Defence Science Journal, Vol 48, No 2, April 1998, pp. 235-243

Study of Energetic Nitramine Extruded Double-Base Propellants

G.K. Gautam, S.M. Pundlik, A.D. Joshi, K.S. Mulage and S.N. Singh
High Energy Materials Research Laboratory, Pune- 411 021.

ABSTRACT

This paper gives the results of an experimental study on nitramine extruded double-base (EDB) formulations containing up to 25 per cent RDX in low and high calorimetric value double-base (DB) propellants. The effect of ballistic modifiers on the burn rate and pressure exponent (η) of promising formulations has also been investigated. The data generated on various parameters reveal that (i) nitramine EDB propellants exhibit relatively superior thermal stability, (ii) tensile strength and percentage elongation are drastically altered if RDX concentration exceeds 15 per cent, (iii) η is lowered significantly in the presence of ballistic modifiers, (iv) characteristic velocity (C*) values are higher to that for the control formulation, and (v) temperature sensitivity of burn rate is on the lower side (0.20 - 0.25 % / °C as against 0.40 % / °C) in the presence of ballistic modifiers.

1. INTRODUCTION

Incorporation of energetic materials like RDX and in the double-base (DB) matrix appreciably enhances the energy output of the propellants by virtue of their favourable heat of formation and low molecular weight combustion products. The other advantages of nitramine double-base (NDB) propellants are, viz., (i) better thermal and chemical stability, (ii) low smoke signature, and (iii) high degree of insensitivity to spall of fragments[1]. However, this class of propellants suffer from major drawbacks, such as low burn rates, high pressure index (η) values and poor ignitability[2]. Further, these propellants are reportedly to resist ballistic modification[3] and no modifiers are found to be effective in improving burn rate and η values[4,5]. Recent studies conducted on nitramine CMDB propellants in the presence of ballistic modifiers, such as lead stearate[6], basic lead salicylate[1], lead stannate[7], and lead citrate[8] have shown remarkable improvement in burn rate and η values. Keeping in view the above facts and also in the absence of adequate data on nitramine extruded double-base (EDB) propellants, it was considered of interest to formulate and process a set of nitramine EDB propellants incorporating RDX as an energetic material with and without ballistic modifiers and to study sensitivity, burning behaviour, chemical, thermal and mechanical properties and ballistic performance of a few promising formulations. This paper reports the results on low and high calorimetric value (cal val) nitramine EDB propellants.

2. EXPERIMENTAL DETAILS

Nitramine double-base (NDB) formulations primarily based on low cal val (860 cal/g) and high cal val (1070 cal/g) propellants containing RDX up to 25 per cent (particle size 35 μ) were processed by solventless extrusion technique[9] in the batch size

Received 09 September 1997, revised 07 October 1997

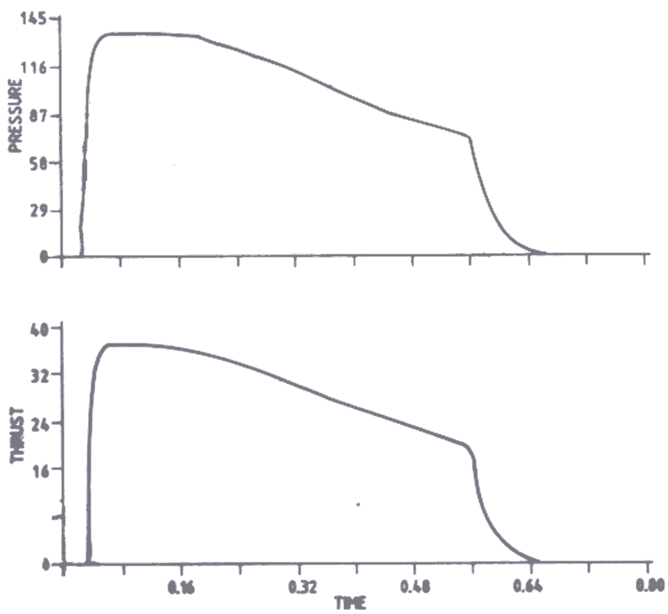


Figure 1. Pressure-time and thrust-time profile for low cal val RDX (5%)-based propellants

1-2 kg RDX and ballistic modifiers were added during the kneading stage. Details of formulations are given in Tables 1 and 2. Sensitivity to impact and friction was determined on propellant powder (5 mg) by fall hammer method using 2 kg weight and Julius Peter apparatus, respectively, whereas sensitivity to spark was determined using indigenous spark sensitivity apparatus. The burn rates of the formulations were determined with a strand burner[10] using Crawford bomb in N_2 atmosphere in the pressure range 35-90 kg/cm^2.

