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STUDIES ON THERMAL STABILITY, AUTOIGNITION AND STABILIZER DEPLETION FOR SHELF LIFE OF CMDB PROPELLANTS

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Summary

This paper reports the results of thermal stability of composite modified double base propellants (CMDB) by using tests applicable for double base propellants (DBP) and shelf life estimation of CMDB propellants by application of the autoignition test and monitoring stabilizer depletion by high performance liquid chromatography (HPLC). The Abel heat test results suggest the stability of CMDB propellants with or without additional stabilizer, whereas the Methyl Violet test indicated that CMDB propellants without resorcinol do not have stability comparable with DBP. Results of the Vacuum stability and B and J tests showed stability of CMDB propellants with resorcinol within acceptable limits. Aging did not change the DTA pattern to any appreciable extent. Autoignition test results gave a shelf life of 27.1 and 157.8 years for CMDB propellants at 40 and 30°C respectively. 2-NDPA depletion studies indicated a half life of 6-7 years and 26-30 years respectively for CMDB propellants at 40 and 30°C whereas carbamite depletion yielded a half life of 8-9 and 40-42 years. The activation energy (E) for aging of CMDB propellants was found to be 33 ± 1 kcal/mol.

1. Introduction

Composite modified double base (CMDB) propellants are comparatively new entrants in the family of solid rocket propellants. In view of their great potential for producing higher specific impulse (I_{sp}) compared to well established double base and composite propellants (DBP & CP), they have found wide application in the propulsion of space vehicles and long range tactical and strategic missiles [1,2].

CMDB propellants are made by incorporating the energetic ingredients of CP systems, such as ammonium perchlorate (AP), high explosives (HMX, RDX), metallic fuel aluminium (Al), etc. into the already energetic matrix of DBP. With the energetic ingredients present in the CMDB propellant formulation, it is expected that storage might result in deterioration of the propellant grain. An increase in autocatalytic behaviour of CMDB over time has been reported by the inclusion of AP [3,4]. During prolonged storage ingre-

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dients may interact with each other or with the atmosphere to produce irreversible changes which may seriously affect both the ballistic and mechanical properties of the propellant.

Estimation of propellant shelf life is important from the point of view of mission reliability, safe handling, safe storage and manufacture. However, in contrast to DBP & CP, very limited information is available on the shelf life of CMDB propellants [3,4,5–8]. Boyars [9] has expressed the influence of propellant aging on chemical stability in terms of shelf life. Rice et al. [3] have claimed that time of autoignition is the most realistic method for determining the shelf life of CMDB propellants. Other researchers have suggested that determining the depletion rate of the stabilizer can be effectively used to compute shelf life of CMDB propellants and chromatographic techniques have been extensively used for this purpose [5,6]. While Beckwith et al. [7] have studied the influence of aging on void formation and bulk compressibility of CMDB propellants, Schmitt [8] investigated the influence of humidity and stresses on strength characteristics of CMDB propellants.

In view of the limited and scattered information available on the life of CMDB propellants, a study was undertaken to investigate the aging behaviour of this class of propellants. The propellants selected for this study are crosslinked CMDB (XL CMDB) with high performance ($I_{sp} > 240$ s) and reasonable mechanical properties (tensile strength – 17 kg/cm^2). This paper reports for CMDB propellants the results of conventional stability tests used for DBP, isothermal gravimetric analysis and differential thermal analysis (DTA) as well as shelf life estimation by applying autoignition test as monitoring stabilizer content depletion by high performance liquid chromatography (HPLC).

2. Experimental

CMDB propellants containing spheroidal nitrocellulose (SNC) [10], NG, AP, Al, nonexplosive plasticizers diethyl and dibutyl phthalates (DEP & DBP) and Stabilizer systems comprising 2-NDPA and carbamite with and without resorcinol were prepared by slurry cast technique [11]. Toluene diisocyanate (TDI) was used to crosslink 10% of unnitrated hydroxyl groups of SNC. Compositional details are given in Table 1.

