# Burning Rate Studies of Energetic Double Base Propellants

V.K. BHAT, HARJDWAR SJNGH, R.R. KHARE & K.R.K. RAO Explosives Research & Development Laboratory, Pune-411021

Received 10 February 1983, revised 16 September 1985

Abstract. A systematic study was carried out on the combustion characteristics of CMDB propellants containing ammonium nitrate, ammonium perchlorate, potassium nitrate, potassium perchlorate, RDX and PETN. While ammonium and potassium perchlorates increased burning rates, other additives maintained either the same burning rate or reduced burning rates marginally. Propellants containing these additives showed marginally higher peak temperatures, indicating interaction among the species of double base propellant decomposition and those of additives.

### 1. Introduction

Higher energy of composite modified double base (CMDB) propellants, as compared to double base and composite propellants, and their flexibility of producing wide burning rates make these propellants suitable for **tractical** missile applications. air to air applications and in dictates of supersonic warfare, CMDB propellants are preferred over the other solid propellants. A number of studies have been carried out in the past on the burning rate-pressure relationship of double base propellants containing high energy materials like β-HMX, PETN, NH<sub>4</sub>ClO<sub>4</sub> etc<sup>1-13</sup>. However, most of this **information** is in the form of patents. The detailed information on the effect of potential oxidisers/energetic materials on the burning of nitrocellulose (NC), nitroglycerine (NG) based double base propellants is not available in the open, literature. Hence, a systematic study was undertaken to study the effect of ammonium nitrate (AN), ammonium perchlorate (AP), potassium nitrate (KN), potassium perchlorate (KP), cyclo-tri-methylene trinitramine (RDX) and pentaerythritol tetranitrate (PETN) on the burning behaviour of double base propellants. This paper reports the results on the effect of these additives on the burning rates, thermal behaviour and combustion characteristics of double base propellants.

## 2. Experimental

Nitrocellulose (NC) of i2.2 percent  $N_2$  content, nitroglycerine (NG) in the form of dynamite (65 parts NG and 35 parts kiesulghur), PETN and RDX of require-d purity were received from Ordnance Factory. Diethyl phthalate (DEP), AP, AN, KN, KP of required purity were obtained through trade. **2-nitro** diphenylamine **(2-NDPA)** prepared on pilot plant scale in our laboratory and having purity of 98.5 percent was used.

Fibrous NC received from Ordnance Factory was first converted into spheroidal NC (dense NC). This conversion involved gel formation, emulsification, solvent removal, drying and sieving <sup>14</sup>. Propellant compositions were made by slurry casting technique <sup>15</sup>. Propellant grains of 100 mm diameter were cast in aluminium casting fixture under vacuum and cured at 60°C for four days. Propellant strands of 5 mm diameter and 150 mm length were cut from , the propellant charges. Burning rates at various pressures were determined by Crawford bomb method <sup>16</sup>. The accuracy of burning rate was of the order of  $\pm$  0.10 mm/sec. Thermal decomposition studies were carried out with the help of simultaneous thermal analyser NETZCH Instrument. Nitrogen was used as inert gas and gas flow rate of 10 litres/hour was maintained in all the experiments. Platinum-10 percent Rh-platinum thermocouples were used.

### 3. Results and Discussions

Results of theoretical calculations of oxygen balance, heat of formation, calorimetric value (cal. val), flame temperature ( $T_f$ ) and specific impulse ( $I_{sp}$ ) for various propellant' compositions are given in Table 1. Thermo-chemical data of Pike and JANNAF were used <sup>17</sup>18.