The thermal characteristics, viz., initial decomposition temperature (*Ti*) and cal val, were measured using indigenous differential thermal analyser (DTA) in the presence of static air at heating rate of 10 °C/min taking 5 mg sample, and using Parr adiabatic bomb calorimeter taking 1 g sample in the presence of air, respectively. Chemical stability of the formulations was determined by carrying out B and J test at 120 °C using 5 g sample. Mechanical properties, viz. ultimate tensile strength (UTS) and per cent elongation, were determined on standard dumbell-shaped test specimen (55 x 10 x 4 mm^3) on universal material testing machine (Instron Model-1185). The values reported are the averages of five readings. Temperature sensitivity of burn rate, characteristic velocity (C*) and specific impulse (Isp) values were obtained by regressive mode static firing of propellant grains (length 50 mm x outer diameter 40 mm x inner diameter 20 mm) in ballistic evaluation motor (BEM) after conditioning at -20 °C, + 50 °C and ambient temperatures.

Table 1. Nitramine extruded double-base propellant formulations

Code No.	Ingredients (%)					
	NC	NG	DEP	Carbmite.	$CaCO_3$	RDX
LC-00	59.5	30.5	7.0			
LC-01	54.5	30.5	7.0			5.0
LC-02	49.5	30.5	7.0			10.0
LC-03	44.5	30.5	7.0			15.0
LC-04	39.5	30.5	7.0			20.0
LC-05	34.5	30.5	7.0			25.0
HC-00	58.0	37.0	-		3.0	-
HC-01	48.0	37.0	-		3.0	10.0
HC-02	43.0	37.0	-		3.0	15.0
HC-03	38.0	37.0	-		3.0	20.0

LC Low calorimetric values
HC High calorimetric values

Table 2. Nitramine extruded double-base propellant formulations with ballistic modifiers

Code No.		Ballistic modifiers (in parts)			
		B.*Pb*.Sal.	B.*Pb*.St	B.*Pb*.Phth.	B.*Cu*.Sal
LC-021	LC-02	2.0			
LC-022	LC-02		2.0		
LCB-023	LC-02			2.0	
LCB-024	LC-02				2.0
HC-011	HC-01	2.0			
HC-012	HC-01		2.0		
HC-013	HC-01			2.0	
HC-014	HC-01				2.0

B.*Pb*.Sal Basic lead salicylate
B.*Pb*.St Basic lead stearate
B.*Pb*.Phth Basic lead phthalate
B.*Cu*.Sal Basic cupric salicylate

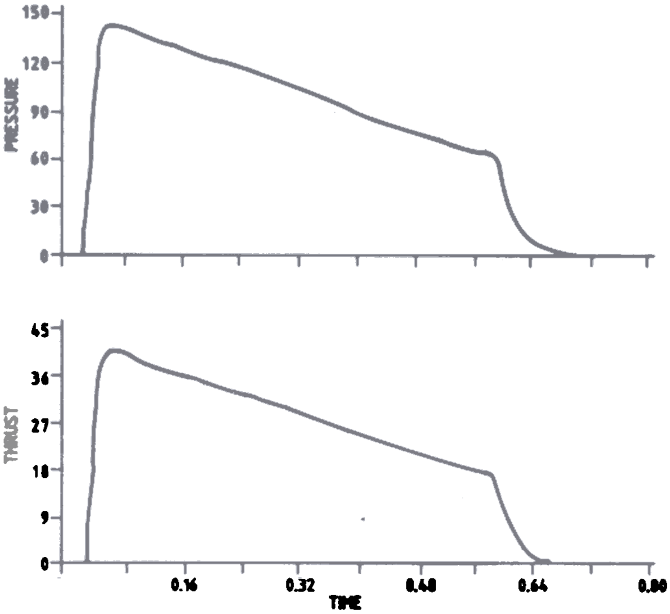


Figure 2. Pressure-time and thrust-time profile for low cal val RDX (10%)-based propellants

