

EFFECT OF HIGH ENERGY MATERIALS ON THE THERMAL STABILITY AND SHELF LIFE OF CMDB PROPELLANTS

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Summary

The results of thermal stability tests indicate higher stability of cyclotrimethylene-trinitramine (RDX), pentaerythritol-tetranitrate (PETN) and their combined formulations with composite modified double base (CMDB) propellants than ammonium perchlorate (AP) containing CMDB propellants. Gas kinetic studies also reveal a similar trend. Activation energies as computed from isothermal gravimetric analysis in the range of 60–80°C, are about 35 kcal/mol for RDX and PETN based compositions, whereas for AP-RDX and AP-PETN based formulations they are about 30 kcal/mol. Autoignition test results also give lower activation energies for AP based CMDB systems. A shelf life of 65–164 year has been obtained for RDX and PETN based CMDB propellants, while on the otherhand the shelf life for AP based formulations ranges from 13–19 year.

1. Introduction

Composite modified double base (CMDB) propellants find wide applications in modern military and space rocketry, in view of their superior performance [1,2]. These propellants basically contain an inorganic oxidizer, such as ammonium perchlorate (AP), or high energy materials dispersed in a double base propellant (DBP) matrix. High energy materials like nitramine or PETN are incorporated to achieve better performance (I_{sp} , which is the specific impulse) and lower smoke level [3,4].

A number of studies have been carried out on the formulation processing and thermal stability of CMDB propellants [5–9]. However, most of the information is patented. The information regarding the influence of high energy ingredients (oxidizers/high explosives) of CMDB propellants on formulation stability and shelf life is vital as regards their handling, processing, transportation and storage. We have reported earlier that the inclusion of ammonium

perchlorate (AP) along with RDX/PETN renders the system more sensitive to impact and friction. On the other side RDX and PETN based compositions are more sensitive to shocks than AP based CMDB propellants [10]. We have also reported that thermal stability of CMDB propellants containing resorcinol, as additional stabiliser, is well within acceptable limits, although autoignition test results showed their lower thermal stability and shelf life span as compared to DBP [11]. The work presented in this paper includes application of various stability tests used for double base propellants (DBP), namely the Abel heat test, the Methyl Violet test, the vacuum stability test and the Bergmann and Junk (B & J) test to assess stability aspects of CMDB propellants containing 30% AP, RDX, PETN and their combinations. Information on isothermal gravimetric analysis (IGA) and gas kinetics was also generated to understand the mechanism of ageing of these systems. Shelf life was estimated from autoignition test results.

2. Experimental

Propellants containing spheroidal nitrocellulose (SNC), NG nonexplosive plasticisers, diethyl and dibutyl phthalate (DEP and DBP) stabilisers, 2-nitrodiphenylamine (2-NDPA) and carbamate and oxidisers/high energy materials (AP, RDX, PETN) were prepared by slurry cast technique [12]. Compositional details are given in Table 1.

The Abel heat test (64.5°C), the Methyl Violet test (120°C), the vacuum stability test (90°C) and the B & J test (120°C), as described elsewhere in details, were applied [13]. The B & J test was modified for lower sample weight (1 g) and reduced time (3 h) in view of autocatalytic behaviour of CMDB propellants [5]. In the vacuum stability test only 2.5 g of sample was used instead of the standard 5 g used for DBP.

For gas kinetic studies an assembly similar to that for the vacuum stability

TABLE 1

Composition details

Composition No.	SNC ^a	CL ^b	AP	RDX	PETN
1	30	40	30	-	-
2	30	40	-	30	-
3	30	40	-	-	30
4	30	40	15	15	-
5	30	40	15	-	15
6	30	40	-	15	15

^aSNC composition: NC (12.2% N by weight) 88.9, NG 7.1, DBP 1.4, Carbamate 2.6.

^bCasting liquid (CL) composition: NG 80, DEP 18, 2-NDPA 2 wt.%.

test was used. In this experiment 2.5 g of sample was heated under vacuum at various temperatures (80, 90 and 100°C) and the volume of gas evolved at different time intervals was determined [14,15]. Isothermal gravimetric analysis was carried out by heating the samples at constant temperatures of 60 and 80°C in incubators and monitoring the changes in weight at different time intervals.

The autoignition test described by Rice et al. [10] was applied to assess shelf life. The propellant sample (200 mg) was heated at constant temperature ($\pm 0.1^\circ\text{C}$) and the time to autoignition (TAI) was recorded, using chromel–alumel thermocouples in conjunction with a pen recorder, in the range of 130–170°C.

