Defence Science Journal, Vol 42, No 3, July 1992, pp 201-204

SHORT COMMUNICATION

Thermal Behaviour of AP-Based CMDB Propellants with Stabilizers

S.N. Asthana, C.N. Divekar, R.R. Khare and P.G. Shrotri

Explosives Research & Development Laboratory, Pune-411 008

ABSTRACT

Stability test results and DTA studies indicate the superiority of molecular sieve (MS) over zirconium silicate ($ZrSiO_4$) as the stabilizer for a composite modified double base (CMDB) system. Shelf life as computed from autoignition test results was 30 years for MS-based composition which is almost double the life of $ZrSiO_4$, but approximately half the life of resorcinol-based composition which was used as a reference. Higher stabilizing effect of MS as compared to $ZrSiO_4$ has been explained on the basis of the presence of channels and cavities in its structure, which makes it an effective adsorbent for decomposition catalysing species. Poor stabilization capability of *m*-dinitrobenzene as compared to resorcinol suggests the catalytic involvement of acidic decomposition products of nitrate esters in autodecomposition process of CMDB propellants.

The composite modified double base (CMDB) propellants are superior to double base and composite propellants, because of their higher performance. They offer advanced propulsion systems for both space vehicles and long range military missiles[1]. Asthana and Singh[2] have reported lower life for conventional AP-based CMDB propellants as compared to RDX- and PETN-based CMDB propellants Strong autocatalytic behaviour of AP-based CMDB propellant is attributed to the interaction between the decomposition products of nitrate esters and AP or its decomposition products, particularly $HClO_4$ [3,4]. To overcome this problem, supplementary stabilizers like resorcinol, alkoxy-phenoxy-benzenes or metal oxides are generally incorporated[5-7]. Baczuk[8] has recommended dual stabilizer system comprising *p*-nitrate *N*-methyl aniline and aluminium silicate molecular sieves (MS).

The search for better stabilizers for CMDB propellant systems is on. This study was undertaken to evaluate alumino silicate, MS and zirconium silicate ($ZrSiO_4$) in view of their capability to absorb acidic decomposition products of nitrate esters which further catalyse the autodecomposition process. These systems were evaluated with reference to resorcinol which is reported to be most effective in CMDB propellant[3,5,9]. The results obtained by Asthana and Singh for resorcinol-stabilized CMDB composition are included as reference[9]. *m*-dinitrobenzene was also assessed as a stabilizer with reference to resorcinol. This study reports the results of stability tests, namely, Abel heat test, methyl violet test, vacuum stability test, DTA, isothermal gravimetric analysis (IGA) and time-to-autoignition (TAI) test.

The propellant compositions containing 30 per cent spheroidal nitrocellulose, 35 per cent casting liquid (NG desensitised with 20 per cent diethyl phthalate) and 35 per cent AP were prepared by the slurry cast technique[10]. MS (in powder form), $ZrSiO_4$, *m*-dinitrobenzene and resorcinol of 99 per cent purity were incorporated in two parts over the composition.

The stability tests were performed as prescribed for double base propellants[11-14]. DTA studies were carried

Received 13 January 1992, revised 18 May 1992

Table 1. Results of stability tests of CMDB propellants

Stabilizer (2 parts)	Abel heat test at 65.5 °C (min)	Methyl violet test at 120 °C (min)		Vacuum stability test at 90 °C* (ml)
Resorcinol	20	Colour change	85	0.8
		No brown fumes	300	
		No explosion	300	
Molecular sieve	20	Colour change	80	0.9
		Brown fumes	215	
		Explosion	270	
Ziroconium silicate	12.5	Colour change	60	
		Brown fumes	75	
		Explosion	140	
m-dinitrobenzene	14	Colour change	75	1.2
		Brown fumes	115	
		Explosion	195	

* volume of gases evolved

out using 5 mg sample at a heating rate of 20 °C/min under atmospheric conditions. For IGA, 200 mg sample was heated at a constant temperature of 120 and 140 ± 0.5 °C in the incubators and the change in weight was monitored. The TAI test was applied to estimate the shelf life of compositions as described earlier[2,3,13].