3. RESULTS & DISCUSSION

The experimental data generated for various parameters for nitramine EDB propellant formulations based on low and high cal val are discussed below:

3.1 Sensitivity

Data on sensitivity to impact and friction (Table 3) of nitramine EDB compositions reveal that the sensitivity increases with increase in RDX concentration for both classes of propellants. This is in agreement with observations reported in literature[11]. The enhancement in sensitivity is due to the sensitive nature of RDX[12]. Further, it was also observed that high cal val formulations were more sensitive to impact than the low cal val formulations. This may be attributed to the high NG content, which shifts the O_2 balance towards positive side, rendering the high cal val composition comparatively O_2-rich. However, both classes of formulations were insensitive to spark up to 5 J. It is thus inferred that these formulations possessed more or less similar order of sensitivity as observed for conventional EDB propellants.

3.2 Burn Rate

From the burn rate results (Table 4 and Fig. 1), it is obvious that the burn rate decreases with increase in RDX concentration in both classes of formulations and η was relatively high as compared to those for their respective control formulations. Reduction in burn rate could be explained on the basis of combustion phenomenon of RDX-based propellant, wherein RDX forms a molten layer on the burning surface and vaporises, causing substantial loss of heat energy, thereby reducing the burning surface temperature, which may ultimately result in lowering the burn rate[2,13].

3.3 Effect of Ballistic Modifiers

Data on burn rate after incorporation of ballistic modifiers in low and high cal val formulations containing RDX (10 per cent) are summarised in Table 5 and presented in Fig. 2. From the results, it is evident that each modifier plays a remarkable role in lowering the η value in a particular pressure range. Basic lead salicylate suppresses the η value in the entire pressure range for both types of propellants, whereas basic lead stearate effectively lowers η value in the same pressure range for low cal val formulation only. The η value is 0.04 in the pressure range 70-90 kg/cm^2 showing plateau effect. However, for high cal val formulation, the suppression in η value is marginal in the case of basic lead stearate. On the contrary, with basic lead phthalate η value has been drastically reduced in the pressure range 35-70 $kg/cm^2$for low cal val formulation showing tendency of near plateau effect (η=1 5), whereas for high cal val compositions, the reduction in η value is appreciably less (0.44 as against 0.74 for control formulation) in the same pressure range. However, basic cupric salicylate was found to be effective in lowering pressure index value in the lower pressure range (35 - 50 kg/cm^2) in both low and high cal val propellants (η = 0.27 and 0.44 respectively).

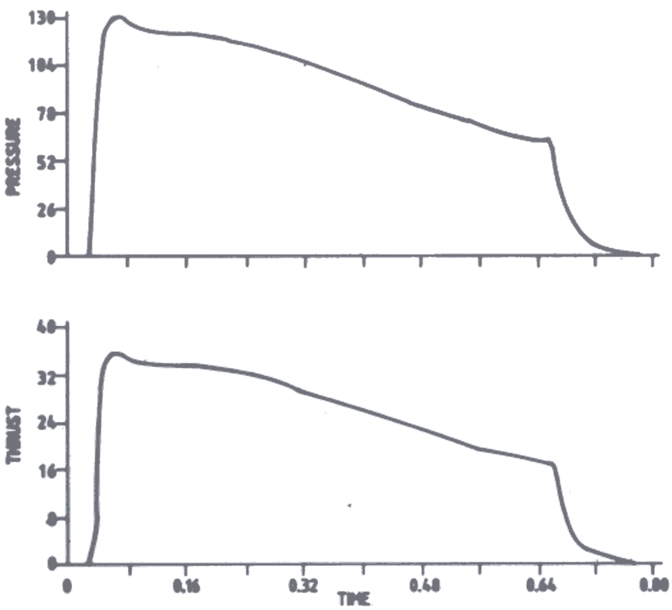


Figure 3. Pressure-time and thrust-time profile for low cal val RDX (15%)-based propellants.