Table 1	Results of propellant parameters of energetic double base propellants.
(NC = 45%)	$_{5}$ , NG = 43.60%, DEP = 9.00%, Carbamite = 1.4%, 2-NDPA = 1.0%)

Additives (10 parts	Density	Oxygen balance	Heat of forma-	Cal. Val	Flame temp	Specific impulse secs
per 100 parts)	(g/cc)		tion (cal/g)	(°K)	(°K)	at 70 kg/cm* pressure
Control	1.57	<b>-</b> 38.2	-540	974	2504	229
A N	1.58	<b>-</b> 32.9	-590	1017	2542	231
AP	1.60	-31.6	<b>-</b> 546	1031	2693	235
KN	1.62	-31.1	<b>5</b> 97	1016	2570	224
KP	1.66	-30.5	-558	1037	2715	229
RDX	1.59	-36.7	-484	1009	2590	233
PETN	1.59	<b>35.7</b>	<b>=</b> 527	1019	2617	234

Inclusion of potential exidisers and **enorgetic** materials increased the density of propellants from 1.57 to 1.58-I .66 gm/cc level. The maximum increase in density was obtained with potassium perchlorate (1.66 gm/cc) and minimum with AN (I .58 gm/cc) based compositions. Their inclusion raised oxygen balance from about – 38 to – 30.5. The energy content of the modified propellant compositions was also raised, as cal. val figures were enhanced from 974 cal/gm to 1037 cal/gm with KP, followed by 1031 cal/gm with AP.

As expected, the maximum flame temperature  $T_f$  was obtained for KP based composition followed by AP based composition. However,  $I_{sp}$  of 235 seconds was obtained for AP based composition, followed by PETN ( $I_{sp}$ -234 sec) based composition. These results show that although flame temperature was maximum with KP (2715°K),  $I_{sp}$  figures were highest for AP and PETN based compositions, thereby indicating that the mean molecular weight of the combustion products was higher in the former case.

The influence of these additives (10 parts each) on the burning rates of propellants containing spheroidal NC-45 percent, NG-13.6 percent, DEP-9 percent Carbomite 1.4 percent and **2-NDPA-1** percent was studied, The results are given in Table 2.

Additives	Burning rates (mm/sec		
(10 parts per 100 parts)	Atmospheric pressure	70 <b>kg/cm²)</b>	
Control	1.4	6.6	
A N	1.0	4.5	
AP	1.6	7.8	
KN	0.9	6.5	
KP	1.4	7.8	
RDX	1.3	6.0	
PETN	1.7	7.0	

**Table 2.** Effect of oxidisers'energetic materials on the burning rate of double base propellants.

At atmospheric pressure, burning rate was marginally higher for AP and PETN based compositions, whereas in case of KP and RDX based compositions burning rates were more or less the same as those of control. In AN and RN based compositions, burning rates were lower than the control. This may be due to their endothermic decompositions/melting or phase transfermation near the surface temperature of double base propellant.

At 70 kg/cm' pressure, burning rates were enhanced with AP, KP and PETN, whereas burning rates were almost the same as those of control with RDX and KN.

Of all the compositions studied, only AN based composition gave lower burning rate than the control. A comparison of the results of flame temperature and burning rates suggest that there is no direct relationship between those two parameters. These results, therefore, suggest that increase of burning rate with increase of flame temperature, generally applicable to conventional double base propellants, is not applicable to energetic double base propellants. The results obtained indicate that the potential **oxidisers/high** energy materials studied do not seem to affect the course and **energetics** of the reactions in the propellant surface or subsurface zone.

During the steady combustion conditions double base propellants are known to burn in four zones namely, foam, fizz, dark and luminous flame **zones**<sup>19</sup>. Kubota et al<sup>20</sup> reported that' the burning rate of basic double base propellants increased considerably with AP. Gas phase observations with the help of high speed photography revealed that flame zone of AP containing double base propellant was more like the flame of AP based composite propellant rather than like double base propellant. The dark zone generally observed with double base propellant was eliminated by the addition of AP and luminous flame was closer to the burning surface. According to Kubota et al<sup>21</sup>, burning rate is controlled by the heat feed back from the diffusion flame between AP decomposition products and fizz zone products of double base propellants.

To find out the probable role of the energetic materials studied on the burning behaviour of propellant, the thermal decomposition of modified propellants was studied. The results are given in Table '3. Thermal decomposition studies of ingredient used were not undertaken seperately as these are well reported in the **literature**<sup>22</sup>? 3.

Table 3. Thermal decomposition temperatures of energetic double base propellants.