The Abel Heat test (64.5 °C), Methyl Violet test (120 °C), Vacuum Stability test (90 °C) and B & J test (120 °C) were applied to test thermal stability [12]. However, the B & J test was modified to lower the sample weight (1 g) and reduce the time (3 h), in view of reported strong autocatalytic behaviour of CMDB propellants [3,4]. Thermal behaviour was investigated by isothermal gravimetric analysis at 80 °C [13]. Influence of aging on DTA pattern was studied by using a NETZCH DTA at heating rate of 10 °C/minute. The sample size was 5 mg.

The autoignition test described by Rice et al. [3] was applied to assess safe

TABLE 1

Compositional details of CMDB & DB propellants

Ingredients	Percentage composition[a,b] (w/w)		
	CMDB-1 (with resorcinol)	CMDB-2 (without resorcinol)	DBP
NC (12.2% N)	25.76	25.76	53.33
NG	29.11	29.11	36.27
AP	19.89	20.29	–
Al	13.52	13.52	–
DEP	6.09	6.09	7.20
DBP	0.55	0.55	0.80
2-NDPA	0.62	0.62	0.80
Carbamite	0.68	0.68	1.60
Resorcinol[c]	0.40	–	–
Fe_2O_3	1.93	1.93	–
TDI	1.45	1.45	–

[a]SNC composition NC (12.2% N) 88.9, NG 7.1, DBP 1.4, Carbamite 2.6 wt.%.
[b]SNC ingredients are taken into consideration in above compositions.
[c]Resorcinol was coated on AP.

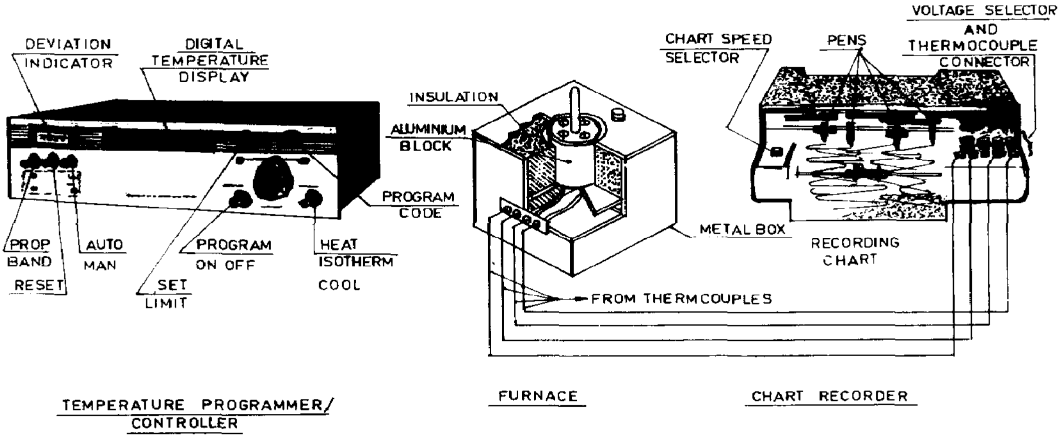

Fig. 1. Autoignition test equipment.

storage life. Instrumentation for the test consisted of a furnace, temperature controller and chromel–alumel thermocouples in conjunction with a pen recorder. (The complete set of equipment is shown in Fig. 1.). The propellant sample (200 mg) was heated in a closed system at constant temperature ($\pm 0.1\,^\circ C$) and the time to autoignition (TAI) was recorded.

Changes in the stabilizer contents with aging were monitored using HPLC.

Equipment supplied by Du Pont with a C-8 column was used for resolution. The mobile phase was an alcohol–water mix. The samples for aging studies were confined in two layers of aluminium foil and aged at 70, 80 and 100°C. These conditions are similar to those used by Volk for aging studies of DBP [13,16,17].