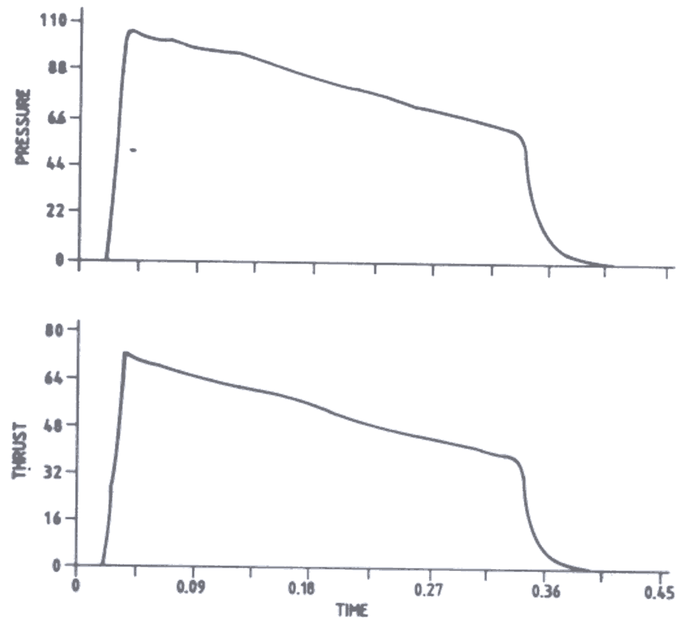


Figure 4. Pressure-time and thrust-time profile for high cal val RDX (10%)-based propellants.

Finally, it has been observed that basic lead stearate is a promising ballistic modifier for low cal val compositions, whereas basic lead salicylate and basic lead phthalate are very effective for both types of nitramine EDB formulations.

Table 3. Sensitivity characteristics of nitramine extruded double-base propellant formulations

Code No.	Friction sensitivity (kg)	Impact sensitivity (Ht. for 50 % explosion) (cm)	Spark (insensitive up to) (J)
LC-00	28.8	54.0	5
LC-01	28.8	50.5	5
LC-02	24.0	44.0	5
LC-03	24.0	45 .0	5
LC-04	21.6	43.0	5
LC-05	21.6	41.0	5
HC-00	28.8	36.5	5
HC-01	25.2	25.5	5
HC-02	24.0	27.0	5
HC-03	21.6	24.0	5

LC Low calorimetric values

HC High calorimetric values

3.4 Thermal & Chemical Characteristics

3.4.1 Thermal Decomposition

Data on thermal characteristics are presented in Table 6. The DTA results for both classes of formulations reveal that the initial decomposition temperature (*Ti*) increases with increase in RDX concentration. It is further observed that all

Table 4. Burn rate for nitramine extruded double-base propellant formulations

Code No.	Burn rate (mm/s) at pressure (kg/cm^2)				η value over pressure range (kg/cm^2)		
	35	50	70	90	35-50	50-70	70-90
LC-00	4.5	5.5	7.0	8.2	0.56	0.72	0.63
LC-01	4.2	5.3	6.9	8.1	0.65	0.72	0.68
LC-02	4.0	5.2	6.6	8.0	0.73	0.71	0.76
LC-03	3.8	5.0	6.4	7.4	0.76	0.73	0.70
LC-04	3.6	4.7	6.0	7.2	0.74	0.72	0.72
LC-05	3.3	4.3	5.5	6.6	0.74	0.73	0.72
HC-00	8.9	11.4	13.5	15.5	0.69	0.50	0.55
HC-01	8.6	11.2	13.2	15.3	0.74	0.60	0.59
HC-02	8.3	10.3	12.8	15.0	0.60	0.64	0.63
HC-03	8.0	9.8	12.6	14.6	0.57	0.75	0.64