The shelf life of the propellant compositions was computed by extrapolating the results to 30°C in view of the findings of Hartman and Musso [5], which bring out that the decomposition pattern of CMDB propellants does not change over the entire temperature range of 38–160°C and that high temperature measurements of various properties, like self heating and induction time, may be extrapolated to the temperature region of interest. A reliability test was run to assess the validity of the TAI test in the present study. It is established that the time to ignition can be determined in this test with a standard deviation of ± 10 seconds and the activation energy with a standard deviation of ± 0.02 kcal/mol, which corresponds to a standard deviation of ± 1.47 y in the shelf life estimate. In general shelf life can be assessed from the present experimental setup with an overall relative accuracy of 6%.

3. Results and discussion

Results of qualitative and quantitative tests are given in Table 2. The obtained Abel heat test values of 27 to 30 min for CMDB compositions containing AP, RDX, PETN and combinations thereof, were within the acceptable limit (> 15 min, which is taken as minimum in this test). The Methyl Violet test results of 85–105 min for colouration to occur were also well above the minimum requirement of 65 min and comparable to the results found with DBP (90 min). However, unlike RDX and PETN based CMDB propellants, AP, AP–RDX and AP–PETN based formulations exploded within 145–220 min at 120°C, which indicates that compositions containing AP exhibit lower thermal stability. ‘Puffing time’ results also showed a similar pattern as propellants containing RDX, PETN and their combinations, but did not ignite upto 300 min, whereas AP based formulations ignited within 165–235 min.

Results of the quantitative vacuum stability test corroborate these findings. The volume of gases that evolved from RDX and PETN based compositions was less (1.5–1.7 ml) than from DBP (2 ml). Ammonium perchlorate based compositions produced higher amounts of gases indicating that AP based formulations need additional stabiliser, whereas RDX and PETN based compo-

TABLE 2

Results of various stability tests for CMDB propellants containing AP, RDX and PETN

Compo- sition	High energy additive	Abel heat test @ 64.5°C (min)	Methyl Violet test @ 120°C (min)	Puffing time test @ 120°C (min)	Vacuum stability test @ 90°C (ml of decomposition gases)	B & J test @ 120°C (ml of NO ₂)
Control SNC 55 CL 45	—	15	I) Colour change 90 II) No explosion	300	2.0	0.2
1	AP	28	I) Colour change 105 II) Explosion 150	165	2.2	—
2	RDX	29	I) Colour change 100 II) No explosion	300	1.7	0.4
3	PETN	28	I) Colour change 85 II) No explosion	300	1.6	0.5
4	AP-RDX	28	I) Colour change 105 II) Explosion 145	172	2.2	—
5	AP-PETN	30	I) Colour change 95 II) Explosion 175	235	1.8	—
6	RDX-PETN	29	I) Colour change 95 II) No explosion	300	1.5	0.4

sitions do not. A similar trend was revealed in the results of the combinations of AP-RDX, AP-PETN and RDX-PETN. In view of the above observations, the B & J was applied only to the thermally stable RDX, PETN and RDX-PETN based compositions. The volume of NO_x that evolved for these compositions was within the acceptable limits of 0.6 ml, nevertheless higher than that for DBP.

Gas kinetics data for CMDB compositions at 80, 90 and 100°C are given in Table 3. The evolved gas volume after 72 h at 80°C was maximum with AP, mixtures of AP-RDX and AP-PETN (0.9–1.4 ml). RDX, PETN and mixtures thereof produced 0.3–0.4 ml of gases. At 90°C AP based compositions produced a gas volume of 19.6 ml in 48 h, while RDX and PETN based formulations gave 1.1–1.2 ml of gases only. Gas volume was around 1.3 ml with RDX and PETN based formulations, but around 1.4–1.5 ml with AP-RDX and AP-PETN combinations. At 100°C thick brown fumes (NO_x) were observed after 30 h with AP based compositions and the volume of gases evolved totalled 12.7 ml. For RDX and PETN based formulations only 2.8–3 ml of gas was measured. After 48 h and 100°C, compositions containing AP-RDX exploded. Similar observations were made with the AP-PETN based composition. However, RDX and PETN based formulations did not explode (gas volume of 4.8–6 ml). These results suggest that RDX and PETN based CMDB propellants are much more thermally stable than AP, AP-RDX and AP-PETN based formulations.

