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Mechanism of Ageing of Composite Solid Propellants

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INTRODUCTION

Composite propellants mostly consist of two major ingredients: oxidiser and binder. It has almost been established now that propellants undergo slow decomposition during the course of ageing [1-3]. To increase the longevity of the propellants, it is necessary to know the mechanism of the ageing process. Thus it has to be established whether the rate-controlling step lies in the oxidiser decomposition or in the binder decomposition. The objective of the present investigation, therefore, is to identify the constituent responsible for the ageing.

It may be noted that contrary to the available literature on the mechanism of the ageing of double-base propellants, very little is known about the mechanism of composite propellant ageing [4-11]. From accelerated ageing studies in the temperature range 40-75°C of five cast composite propellants, Kuletz and Pakulak [4] have shown that the primary component altered at the exposed surface is the binder, whereas in the interior it is the oxidiser. However, they found the activation energy (E) for surface, subsurface, and bulk material to be almost similar (23-27 kcal/mole). Schedlbauer [6] observed that polyurethane and carboxy terminated polybutadiene (CTPB)-based propellants harden during ageing, which he attributed to cross-linkage through the double bonds present in the main chain. He suggested that $HClO_4$ generated due to the interaction of AP and moisture may act as an excellent cross-linkage

agent for double bonds. Myers [7] also observed the hardening of the CTPB propellant, which he explained on the basis of cross-linkage reactions due to the oxidative attack of AP on CTPB double bonds. Layton [9-11] correlated the chemical structural changes of CTPB, hydroxy terminated butadiene (HTPB), and terepolymer of butadiene, acrylic acid, and acrylonitrile (PBAN)-based propellants with the change in their mechanical properties during the ageing process. He proposed that the cross-linkages are formed along the polymer chains at the unsaturated sites, with the maximum percentage at the pendant vinyl group. He estimated energy (E) values (5-7 kcal/mole) for the chemical and mechanical changes during ageing and attributed this to the diffusion process. It may be seen from the works of Kuletz and Pakulak [4] and Layton [9-11] that there is controversy over the E values for the ageing process. Another objective of the present work, therefore, is to estimate the E values for changes occurring in the mechanical properties, burning rate ($\dot{r}$), and thermal decomposition (TD) during ageing and to see whether there is a correlation between them.

EXPERIMENTAL

The preparation of propellant based on polystyrene (PS) and ammonium perchlorate (AP) and the method of ageing in air are described in our recent paper [2]. Propellants based on different binders

[PS, polymethylmethacrylate (PMMA), and phenol formaldehyde (PPF)] and different oxidisers [AP, $KClO_4$(KP), and NH_4NO_3(AN)] were also processed in a similar manner. The dummy PS/NaCl propellant was also made in a similar way. In all the above systems oxidiser:fuel ratio (3:1) was kept constant.

Ageing studies of PS/AP (75%) propellant in vacuum and in nitrogen atmospheres at 100°C storage temperature were also carried out. For vacuum storage, the propellant strands were suspended in a vacuum oven (20-mm pressure). There was no significant change in pressure in the vacuum oven during storage of up to 25 days.

The ageing studies of pure AP having a particle size of (53–105 μs) were carried out at 75°, 100°, 125°, and 150°C for 12 days of storage time. The samples were stored in open weighing bottles. The TD studies of the aged samples were carried out at 230°C immediately after removal from the oven.

Isothermal thermogravimetric (TG) studies of unaged and aged propellants were carried out on a homemade assembly as described earlier [2]. The TD rate was calculated for 25% decomposition from the TD plot of percent weight loss vs time. Differential thermal analysis (DTA) thermograms were obtained on an automatic Wagnomat DTA-02-Universal Instrument (Firms Franz Wagner, East Germany). The burning rate ($\dot{r}$) measurements for the unaged and aged propellants were carried out at ambient conditions. A fine and visible circular marking on the coated strands was done with a fine pointed needle on a lathe at three points, and the distance between the marks was measured with vernier calipers (least count 0.002 cm). The distance between the top surface and the first mark was kept at about 0.7 cm. A stopwatch with 1-sec time accuracy was used to note the burning time. The $\dot{r}$ measurements were also done with an electronic timer, and the accuracy in the $\dot{r}$ measurements in both the cases was the same. The propellant strand was fixed to a stand, and the top surface was ignited with an electrically heated nichrome wire. Two stopwatches were used simultaneously to note the time from first mark to second mark and from second mark to third mark. The distance divided by the time gave the $\dot{r}$ in cm/sec.