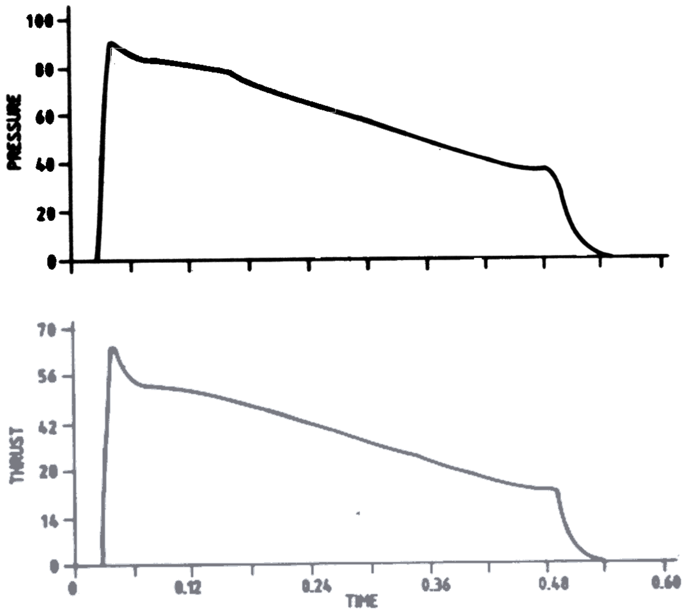


Figure 5. Pressure-time and thrust-time profile for high cal val RDX (15%)-based propellants.

formulations are superior in thermal stability as compared to their respective control formulations. This may be attributed to greater consumption of heat energy in the activation of RDX, resulting in enhancement of *Ti*.

Table 5. Effect of ballistic modifiers on the burn rate of nitramine extruded double-base propellant formulations

Code No.	Burn rate (mm/s) at pressure (kg/cm^2)				η value over pressure range (kg/cm^2)		
	35	50	70	90	35-50	50-70	70-90
LC-02	4.0	5.2	6.6	8.0	0.73	0.71	0.76
LC-021	6.7	8.0	9.1	10.0	0.50	0.38	0.28
LC-022	6.4	7.3	7.6	7.8	0.37	0.12	0.04
LC-023	7.2	7.6	8.2	9.3	0.15	0.15	0.51
LC-024	4.9	5.4	6.5	7.8	0.27	0.55	0.72
LC-01	8.6	11.2	13.2	15.3	0.74	0.60	0.59
HC-011	10.1	12.2	14.8	16.2	0.53	0.34	0.36
HC-012	8.5	10.1	12.0	14.0	0.48	0.51	0.61
HC-013	9.3	11.0	12.6	14.8	0.44	0.40	0.64
HC-014	8.7	10.2	12.2	14.2	0.44	0.53	0.60

3.4.2 Calorific Values

Calorific values (Table 6) have been found to be in ascending order with increase in RDX concentration for both classes of propellants because of the energetic nature of RDX.

3.4.3 Chemical Stability

Data on chemical stability, as determined by B and J test (Table 6), show that both classes of formulations are chemically stable and thus RDX appears to be compatible with double base matrix.

3.5 Mechanical Properties

Data on UTS and percentage elongation (Table 7) clearly show that tensile strength decreases and per cent elongation increases with increase in RDX concentration for both formulations. However, tensile strength is drastically reduced beyond 15 per cent RDX concentration. This may be due to alteration of NC/NG, which is primarily responsible for the physical strength of the propellant.

3.6 Performance Evaluation

Data on ballistic performance of low and high cal val nitramine propellants are presented in Table 8.

3.6.1 Characteristic Velocity & Specific Impulse

From pressure-time and thrust-time profiles data (Table 8 and Figs 3-7), it is seen that C^* and Isp values of nitramine propellants are in ascending order with increase in RDX concentration from 5 to 15 per cent and higher than those for their respective control formulations. The superior performance may be attributed to the positive heat of formation (+14.9 K cal/mole) of RDX, which may be responsible for increasing the flame temperature. Further, the smooth nature of pressure-time profile indicates that RDX-based EDB propellants generally do not undergo unstable combustion.

