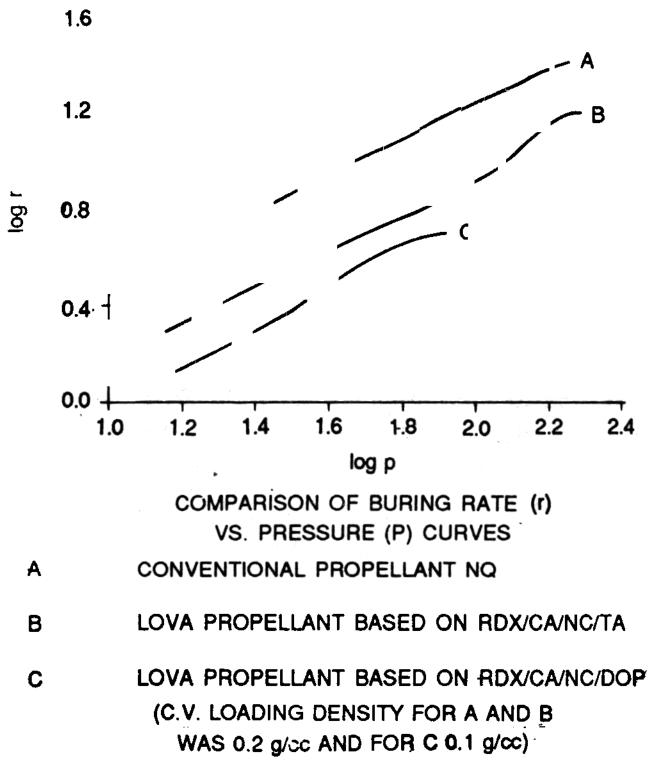

Figure 1. Comparison of buring rate (r) vs pressure (P) curves. (A, Coventional propellant NQ; B, LOVA propellant based on RDX/CA/NC/TA; and C, LOVA propellant based on RDX/CA/NC/DOP. CV loading density for A and B was 0.2 g/cc and for C 0.1 g/cc.)

as impact and friction sensitivity. However, the removal of NC results in decrease in compression strength of the propellant.

3.2 Burning Characteristics of RDX/CA Formulations

LOVA propellants in general have high pressure exponents (α) and lower linear burning rate coefficients (β_1) than the conventional nitrate-ester based propellants[13,14]. The α values for LOVA propellants in the present work were in the range 0.74-1.25 and β_1 values in the range of 0.0601-0.214 cm/s/MPa (Table 3). In general, LOVA propellants based on both RDX/CA/DOP/NC and RDX/CA/TA/NC systems have low burning rates compared with those for conventional NQ propellant (Fig. 1).

3.3 Force Constant & Thermochemical Data

The observed force constant (F) for LOVA propellants is in the range 1027-1134 J/g as against 1063 J/g for propellant NQ (Table 3). The theoretically calculated values are in the range 1063-1113 J/g (Table 2). The calorimetric values for LOVA propellants are in the range 795-941 cal/g as against 880 cal/g for propellant NQ. Thus, LOVA propellants based on RDX/CA/DOP/NC or RDX/CA/TA/NC systems have comparable or in some cases, better energy levels than those of the NQ propellant.

Adiabatic flame temperatures for the candidate LOVA propellants are in the range of 2640-2897 K as against 2800 K for the propellant NQ. For formulations with TA, the adiabatic flame temperature is higher as compared to the formulations with DOP which is expected due to higher calorimetric value of TA. This can be attributed to the higher oxygen content in TA than in DOP.

The higher values of co-volume for LOVA propellants as compared to conventional triple base NQ propellant indicate the formation of low molecular weight product gases during the combustion of these formulations. According to Heiney[15] this need not be considered as a drawback of the LOVA propellant.

3.4 Vulnerability of LOVA Propellants

The vulnerability aspects of LOVA formulations processed in the present work were compared with those of propellant NQ on the basis of data obtained on impact sensitivity, friction sensitivity and ignition temperature. The data given in Table 4 shows that ignition temperature for all the propellants is in the range 210-235 °C, which is significantly higher than that for propellant NQ (175 °C) and most of the conventional propellants based on NC, NG composition. Thus, these LOVA propellants are less sensitive to ignition than the NQ propellant.

Impact sensitivity values in terms of height for 50 per cent explosion (2 kg falling weight) are listed in Table 4. These values are in the range 43-65 cm as against 29 cm for the propellant NQ. The LOVA propellants have been found to be insensitive to friction up to 36 kg wt as against 16 kg wt for NQ propellant.

Thus, as far as sensitivity to heat, impact and friction are concerned the LOVA propellants reported here are found to be less vulnerable to these stimuli than the NQ propellant.

3.5 Mechanical Properties

In general, the propellants with CA/TA system had better compression strength and also higher densities as compared to the propellants with CA/DOP system; this indicated that TA has better plasticizing effect with CA as compared to DOP (Table 5). Thus, compression strength for formulation No. 2 with DOP as plasticizer is 309 kg/cm^2 as against 487 kg/cm^2 for formulation No. 4 with TA as plasticizer. All other ingredients remain the same. This trend was observed even in bimodal RDX formulations. Thus, the compression strength of the propellant containing bimodal RDX (90 per cent RDX of 5 µm and 10 per cent RDX of 20 µm) and DOP as plasticizer (formulation No. 1) was 232 kg/cm^2 as against 387 kg/cm^2 for the same propellant composition but containing TA as the plasticizer (formulation No. 3). The presence of similar moieties (viz. $-O-CO-CH_3$) in both CA and TA is expected to lead to better intermixing of these two as compared to the DOP and CA combination. In addition, TA being an aliphatic plasticizer is expected to interact better with CA which is also aliphatic in nature as compared to DOP which is aromatic in nature.

Cellulose acetate has free hydroxyl groups (0.5 per repeating unit in its molecular structure). If these hydroxyl groups are cross-linked by toluene diisocyanate (TDI), the mechanical strength of the propellant is expected to be improved. The cross-linking of CA up to 10 per cent of total available hydroxyl groups with TDI showed better compression strength compared to non-cross-linked propellant. Thus, compression strength for formulation No. 5 (with cross-linking of CA) was 589 kg/cm^2 as against 494 kg/cm^2 for formulation No. 6 (without cross-linking) (Table No. 5).

Table 5. Compression strength and densities of the LOVA propellants based on RDX/CA systems

	Formulation No.							
				4	5	6		
Compression strength (kg/cm^2)	232	309	387	487	589	494	261	282
Density at 27°C (g/cc)	1.35	.33	1.63	.62	.66	1.63	1.57	.1.67

Note : Compression strength determined using Instron 1185, UK. Cylindrical samples of *L/D* = 1 used for the test.

CONCLUSIONS

(a) Formulations based on RDX/CA/TA/NC compositions offer LOVA gun propellants whose ballistic performance, and energy content are comparable with the conventional gun propellant NQ. They can be easily processed with the existing setup being used for conventional double/triple base propellants. RDX/CA/DOP/NC based compositions resulted in poor mechanical properties and low densities.

(b) All LOVA propellants reported here, based on RDX/CA/TA/NC compositions, have significantly higher ignition temperature (>210 °C) and they are less vulnerable than conventional NQ propellant, as far as heat, impact and friction sensitivities are concerned.

(c) The use of bimodal RDX (5 μm and 20 μm) in LOVA formulations resulted in increased α value though such compositions did not show any adverse effects on ignition temperature and impact and friction sensitivities. The cross-linking of CA with TDI showed scope for improvement in mechanical properties of the propellant.

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