RESULTS AND DISCUSSION

Data for changes in $\dot{r}$ and TD rate for the propellants with different oxidisers and the same binder are given in Table 1. To compare the behaviour of different oxidisers on the storage stability of the propellants, the TG, DTA, and $\dot{r}$ results are summarised in Table 2. A similar comparison of the propellants having the same oxidiser and different binders is also presented in Table 2. Analysis of the data presented in Table 2 suggests strongly that the ageing characteristics of the propellants are related to the themal stability of the oxidiser, and not to that of the binder. In addition, the following results also support evidence that the ageing of the propellant is governed by the oxidiser decomposition alone.

1. Comparative ageing study [12] of PS/AP and PS/NaCl (dummy) propellants has very clearly indicated that the ageing is due to the oxidiser decomposition present in the propellant matrix and that the atmospheric oxidation is negligible; that is, after storing at 100°C for about 25 days it was observed that the PS/AP sample turned yellow homogeneously throughout the bulk of the material, whereas the dummy propellant looked similar to that of the unaged propellant. Infrared (IR) analysis [3, 12] of the binder portion of the PS/AP and PS/NaCl systems show that peroxide formation takes place in the PS/AP system, and not in the PS/NaCl system, which indicates that the oxygen for peroxide formation comes from AP decomposition rather than from the air.

2. The ageing studies were carried out in air, nitrogen, and vacuum, and the data on $\dot{r}$ and TD are summarised in Table 3. The data presented in Table 3 show that the changes in $\dot{r}$ and TD rate were almost similar in different environments of ageing, indicating that the propellant decomposition is unaffected by aerial oxidation and that it depends only on the constituents of the propellant.

3. It was observed [13] that the easily decomposible ammonium salts that readily evolve ammonia [e. g., $(NH_4)_2HPO_4$, NH_4F, NH_4Cl, and NH_4Br], which reduce the TD and deflagration rate of AP, bring about an increase in the

TABLE 1

Comparison of Ageing Characteristics of Propellants Containing PS as Binder and Having Different Oxidisers[a]

System	Storage time (days)	$\dot{r}$ (mm/sec)	Change in $\dot{r}$ (%)	Thermal decomposition rate (min^{-1} × 10^{-3}), TG temp. = 230°C	Change in TD rate (%)
PS/KP (75%)	Unaged	0.490	0.00	2.51	0.00
Propellant	15	0.520	6.12	2.64	5.18
	30	0.540	10.20	2.72	8.37
	50	0.600	22.45	2.87	14.34
PS/AP (75%)	Unaged	0.880	0.00	5.43	0.00
Propellant	5	0.950	7.95	5.75	5.89
	10	1.000	13.64	6.45	19.52
	15	1.050	19.32	6.94	27.81
	20	1.090	23.86	8.13	49.72
PS/AN (75%)	Unaged	0.048	0.00	5.78	0.00
Propellant	7	0.056	16.67	6.85	18.51
	11	0.062	29.17	7.25	25.43
	15	0.069	43.75	8.40	45.33

[a] Storage temperature = 100°C, error in $\dot{r}$ = 2–5%, oxidiser particle size = 53–105 μ, room temperature = 25 ± °C.

terminal stability of the propellant. These results confirm that the ageing behaviour of the propellant is controlled by the oxidiser decomposition characteristics.