3.6.2 Temperature Sensitivity of Burn Rate

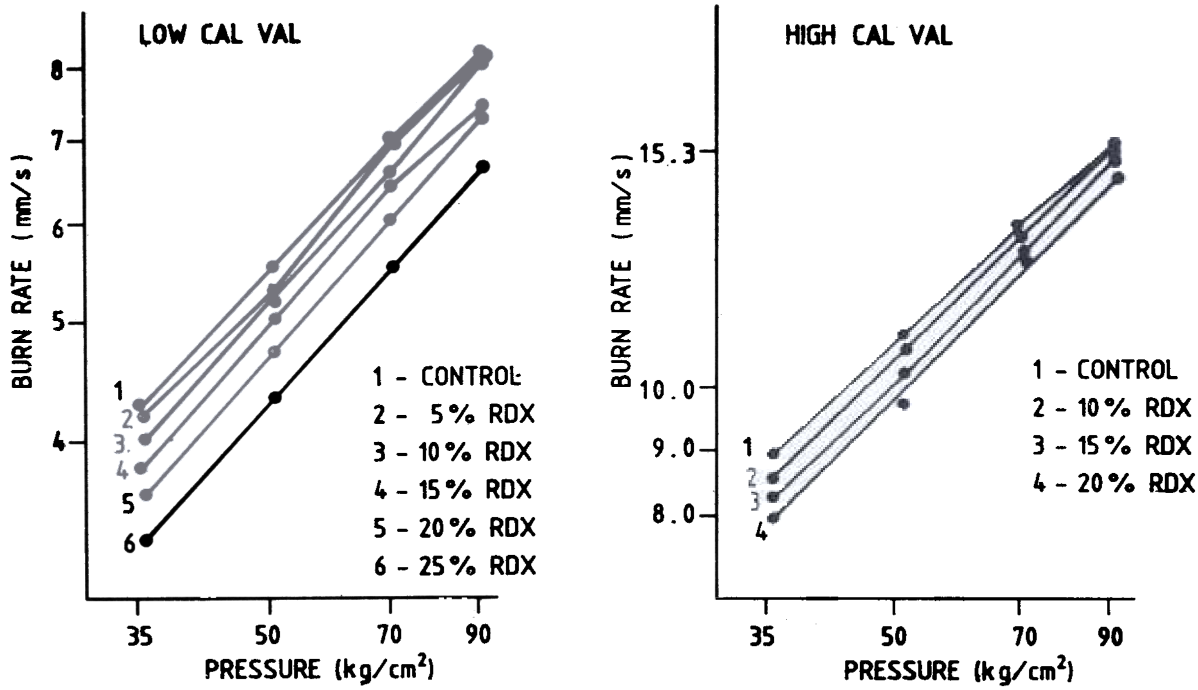


Figure 6. Effect of RDX concentration on burn rates of EDB propellants.

The data on temperature sensitivity of burn rate $(\pi r)p$ between -20 °C and +50 °C at 70 kg/cm^2 on promising nitramine compositions containing 10 per cent RDX* for low and high cal val indicate marginal lowering of $(\pi r)p$ value (0.36 % / °C for low cal val as against 0.40 % /°C for control and 0.38 % /°C for high cal val as against 0.42 % /°C for control formulation). However, addition of basic lead salicylate in the same composition has resulted in appreciable lowering of $(\pi r)p$ values which are of the order of 0.20 - 0.25 % / °C.

Table 6. Thermal and chemical stability of nitramine extruded double-base propellant formulation

Code No.	Thermal decomp. temperature *Ti* (°C)	*Tm* (°C)	Calorimetric value cal/g)	Chemical stability at 120 °C (ml/5g)s
LC-00	175	187	870	2.2
LC-01	184	191	889	2.2
LC-02	185	193	904	2.0
LC--03	189	195	923	2.0
LC-04	190	197	940	2.2
LC-05	192	200	970	1.9
HC--00	170	183	1060	1.9
HC-01	172	190	1116	1.8

4. CONCLUSIONS

- In the presence of ballistic modifier, pressure exponent values η of both classes of formulations are reduced significantly. Basic lead stearate shows plateau effect in the pressure range 50-90kg/cm^2, whereas basic lead phthalate produces near-plateau effect in the pressure range 35-50 kg/cm^2 for low cal val formulations only.
- C* values are enhanced by 2-3 per cent and Isp by 5-6 per cent as compared to those for control formulations.
- Nitramine EDB propellants are thermally stable.
- Mechanical properties are drastically altered beyond 15 per cent RDX concentration.