The CMDB composition containing $ZrSiO_4$ recorded lower heat test and methyl violet test times as compared to MS- and resorcinol-based compositions. In the vacuum stability test, the volume of the gas evolved was 0.8, 0.9 and 1 ml for resorcinol, MS and $ZrSiO_4$ based compositions, respectively. These results suggest that MS is a more effective stabilizer than $ZrSiO_4$, but is inferior to resorcinol (Table 1).

DTA results (Table 2) indicate the peak temperature of 171 °C for MS-based composition, which is lower than the peak temperature for resorcinol-based composition (185 °C). The composition containing $ZrSiO_4$ decomposed at the peak temperature of 168 °C. Similar trend was observed in IGA studies also (Table 3). Activation energies (120-140 °C), as computed from IGA results by applying Arrhenius equation, are 26 and 23.5 kcal/mol for MS- and $ZrSiO_4$-based compositions, respectively as compared to activation energy value of 30 kcal/mol for resorcinol-based composition. These values give a measure of relative stability. The compositions were subjected to TAI test to get realistic estimates of activation energy from slope of Arrhenius plot of reciprocal of autoignition time against inverse of storage temperature[15].

In TAI test, MS-based composition recorded autoignition times of 87, 36, 17, and 7 min at 130, 140, 150 and 160 °C, respectively (Table 4). Whereas for $ZrSiO_4$-based composition, it was 78, 33.5, 16 and 6.7 min, respectively. These values are lower than those for resorcinol-stabilized composition. The activation energy value for $ZrSiO_4$-based composition was 28 kcal/mol as against 31 kcal/mol for resorcinol-based composition corresponding to shelf life of 16 and 73

Table 2. Results of differential thermal analysis of CMDB propellants

Stabilizer (2 parts)	Decomposition temperature (°C) Initial	Peak	Final	Percentage weight loss
Resorcinol	179	185	193	71
Molecular sieve	148	171	191	78
Zirconium silicate	147	168	189	83
m-dinitrobenzene	140	164	187	91

Table 3. IGA results of CMDB propellants

Stabilizer (2 parts)	Time required for 5 % weight loss (min) At 120 °C	At 140 °C	Activation energy (kcal/mol)
Resorcinol	136.7	21.2	30.0
Molecular sieve	93.0	19.0	25.6
Zirconium silicate	73.0	17.0	23.5
m-dinitrobenzene	60.2	15.6	21.7

Table 4. Results of TAI test of CMDB propellants

Stabilizer (2 parts)	Time-to-autoignition (min)				Activation energy (kcal/mol)	Life time at 30 °C (years)
	130 °C	140 °C	150 °C	160 °C		
Resorcinol	101.0	39.8	18.6	7.9	30.9	73
Molecular sieve	87.0	36.0	17.0	7.0	29.2	30
Zirconium silicate	78.0	33.5	16.0	6.7	28.0	16
m-dinitrobenzene	44.2	21.1	11.3	5.5	24.1	2

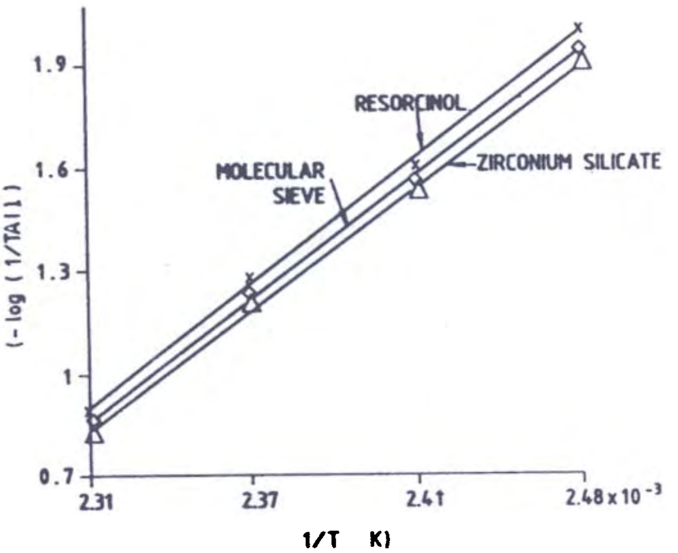

Figure 1. MS-based composition.