3. Results and discussion

3.1 Thermal stability of CMDB propellants

The results of the Abel heat test, Methyl Violet test, Vacuum Stability test and B & J test on CMDB propellants are given in Table 2. For comparison, the values obtained for DBP are also included in the table. As approximation the thermal stability values accepted for DBP were taken as the criterion of stability for CMDB propellants. The Abel Heat test values obtained for CMDB propellants, with and without resorcinol (21 and 13 min respectively) show equal or better stability than DBP (13 min) and suggest that addition of supplementary stabilizer resorcinol enhances stability. For the Methyl Violet test, CMDB propellants with and without additional stabilizer resorcinol required 110 and 105 min respectively for a change in the colour of the paper (DPB 90 min). However, the CMDB propellant without resorcinol gave brown fumes (NO_2) after 235 min and exploded within 295 min. Thus, the Methyl Violet test indicated that the thermal stability of CMDB propellant with resorcinol

TABLE 2

Results of stability tests for CMDB and DBP propellants

Test	Propellant system		
	DBP	CMDB-1	CMDB-2
Heat Test at 64.5°C (minutes to change of color)	13	21	13
Methyl Violet Test at 120°C (minutes)	i) Color change 90 ii) No brown fumes iii) No explosion	i) Color change 110 ii) No brown fumes iii) No explosion	i) Color change 105 ii) Brown fumes 235 iii) Explosion 295
Vacuum Stability Test at 90°C (ml of decomposition gases)	1.84	2.40	–
B & J Test at 120°C (ml of NO_x)	0.20	0.35	–

was similar to that of DBP (no evolution of brown fumes and no explosion within 300 min), but the CMDB propellant without resorcinol was comparatively unstable. Hence, for further studies CMDB propellant containing 2-NDPA, carbamite and resorcinol stabilizers was selected.

The Vacuum Stability and B & J tests showed that the total evolved gasses, including oxides of nitrogen were 2.4 and 0.35 ml respectively. These values are higher than those for DBP (1.84 and 0.20 ml respectively) and suggest that CMDB propellants, even containing additional stabilizer (resorcinol), are relatively less stable than DBP. However, nitrogen oxide evolution up to 0.6 ml as per modified B & J test may be considered the limit for the acceptable stability. Hence, CMDB propellants studied can be considered thermally stable for all practical considerations.

3.2 Isothermal gravimetric analysis

A temperature of 80 °C was selected for isothermal gravimetric analysis of the CMDB-1 propellant. The results are given in Table 3. A plot of percentage loss against time is given in Fig. 2, which shows that while the CMDB-1 propellant required 5.7 h, DBP required 10.3 h for 3% weight loss. Further, the weight loss within 15 h was 5.2% for the CMDB-1 propellant as compared to 3.8% for DBP. These results indicate that under similar conditions CMDB propellants show a higher weight loss than the DBP matrix of which they are made, indicating that AP inclusion in DBP matrix may be responsible for this behaviour (i.e., stronger autocatalytic decomposition of nitric esters at elevated temperatures).

3.3 DTA of fresh and aged CMDB propellants

DTA results for unaged and aged CMDB-1 propellants are given in Table 4. The samples aged at 70 and 100 °C for 42 and 0.5 days respectively, gave inception temperatures (T_i) identical to that for the unaged sample (149 °C). The peak temperatures (T_m) of the aged samples were 173 and 174 °C which are marginally lower than T_m for the unaged sample (176 °C). The final temperatures (T_f) for the aged samples were slightly lower than the T_f for the