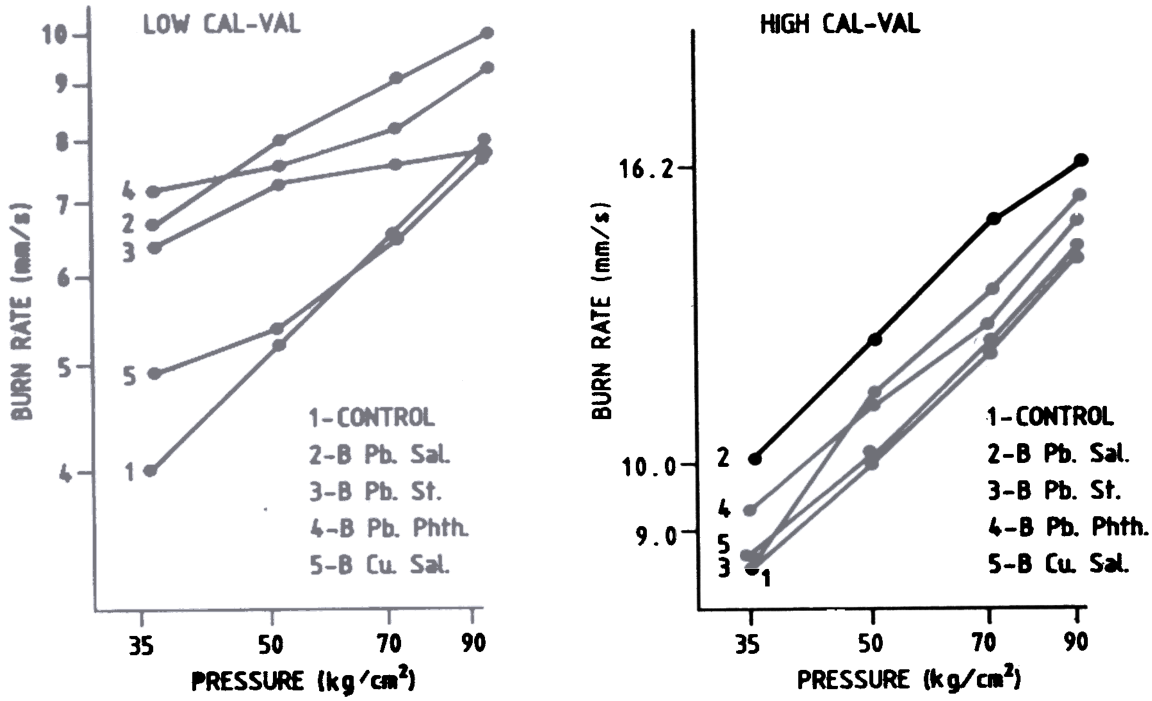


Figure .7 Effect of ballistic modifiers (2 pt.) on burn rates of RDX (10 %)-based propellants

ACKNOWLEDGEMENTS

The authors express their deep gratitude to Dr Haridwar Singh, Director, HEMRL, Pune, for valuable suggestions during the course of the present study. Their thanks are also due to Shri P.A. Phawade, Sci D and his colleagues for ballistic evaluation of propellant grains by static firing. The cooperation extended by *QARD*, Instrumentation and Pyro Group, in data generation is also acknowledged.

Table 7. Mechanical propertiers of nitramine extruded double-base propellant formulations

Code No.	Ultimate tensile strength	% Elongation
	110	
	108	
	100	
	80	
	56	
	48	
	128	
	120	
	90	
	65	

REFERENCES

1. Asthana, S.N.; Vaidya, M.V. & Shrotri, P.G. Studies on minimum signature nitramine-based high energy propellant. *J. Energ. Mat.*, 1992 , **10**, 01-16.