Isothermal gravimetric analysis (IGA) results for CMDB compositions at 60 and 80°C are given in Table 4. It is seen in Table 4 that while AP, AP-RDX and AP-PETN based propellants required 302, 216 and 209 h, respectively,

TABLE 3

Gas kinetic results for CMDB formulations at 80, 90 and 100°C

Compo- sition	High energy additive	Volume of gases evolved (ml)								
		80°C			90°C			100°C		
		24 h	48 h	72 h	24 h	30 h	48 h	24 h	30 h	48 h
Control SNC-55 CL45	-	0	0.1	0.6	0.6	0.7	1.4	3.0	4.2	-
1	AP	0.2	0.6	0.9	0.9	1.1	19.6 (Brown fumes)	3.5	12.7 (Brown fumes)	-
2	RDX	0.1	0.2	0.3	0.5	0.7	1.2	2.3	3.0	5.2
3	PETN	0.1	0.2	0.4	0.4	0.6	1.1	2.2	2.8	4.8
4	AP-RDX	0.3	0.7	1.2	0.8	1.0	1.5	3.0	4.0	Exploded
5	AP-PETN	0.3	0.9	1.4	0.8	1.0	1.4	2.4	3.0	Exploded
6	RDX-PETN	0.1	0.3	0.4	0.6	0.8	1.3	2.5	3.4	5.8

TABLE 4

Isothermal gravimetric analysis results for CMDB propellants at 60 and 80 °C

Composition	High energy additive	Time required (hr) for 3% wt. loss		<i>E</i> (kcal/mol)
		60 °C	80 °C	
1	AP	302	15.4	34.8
2	RDX	374	18.2	35.3
3	PETN	384	19.0	35.1
4	AP-RDX	216	18.0	29.0
5	AP-PETN	209	15.8	30.2
6	RDX-PETN	336	19.0	35.1

TABLE 5

Results on time to autoignition for CMDB propellants

Composition	High energy additive	Time to autoignition (min)					<i>E</i> (kcal/mol)	Extrapolated shelf life at 30 °C (y)
		130 °C	140 °C	150 °C	160 °C	170 °C		
Control SNC-55 CL-45	-	-	-	20.4	8.3	3.5	32.7	190
1	AP	67.6	28.2	12.5	-	-	28.0	13
2	RDX	-	-	25.7	10.7	4.8	31.9	164
3	PETN	-	-	19.5	8.5	3.8	30.5	65
4	AP-RDX	33.9	14.1	6.0	-	-	29.8	14
5	AP-PETN	69.2	28.2	12.0	-	-	28.9	19
6	RDX-PETN	-	-	24.0	10.0	4.4	31.2	110

for 3% weight loss to occur at 60 °C, RDX, PETN and RDX-PETN based compositions need 374, 384 and 336 h, respectively. A similar trend was observed at 80 °C. The activation energy (*E*), calculated by using the Arrhenius equation, for AP based CMDB propellant was 34.8 kcal/mol as compared to 35.3 and 35.1 kcal/mol for RDX and PETN based compositions. For AP-RDX and AP-PETN based formulations *E* was 29 and 30.2 kcal/mol, respectively. However, for RDX-PETN based compositions *E* was 35.1 kcal/mol.

Results of time to autoignition (TAI) test for different CMDB compositions are given in Table 5. First the experiments were carried out at 150 °C. At this temperature AP based compositions self-ignited after 12.5 min, which is two-third the time required for DBP (20.4 min). On the contrary, RDX and PETN based compositions required 25.7 and 19.5 min respectively. The TAI values for AP-RDX and AP-PETN based formulations were 6 and 12 min, respec-