TABLE 3

Results of isothermal gravimetric analysis at 80 °C

Aging interval (h)	% Weight loss	
	DBP	CMDB-1
5	2.1	3.1
10	2.7	3.7
15	3.8	5.2

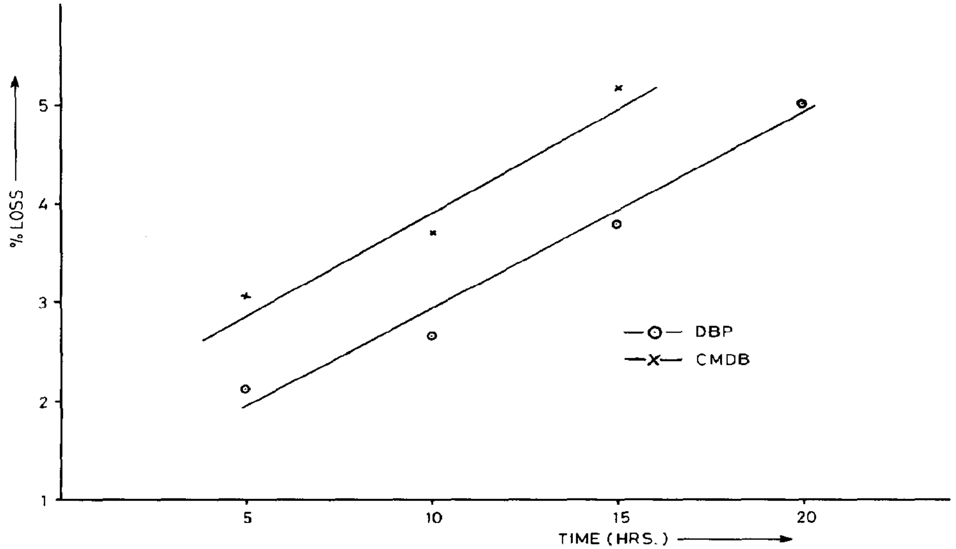

Fig. 2. Plot of percent weight loss versus time of isothermal gravimetric analysis at 80°C.

TABLE 4

Results of DTA studies of unaged and aged CMDB-1 propellants

Aging temperature (°C)	Aging duration (days)	Decomposition temperature (°C)			Area under thermogram (mm^2)
		Inception temperature (T_i)	Peak temperature (T_m)	Final temperature (T_f)	
Unaged sample	—	149	176	212	250
70	42	149	173	209	200
100	0.5	149	174	205	240

unaged sample. The area under the thermogram was found to be lower for aged samples (200 and 240 mm^2) compared to the unaged sample (250 mm^2). These results show that even after accelerated aging, CMDB propellant containing AP and stabilizer (2-NDPA, carbamite and resorcinol) shows a thermal decomposition pattern similar to that obtained for the unaged sample. However, as the area under the thermogram is proportional to heat of reaction during decomposition [14], total heat output of aged samples is lower than that for unaged samples.

3.4 Shelf life estimation

3.4.1 Autoignition test

The autoignition test for CMDB-1 propellant was carried out at 130.5, 139.5 and 150.5°C. For DBP the temperatures used were 150.5, 160.5 and 169.5°C due to the long autoignition time of DBP at temperatures lower than 150°C. Results are given in Table 5. CMDB-1 propellant containing AP and Al required 95.2 and 42.5 min at 130.5 and 139.5°C respectively for autoignition. At 150.5°C, while CMDB propellant ignited after 12.7 min, DBP required 18 min, suggesting thereby that the decomposition reactions are faster for CMDB propellants compared to DBP. A graph of log (time of autoignition)$^{-1}$ vs. (temperature)$^{-1}$ is shown in Fig. 3. From the slope of this line, the activation energy (E) may be calculated using the relationship $E = 2.303\ R$ (slope of line). The E value calculated for CMDB-1 was 32.2 kcal/mol compared to a value of 34.3 kcal/mol for DBP. Extrapolation of the data in Table 5 and Fig. 3, as suggested by Rice et al. [3] and Schubert et al. [13], to lower temperatures for the CMDB propellant gives shelf lifes of 157.8 and 27.1 years for 30 and 40°C respectively which is significantly less than that for DBP – 378 and 61.2 years respectively.

Hartman et al. [4] determined the shelf/storage life of CMDB propellants using a NG degradation technique and depletion of resorcinol. Their results agree closely with those obtained in the present study (Table 5).