2. Cohen-Nir, E. Combustion characteristics of advanced nitramine-based propellants. International Symposium on Combustion (18), 1991. pp. 195-205.

Table 8. Data on C*, Isp and temperature sensitivity of nitramine extruded double-base propellant formulations

Code No.	C* values (m/s)		Isp (s)		(πr) p at (70 kg/cm ^{2})
	Theo.	Exptl	Theo.	Exptl.	
LC-00	1381	1330		207	0.40
LC-01	1395	1347		210	0.38
LC-02	1410	1364		219	0.36
LC-03	1426	1390		221	
LC-021	1400	1349		216	0.20
HC-00	1464	1446		231	0.42
HC-01	1490	1476		227	0.38
HC-01	1478	1462		224	0.24

C* Characteristic velocity

3. Cohen, N.S.; Lo, G.A. & Crowley, J.C. Model and chemistry of HMX combustion. *AIAA Journal*, 1985, **23** (2), 276-82.

4. Raman, K.V. & Singh, H. Ballistic modification of RDX-based CMDB propellants. *Prop. Expl. Pyrotech.*, 1988, **13** (5), 149-51.

5. Fifer, R.A. Chemistry of nitrate ester and nitramine propellants. *In* Fundamentals of solid propellant combustion, edited by K.K,Kuo & M.Summerfield, **90**, 1984. pp. 215 -18.

6. Kubota, N. Determination of plateau effect of catalysed double-base propellant. International Symposium on Combustion (17), 1978. pp. 1435-441.

7. Stack, S.J. Combustion catalysts for propellants. USA Patent 3, 954, 667. 1976.

8. Kubota, N & Sonobe, T. Burning rate catalysis of azide/nitramine propellants. International Symposium on Combustion, (23), 1990, pp. 1331-337.

9. Warren, F.A. Rocket propellants. Reinhold Publishing Corporation, New York, 1960.

10. Crawford, B.L.; Huggett,C.; Daniels, F. & Wilfong, E. *Analytical Chemistry*. 1947, **19**, 630.

11. Gautam, G.K.; Singh, H. & Rao, K.R.K. Sensitivity and ballistic properties of RDX & PETN-based double-base propellants. *Ind. J. Technol.*, 1987, **25**, 75-78.

12. Dhar, S.S.; Asthana, S.N.; Shrotri, P.G. & Singh, H. Sensitivity aspects of GAP. Proceedings of International Symposium on Compatibility of Plastics and other materials with Explosives, Propellants, Pyrotechnics and processing of Explosives, Propellants & Ingredients. American Defence Preparedness Association, San Diago, California, 1991, pp. 213 - 18.

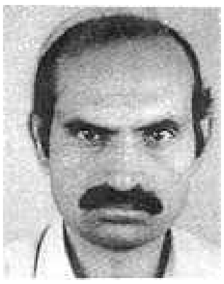
13. Kubota, N. Survey of rocket propellants and the combustion characteristics. *In* Fundamentals solid propellant combustion, edited by Kuo Summerfield, 1984, **90**. pp. 30-31.

Contributors

Mr GK Gautam obtained his MSc in Organic Chemistry from University of Poona, Pune. He l been working in the field of solid double-base rocket propellant for the past 20 years.

Mr SM Pundlik obtained his MSc in Organic Chemistry from University of Poona, Pune. He has been working in the field of extruded double-base rocket propellant for the past 25 years.

Mr AD Joshi obtained his MSc in Inorganic Chemistry from University of Poona. He has been working in the field of extruded double-base rocket propellant for the past 25 years.



Mr KS Mulge obtained his BSc in Chemistry from Shivaji University, Kolhapur. He has been working in the field of double-base rocket propellants for the past 14 years.

Dr SN Singh obtained his PhD in Chemistry from Banaras Hindu University in 1971. He has contributed significantly in the field of high explosive, pyrotechnics and solid rocket propellants. He is presently engaged in the development of advanced solid rocket propellants, particularly nitramine EDB propellants.