4. The results on oxidiser loading [3] indicate that TD rates of aged and unaged propellants behave in a similar fashion; increasing the oxidiser loading reduces the TD rate in the orthorhombic region, and the reverse is true in the cubic region. These results are akin to that observed

for the effect of precompression pressure on AP decomposition; in other words, AP decomposition rate is reduced in the orthorhombic region and increased in the cubic region as the precompression pressure is increased.

All these observations lead to the fact that the agency responsible for the ageing in the propellant is the TD of the oxidiser contained in it.

Although it has been shown beyond doubt that the oxidiser governs the ageing of the composite

TABLE 2

Comparison Between Thermal Stability of Oxidisers and Binders on Ageing of Corresponding Propellants

Propellant system	Extent of decomposition at 230°C (TG) (%)	Oxidiser or binder decomposition temperature[a] (°C)			Aged at 100°C for 15 days for samples 1-3 and 12 days for samples 4-7	
		Sample	Start	End	Change in $\dot{r}$ (%)	Change in TD rate (%)
1. PS/KP (75%)	~25	KP	~550	~765	6.12(+)	5.18(+)
2. PS/AP (75%)	~45	AP	~290	~460	19.32(+)	27.81(+)
3. PS/AN (75%)	100	AN	~225	~300	43.75(+)	45.33(+)
4. PA/AP (75%)	~45	PS	~440	~660	17.05(+)	23.57(+)
5. PMMA/AP (75%)	—	PMMA	~278	~415	12.12(+)	27.27(+)
6. PPF/AP (75%)	—	PPF	~290	~600	13.14(+)	32.28(+)
7. CTPB/AP (80%)	—	CTPB	~390	~534	5.63(+)	13.00(+)

[a] Data derived from the DTA traces; (+) increase in the value.

TABLE 3

Comparison of Ageing Characteristics of PS/AP (75%) Propellants Aged at 100°C in Atmospheres of Air, Vacuum and Nitrogen[a]

Atmosphere	Storage time (days)	$\dot{r}$ (mm/sec)	Change in $\dot{r}$ (%)	Thermal decompostion rate (min^{-1} × 10^{-3}) TG temp. = 230°C	Change in TD rate (%)
Air	Unaged	0.880	0.00	5.43	0.00
	5	0.950	7.95	5.75	5.89
	10	1.000	13.64	6.49	19.52
	15	1.050	19.32	6.94	27.81
	20	1.090	23.86	8.12	49.72
Vacuum	5	0.940	6.82	5.68	4.60
(20 mm)	10	0.990	12.50	6.33	16.57
	15	1.030	17.05	6.80	25.23
	20	1.060	20.45	8.00	47.33
Nitrogen	5	0.940	6.82	5.71	5.16
(1 liter/min)	10	0.990	12.50	6.37	17.31
	15	1.040	18.18	6.90	27.07
	20	1.070	21.59	8.00	47.33

[a] Error in $\dot{r}$ = 2 to 4%, AP particle size = 53–105 μ, room temperature = 26 ± 1°C.

solid propellant, this may be quantitatively support if it could be shown that the energy of the propellant decomposition is the same as that for the oxidiser decomposition. For AP decomposition it has now been fairly well established that in the temperature range 200–400°C there are three

TABLE 4

Energy data for AP and PS/AP Propellant

System	E (kcal mole^{-1})			
	50–150°C	200–250°C	250–350°C	350–450°C
AP	13[a]	30[b]	20[b]	60[b]
PS/AP (75%) Propellant	13[a]	29	19	–
PS/AP (75%) Propellant (aged at 100°C for 15 days)	–	28	18	–

[a] Values obtained by indirect method; that is, the samples were aged in the temperature region 50–150°C for 12 days and TD rate of the aged samples was calculated at 230°C.

[b] Values obtained by Kishore and Pai Verneker [20].