3.4.2 Stabilizer depletion

2-NDPA depletion in CMDB-1 propellant upon aging at 70, 80 and 100°C, determined using HPLC, is shown in Table 6. The residual stabilizer content was plotted against time interval (Fig. 4). Using the Woolwich formula [15], the half life of propellant at 70 and 80°C (time required for depletion of stabilizer content from 0.6 to 0.3 wt.%) was determined to be 45.1 and 11.9 days respectively. A factor corresponding to increase in propellant aging on increase in temperature by 10°C was obtained by dividing the propellant half life at

TABLE 5

Results of time to autoignition test for CMDB and DB propellants at various temperatures

Propellant system	Time to autoignition (minutes) (at temp. °C)					Activation energy (kcal/mol)	Predicted life at 40°C (years)	Predicted life at 30°C (years)
	130.5	139.5	150.5	160.5	169.5			
DBP	–	–	18.0	6.9	3.4	34.4	61.2	378.0
CMDB	95.2	42.5	12.7	–	–	33.2 (35.5)[a]	27.1 (35)[a]	157.8 (165)[a]

[a]Values reported by Hartman for CMDB propellants [4].

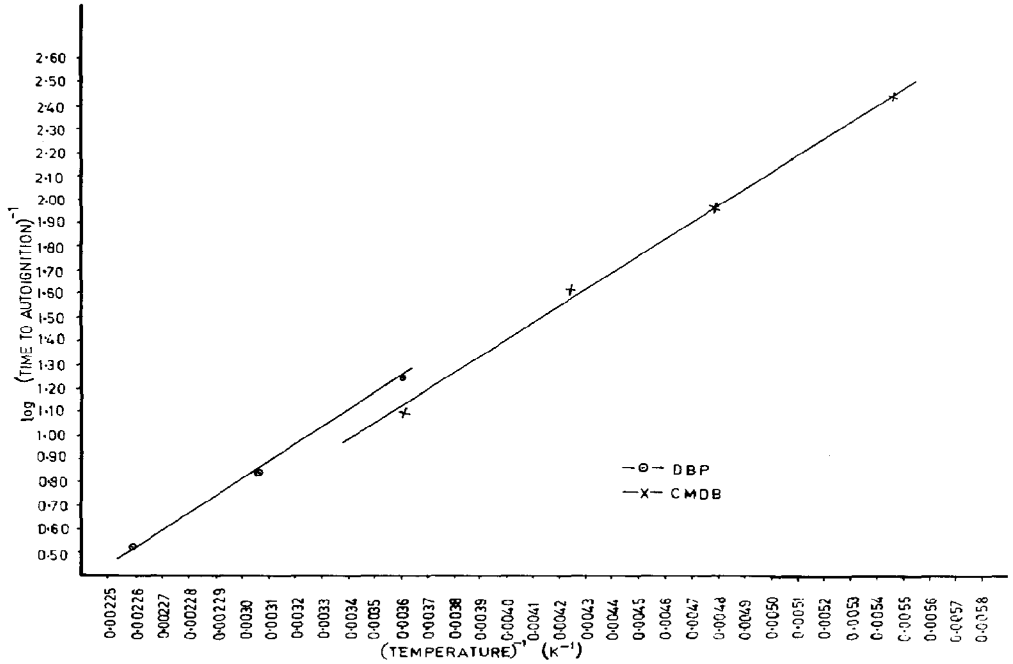

Fig. 3. Arrhenius plot of time to autoignition from test results.

70 °C with that at 80 °C. The value for the factor thus obtained was 3.79. This factor was verified by applying it to the experimentally determined half life obtained by 2-NDPA depletion at 100 °C (0.86 day) and back calculating the half life at 70 and 80 °C. These computed half lives are well in agreement with the values obtained directly by Woolwich's formula. By establishing the factor in this way the half life of the propellant at 30 and 40 °C was calculated from its half life at 70 °C. This gave the half life of 25.5 and 6.7 years respectively.

2-NDPA depletion times obtained were also used to determine activation energy for the decomposition of the propellant. The activation energy was 32.2 kcal/mol. The time for depletion of 2-NDPA content to zero was determined by extrapolation in Fig. 4. The time thus obtained was 47.5 days. Using these values of activation energy and time, the life of the CMDB-1 propellant at 30 and 40 °C corresponding to total 2-NDPA consumption was determined to be 65.9 and 12 years respectively, which are approximately double their half lives determined above.