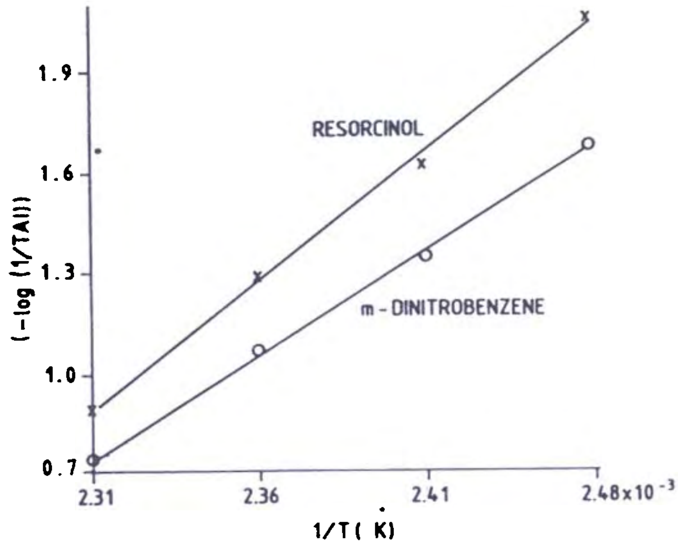

Figure 2. Activation energy computed from the slope of Arrhenius plot.

years, respectively. The MS-based composition occupies intermediate position with activation energy of 29 kcal/mol and shelf life of 30 years (Fig. 1).

These results established that MS, as a stabilizer, is superior to resorcinol monoacetate, resorcinol diacetate, MgO and cobaltic oxide, and its stabilization effect is comparable to that of PNMA in a CMDB system[9]. However, MS appears to be relatively less effective than resorcinol.

The CMDB composition containing *m*-dinitrobenzene, where both the OH groups of resorcinol are replaced by NO_2, was also evaluated. This formulation exploded during methyl violet test within 195 min. In IGA, the time required for a loss in weight of 5 per cent at 120 °C was less than half the time for resorcinol-based composition. Similarly, in TAI test at 130, 140 and 150 °C, TAI values obtained for *m*-dinitrobenzene-based composition were almost half the values for resorcinol-based composition. The activation energy computed from the slope of Arrhenius plot (Fig. 2) comes to 24 kcal/mol corresponding to shelf life of two years as compared to shelf life of 73 years for resorcinol. This study suggests that *m*-dinitrobenzene is a poor stabilizer for a CMDB system like *m*-nitrophenol[9] and establishes that the replacement of the electron donating OH group by the electron withdrawing NO_2 group renders aromatic compounds ineffective as stabilizer. These findings bring out that acidic elements like nitrogen oxides and acids have a role in catalysing autodecomposition reactions and support the view points of Asthana and Singh[9], and Hartmann and Musso[16] that resorcinol acts as an effective stabilizer for a CMDB system by offering an activated aromatic ring with electron-rich ortho and para position, due to mesomeric effect of hydroxyl group. These positions are readily available to bind autodecomposition catalysing species. The replacement of OH group by nitro group, as in case of *m*-dinitrobenzene, leads to electron-deficient aromatic ring because of strong electron withdrawing inductive and mesomeric effect of NO_2 group.

As regards mechanism of action of MS, Baczuk[8] has suggested that it acts as a stabilizer by rendering nitric acid harmless primarily because of the acid-base interaction. Higher effectiveness of MS as compared to $ZrSiO_4$ can be explained on the basis of difference in their structures. $ZrSiO_4$ is basically an ortho silicate with discrete anion structure[17] while MS has the extended anions. Their main characteristic is the openness of the $(Al.Si)O_2$ framework which results in the formation of channels and cavities of sizes ranging from 2-11Å in diameter enabling effective trapping of catalysing elements like NO_2 and HNO_3 in the holes thereby removing them away from the sphere of action[18].

CONCLUSION

Molecular sieve is superior to $ZrSiO_4$ as a stabilizer for a CMDB system. Life of MS-based CMDB composition is 30 years. Its stabilization potential is comparable to PNMA; however, it is less than that of resorcinol. MS appears to be stabilizing CMDB system by effectively removing elements like nitric oxides and acids through acid-base interaction due to its extended anion framework.

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