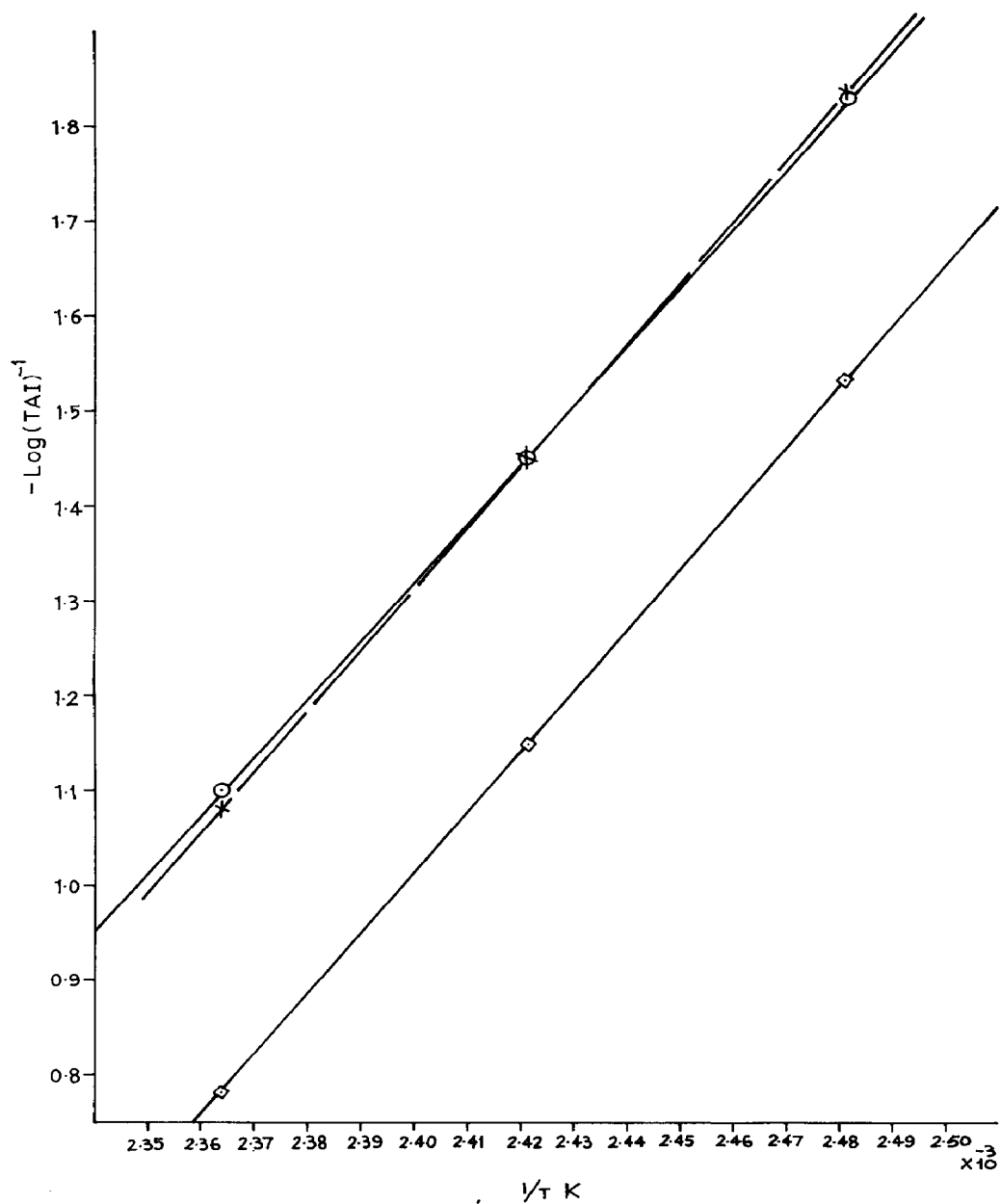


Fig. 1. Arrhenius plot of TAI vs. temperature for several AP containing CMDB formulations: \odot AP, \square AP+RDX and \times AP+PETN.