To verify the above observations, results on carbamite depletion at 70 and 80 °C (Table 7, Fig. 5) were used to predict shelf lives at 70 and 80 °C. Measured half lives were 49.7 and 12.0 days respectively, giving a factor of 4.13 for decrease in half life of propellant per 10 °C temperature increase. Using the half life data obtained at 100 °C (0.75 day) and multiplying by the factor $(4.13)^3$

TABLE 6

Results of 2-NDPA depletion on aging of CMDB-1 propellant using HPLC

Temperature (°C)	Interval (days)	% Residual 2-NDPA content	Half life as per Woolwich's formula [15] (days)	Half life computed from half life at 100°C using factor 2.79 (days)	Half life (years) computed from 70°C data & factor 3.79		Activation energy (kcal/mol)	Life from activation energy & data at 70°C (years)	
					30°C	40°C		30°C	40°C
	0	0.60							
	14	0.53							
70	28	0.50	45.1	46.8					
	35	0.40							
	42	0.18			25.5	6.7	32.2	65.9	12
	0	0.60							
80	3	0.55	11.9	12.4					
	6	0.44							
	9	0.41							
100	0.75	0.37	0.86	–					

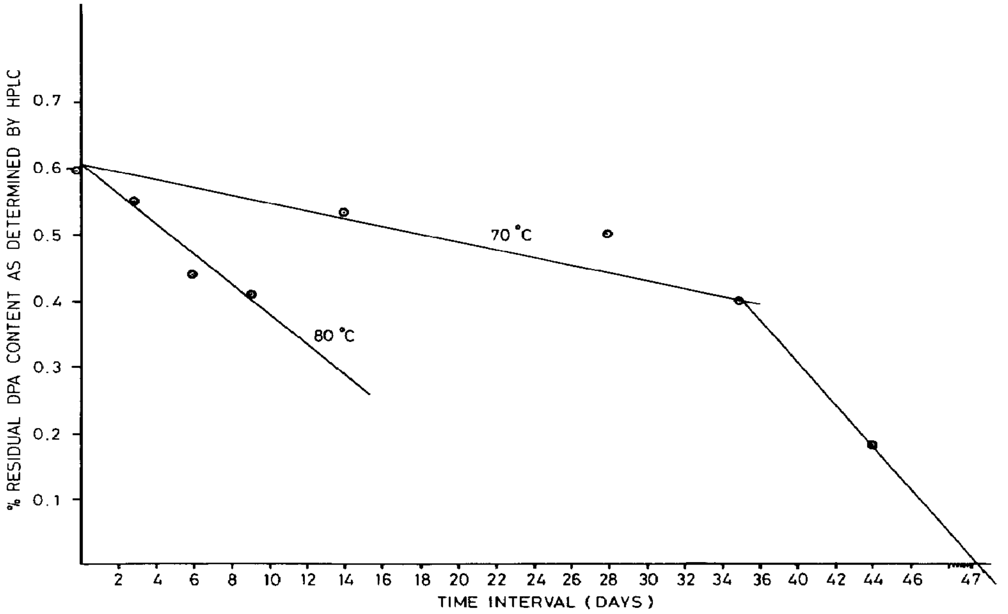

Fig. 4. Residual DPA content vs. time interval.

TABLE 7

Results of carbamite depletion on aging of CMDB-1 propellant using HPLC

Temperature (°C)	Interval (days)	% Residual carbamite content	Half life as per Woolwich's formula [15] (days)	Half life computed from half life at 100°C using factor 4.13 (days)	Half life (years) computed from 70°C data & factor 4.13		Activation energy (kcal/mol)	Life from activation energy & data at 70°C (years)	
					30°C	40°C		30°C	40°C
70	0	0.66							
	14	0.60	49.7	52.8					
	28	0.54							
	35	0.50							
	42	0.20			39.6	9.6	34.1	94.7	15.5
	0	0.66							
80	3	0.55							
	6	0.44	12.0	12.8					
	9	0.41							
100	0.75	0.37	0.75	–					