E values (See Table 4). Below 200°C the E value for TD of AP has not been reported in the literature, which may be because the decomposition is extremely slow. In the present context the knowledge of the E value of AP and PS/AP propellant below 200°C is extremely important because the ageing is carried out in this region. An indirect method was adopted to estimate the E value of AP and PS/AP propellant in the temperature range 75–150°C. The samples were aged at these temperatures for a period of 12 days, preheated (aged) material was decomposed at 230°C, and the TD rate was calculated for 25% decomposition. The E values were obtained from the Arrhenius plots, and the data are shown in Table 4. The similarity of the E values for the propellant decomposition during the course of ageing below 200°C supports the belief that the constituent responsible for ageing is the oxidiser.

Isothermal TG studies of PS/AP (75%) propellants were carried out at 205°, 215°, 225°, 240°, 250°, 260°, 270°, 281°, 290°, 299°, and 310°C. Above 310°C the TG studies could not be carried out because the propellant becomes ignited. The E-value calculations were in accordance with the Jacobs–and Kureishy technique [21] using the TD rate of 5–30% decomposition. The Arrhenius plot

TABLE 5

Thermal Decomposition Data of AP Aged at Different Temperatures at a Fixed Storage Time (12 Days)[a]

System	Storage temperature (°C)	Thermal decomposition rate $(min^{-1}) \times 10^{-3}$ (25% decomposition)	Change in TD rate (%)
Pure AP	Unaged	6.58	0.00
	75	6.90	4.86
	100	7.81	18.69
	125	8.93	35.71
	150	10.00	51.98

[a] Thermal decomposition temperature $= 230°C$, AP particle size $= 53–105\ \mu$.

is shown in Fig. 1. The break in the Arrhenius plot is due to the phase transition of AP around 240°C. The E values for the unaged PS/AP (75%) propellant thus obtained are presented in Table 4. On comparing the E values of the propellant with that of AP in Table 4, one can strongly say that the rate-determining step in the propellant is the same as that in the AP decomposition in all the temperature ranges studied. To determine whether the rate-controlling process observed for the unaged propellant is the same for the aged propellant, the E value for PS/AP (75%) propellant aged at 100°C for 15 days was estimated in a manner similar to that for the unaged propellant, (see Table 4). The similarity of the E values for the unaged and aged propellants show that the rate-controlling step does not change during ageing.

The next step was to understand the significance of the E value below 200°C, that is, to which process the E value (13 ± 2 kcal/mole) corresponds. From the recent work carried out in our laboratory [22] on the electric field experiments on AP decomposition at low-temperatures the protons have been found to be the charge-carrying species. The electric-field behaviour of the corresponding PS/AP propellants was also examined in the same low-temperature region, and it was again found that the charge-carrying species are only the protons. It may, therefore, be inferred that proton transfer takes place during the AP and

propellant decomposition around 150°C. This conclusion gets credence from the fact that the energy for the proton transfer is of the order of 15–20 kcal/mole, which is very near to the E value obtained in the present work below 200°C, for the propellant as well as for the AP decomposition. There are a few more observations to support the fact that the proton transfer takes place in the low-temperature region (i.e., below 200°C).

1. Boldyrev et al. [14] have studied electrical conductivity through AP crystals below 100°C and found that hydrogen is generated at the cathode. They concluded that the charge carriers were protons, but his conclusion has been challenged as not being conclusive since the hydrogen may be formed during the secondary reactions.

2. Keenan and Ohanian [15] have recently studied the electrical conductivity of AP single crystals below 200°C. They concluded that the proton is the conducting ion in the temperature range 25–100°C.

3. Ellsworth Hackman et al. [16] found from mass spectrometric studies that NH_3 and $HClO_4$ are among the primary species formed during the decomposition of AP in the temperature range 80–165°C and that these species remain as major species throughout the temperature range tested. They observed the following species by using a time-of-flight mass spectrometer:

at 80°C: Cl, ClO, ClO_2, ClO_3, $\underline{HClO_4}$,

at 95°C: ClO, ClO_2, ClO_3, NO, HNO, Cl, $\underline{HClO_4}$,

at 115°C: HCl, N_2O, HNO, Cl, ClO, ClO_2, ClO_3, $\underline{HClO_4}$,

at 135°C: NO, Cl, HCl, HNO, Cl, ClO, ClO_2, ClO_3, $\underline{HClO_4}$,

at 165°C: NO, Cl, HCl, ClO, ClO_2, ClO_3, $\underline{HClO_4}$,

4. Heath and Majer [17] have used a mass spectrometer to study the decomposition of AP. Decomposition products were detected in the temperature range 110–120°C. At very low pressures (i.e., in the absence of gas molecular collisions), species such as NH_3, $NClO_4$, Cl_2,