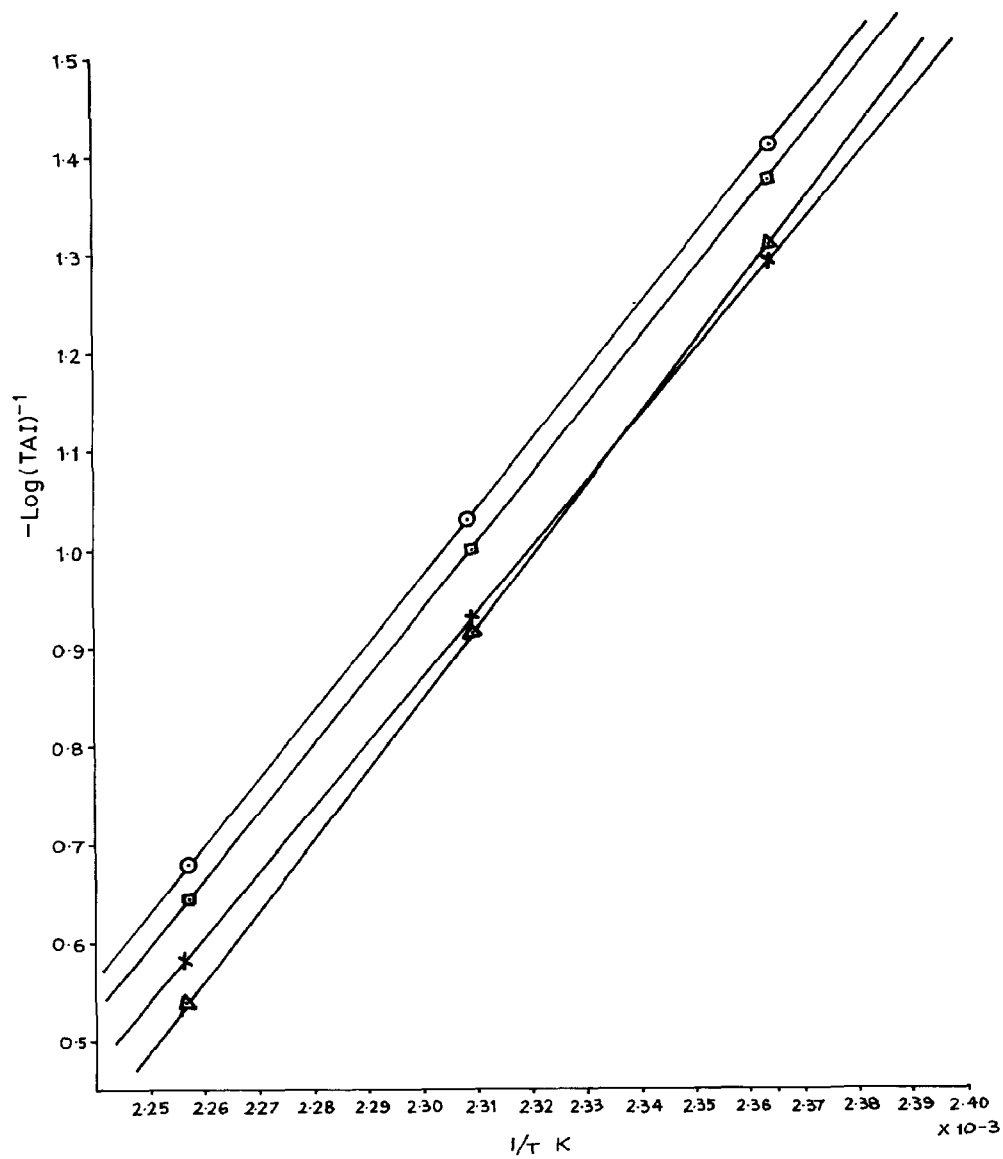


Fig. 2. Arrhenius plot of TAI vs. temperature for CMDB formulation: ○ RDX, × PETN, □ RDX/PETN and △ DBP (control).

tively, which are lower than that for AP based composition. RDX–PETN based composition self-ignited after 24 min, which is intermediate to that for RDX and PETN based individual compositions. The results indicate that in the presence of AP, RDX and PETN containing CMDB propellants undergo self ignition sooner than without AP. This suggests that AP catalyses autodecomposition of RDX and PETN in DBP matrix. In view of these observations, further information on the TAI of AP based formulations was generated at lower test temperatures (130–140 °C), whereas that for RDX and PETN based formulations was determined at higher temperatures (160–170 °C). Activation energy (E) values were calculated from the slope of the Arrhenius plot of log autoignition time against corresponding reciprocal temperature (Fig.1, 2). In general, E for AP, AP–RDX, AP–PETN based compositions was lower (28–30 kcal/mol) as compared to that of RDX, PETN and RDX–PETN based formulations (31–32 kcal/mol). Shelf life computed by extrapolating these values to 30 °C was 13–19 y for AP, AP–RDX and AP–PETN based compositions and 65–164 y for RDX/PETN based compositions.

4. Conclusions

(i) Results of qualitative and quantitative stability tests suggest higher stability for RDX, PETN and their combination based compositions than AP and AP–RDX/PETN based compositions. Results from gas kinetic, isothermal gravimetric analysis and time to autoignition (TAI) measurement further confirm the above trend.

(ii) Shelf life calculated from the Autoignition test results was considerably higher for RDX/PETN based CMDB propellants (65–164 y) than that for AP and AP–RDX/PETN based compositions (13–18 y) at 30 °C.

(iii) Activation energy calculated from the results on isothermal gravimetric analysis (at 60 and 80 °C) and TAI (130–170 °C) was 33 ± 4 kcal/mol, which suggest that a more or less similar mechanism of ageing is involved for AP, RDX and PETN based CMDB propellants.

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