(i) Heating rate 10°C

(ii) Maximum temperature 500°C

Additives	DTA Exotherms				
(10 parts per 100 parts)	Inception (T <sub>i</sub> ) °C	Final decomposition $(T_f)$ $^{\circ}$ C	Peak temp ( <b>T</b> <sub>m</sub> ) °C		
Control	156	237	181		
AN	154	228	184		
AP	156	216	185		
KN	156	230	173		
KP	161	232	185		
RDX	159	232	188		
PETN	161	225	183		

The control propellant containing spheroidal NC, NG, DEP and stabilizers decomposed exothermally in the temperature range 156-237°C, with peak temperature

at 180°C, whereas propellants containing AN, AP and KN decomposed in the temperature region 154-228°C, 156-215°C and 156-230°C, with peak temperatures of 185°C and 173°C respectively. In case of KP, RDX and PETN based compositions, **exother**-mic decomposition commenced between 158 and 161°C. These results suggest that these additives do not affect the decomposition behaviour of double base propellants. However, there may be some interaction between oxidiser and double base propellants species during the course of combustion as revealed from the variation of peak temperatures.

The results of the present study, in general, reveal the burning rate characteristics of CMDB propellant containing potential oxidisers and energetic materials. However, since the thermal and ballistic properties of these materials, particularly RDX and PETN are not well understood, further systematic research work is necessary to understand the complex combustion phenomenon of energetic double base propellants.

### References

- Robert, S., NC propellant compositions containing Inorganic oxidizing agents, U.S. Pat. 3, 779, 826, (1973).
- 2. Hill, W.E., CMDB propellant with very high burning rate, U.S. Pat. 3, 811, 966, (1974).
- 3. Kiriame's. etal, Chem, Abstr., 81 (16), (1974), 93624,
- 4. Suzuki, H., etal., Chem. Abstr., 81 (16), (1974), 932625 t.
- 5. John, C.E., Handerson, L.D., "Incorporating ballistic modifiers in slurry cast double base containing compositions", U.S. *Put.* (1976), 4,000,025.
- 6. Kinamare, S., etal., Chem. Abstr., 81 (10) (1974), 518292 X.
- 7. Kaneke, J., etal., Chem. Abstr., 82 (26), (1975), 173243 C.
- 8. Shinohara's., etal., Chem, Abstr., 83 (4) (1975), 30482.
- 9. Kaneka, J; etal., Chem. Abstr., 83 (10), (1975), 8,2295 a.
- 10. Kloehn, W., Inst. Chem. Tech. Unters Chem, Abstr., 83 (16), (1975), 1344469 g.
- 11. Yokoyama A., etal., Chem. Abstr., 83 (18), (1975), 149778.
- Elrick, D.E., Modified double base propellants with disocyanate crosslinker, U.S. *Put.*, (1975), 3,894,894.
- 13. Tsugikado, etal.. Kogyo Kayaku, 39, (1977), 77-84.
- 14. Varghese, A.O. Manufacture of dense NC M.Sc. thesis, Poona University, 1978.
- Camp A.T., 'Advances in chemistry series 88', (American chemical society, Washington DO), 1969.
- 16. Crawford, B.L. Hugget C. etal., Analytical Chemistry, 19, (1947), 630.
- 17. Pike, Thermochemical data for propellant ingredients and their products of explosion, Armament Research Establishment Report No. 25/49,
- 18. 'JANNAF Thermochemical Tables, (CPIA, Publication), 1971.
- 19. Parr., R.G., Crawford, B.L., J. of Physical Colloidal Chemistry 54, (1950), 929.
- 20. Kubota, N., Chlemiller, H.J., Caveny, L.H., & Summerfield, M., Proceedings of 10th International Symposium on Space Technology and Science, Tokyo, 1973.
- Kubota, N., & Masomato, T., 16th Symposium on combustion (International), Combustion, Institute, 1977, pp 1201-1209.
- 22. Gordon, S & Campbell C., Analytical chemistry, 27 (1955).
- 23. Bohon, R.L., Analytical Chemistry, (1963), 1845.