Fig. 1   Arrhenius plot of the log (time) vs 1/T for the
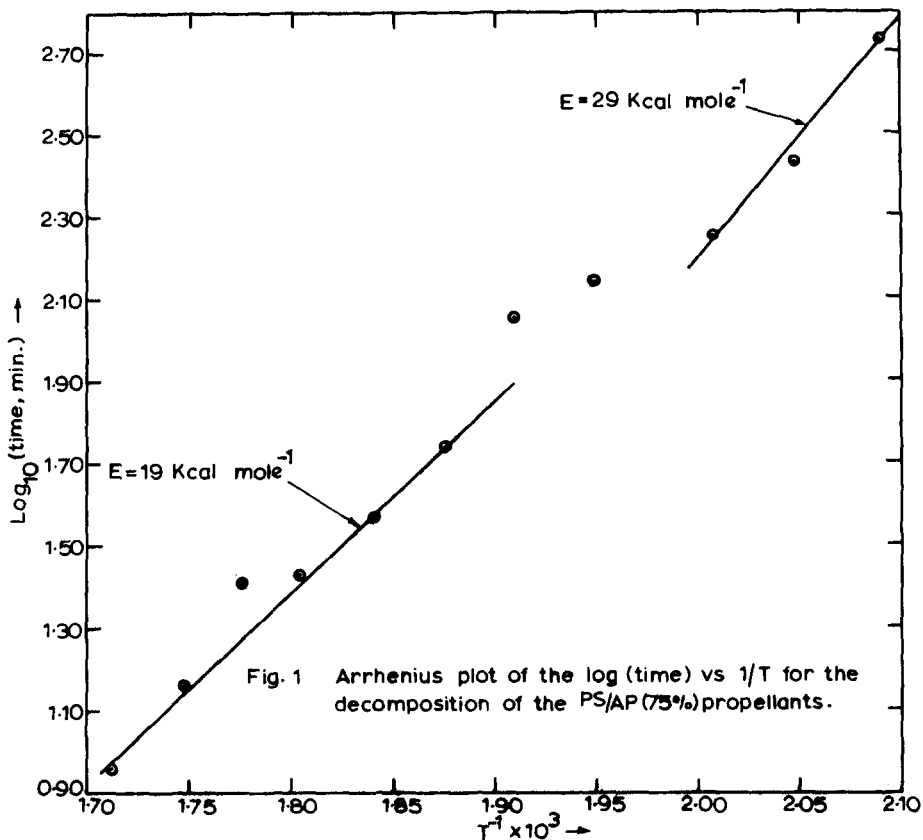decomposition of the PS/AP(75%)propellants.

Fig. 1.

HCl, nitrogen oxides, O_2, and Cl_2 were detected in the decomposition products, indicating that the main decomposition reaction takes place in the crystal rather than the gas phase.

5. Svetlov and Koroban [18] have studied the TD of AP at 150°C by prolonged measurements on a manometer. They have shown that significant amounts of $HClO_4$ are produced, some of which is obsorbed on the residual AP.

6. Recent studies by Kishore et al. [19] have shown that the preheating of AP at 150°C brings about an increase in the rate of AP decomposition during a certain preheating time. This has been explained on the basis of the formation of some acid that perhaps catalyses AP decomposition. Evidence for acid formation during preheating has been confirmed from pH measurements of aged samples.

In conclusion, the present work has shown that the rate-determining step in the ageing process of the solid composite propellant lies in the TD of the oxidiser, and in the case of AP-based propellant the mechanism involves proton transfer below 200°C.

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