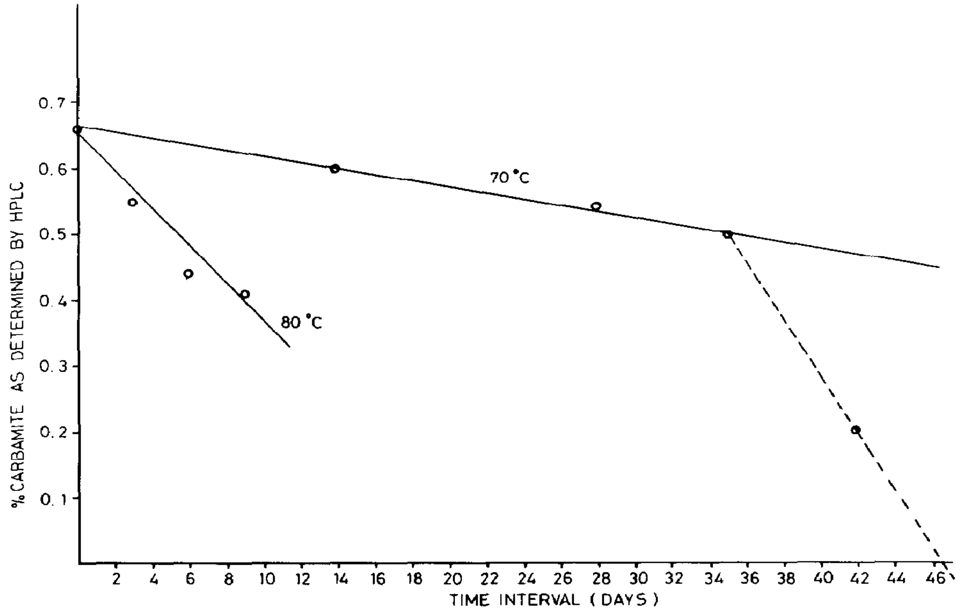

Fig. 5. Residual carbamite content vs. time interval.

and $(4.13)^2$ the half lives of 52.8 and 12.8 days at 70 and 80°C respectively are obtained. These are comparable to the half lives obtained from Woolwich's formula. Using this factor and half life at 70°C, the half lives at 30 and 40°C are 39.6 and 19.6 years respectively. From an activation energy value of 34.1 kcal/mol as obtained for 2-NDPA depletion, and the time obtained for carbamite depletion to zero by extrapolation in Fig. 5, total life at 30 and 40°C are 94.7 and 15.5 years respectively, which is again almost double the half life predicted above.

The life time estimates by autoignition test at 30 and 40°C (157.8 and 27.1 years respectively) are about 2.4 times that of 2-NDPA depletion to zero level (65.9 and 12.0 years respectively) and about 1.7 times that of carbamite depletion to zero level (94.7 and 15.5 years respectively). The difference in the predicted shelf life with regard to 2-NDPA and carbamite depletion may be attributed to a slower decomposition (reaction with nitrogen oxides) rate of carbamite than 2-NDPA. Further, the life estimates from autoignition test are expected to be higher than those from stabilizer depletion to zero level because reaction products of original stabilizers can also impart stability to propellant to a certain extent. The results of the present study of autoignition and stabilizer depletion for CMDB propellants, when compared with the results of Volk [13,16,17] for DBP, suggest close agreement.

An activation energy of about 33 kcal/mol obtained for aging of the CMDB propellant in above experiments corresponds to the energy required for cleavage of $RO{-}NO_2$ bonds in nitric esters. This suggests that the rate determining step during the aging of CMDB propellants is the decomposition of nitric esters.

Conclusions

1. Qualitative and quantitative thermal stability test results reveal acceptable stability of CMDB propellants containing resorcinol as additional stabilizer. Autoignition test results indicate lower stability of CMDB propellants than DBP. Isothermal gravimetric analysis also suggests a similar pattern.
2. Using autoignition test results, a storage life of 157 years and 27 years can be assigned at 30°C and 40°C respectively for the CMDB-1 formulation studied.
3. Factor for increase in depletion of 2-NDPA and carbamite with temperature increase by 10°C are 3.79 and 4.13 respectively. These are in agreement with the values of 2–4 for DBP [16].
4. Aging does not lead to a change in DTA pattern of CMDB propellants. However, it reduces the overall heat output.

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