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THERMAL ANALYSIS OF AMMONIUM PERCHLORATE + POLYSTYRENE + ADDITIVE MIXTURES I.

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The thermolysis of ammonium perchlorate (AP) and AP/polystyrene propellants was investigated with carboxylates of copper as additives. The rate of burning was found to be enhanced considerably. TG and ignition delay studies demonstrated that the high-temperature decomposition of AP is enhanced enormously by these additives, whereas the low-temperature decomposition remains unaffected. It is suggested that the main species catalysing the rate of burning or AP decomposition is CuO. Analysis showed that the increase in the rate of burning is controlled by the catalysis of AP decomposition.

The thermal decomposition of ammonium perchlorate (AP) has previously been thoroughly investigated due to its deflagration characteristics. The initial thermolysis reaction of this salt is proton transfer from NH_4^+ to the anion, liberating adsorbed and gaseous NH_3 and $HClO_4$ [1, 2]. Subsequently, these species react by radical reactions, providing N_2, H_2O, Cl_2, nitrogen oxides, etc. However, the thermal decomposition involves a complex set of competitive reactions.

The presence of metal oxide additives during the decomposition of AP is believed to accelerate the decomposition of ammonia [2-7]. In earlier studies, we reported [6, 7] that the carbonates and freshly prepared oxides of copper and chromium are better burning rate additives than their aged oxides. Therefore, it was planned to prepared carboxylate salts of copper to check their effectiveness as burning rate additives, because these also decompose to CuO as ultimate end-product. Combustion and thermolysis studies on AP, AP + additives, polystyrene (PS), PS + additives, AP + PS and AP + PS + additives have been undertaken in order to understand the role of

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these additives in the decomposition of AP and the combustion of AP/PS propellants.

Experimental

Copper benzoate (CB), copper salicylate (CS), copper malonate (CM) and copper adipate (CA) were prepared and purified by the methods reported earlier [8-10]. These were used as additives (200-400 mesh) in measurements of the burning rates of AP/PS propellants and also in AP thermolysis studies.

AP (Central Electrochemical Research Institute, Karaikudi, Tamil Nadu) having a purity of 99.1% (100-200 mesh) was used as such. Styrene monomer from Synthetics and Chemicals Ltd., Bareilly, was purified and polymerized as reported earlier [6].

Burning rate studies

AP/PS propellants with and without additives (5% by wt.) were prepared, and the rate of burning was measured at ambient pressure as reported earlier [6].

Thermoanalytical studies

The following experiments were performed in thermolysis studies on AP, PS and AP/PS propellants with and without additives.

a) Thermal analysis – Thermogravimetric analysis (TG) on PS with and without additives (5% by wt.) was performed at 548 K with the TG apparatus assembled in our laboratory [11]. TG curves for AP and AP + additive (10% by wt.) samples were recorded at 503 K. This temperature was selected in view of the fact that AP + additive samples deflagrate at 518 K (without undergoing appreciable weight loss). TGA data on AP/PS propellant samples with and without additives (5% by wt.) were obtained at 533 K, as deflagration occurred above 538 K in the presence of additives.

b) Ignition delay - Hot plate [12] (HP) and tube furnace (TF) techniques were employed for ignition delay studies on AP (100-200 mesh, powder form) with and without additives.

The HP was fabricated locally. Its temperature could be varied by means of a dimmerstat in series with the heater wire, and its surface temperature was recorded with a Pt-Pt (Rh 13%) thermocouple whose hot junction was insulated with a mica sheet and whose cold junction was kept in water at a fixed temperature. The maximum fluctuation in the temperature of HP was found to be ±2 deg. Ignition delay data in the temperature range 596-845 K were recorded by taking a sample weight of 100 mg in a cylindrical tube (dia = 2 cm and height = 5 cm) placed vertically on the HP; the mean of the four readings was taken and is reported in Table 3.

In the TF technique, the furnace temperature (range 573-623 K) was recorded with a mercury thermometer and controlled to ±1 deg by means of a dimmerstat. 50 mg of the sample (additive concentration = 0.5% by wt.) was taken in an ignition tube (height = 5 cm and dia = 0.4 cm) and the time gap between the insertion of the sample in the TF and the appearance of a flame was taken to be the ignition delay (t_{id}). The mean of the four runs for each sample was taken and the data are reported in Table 3.

Discussion

The data in Table 1 clearly show that the rate of burning was enhanced when, CB, CS, CM and CA were present as additives in AP/PS propellants. The rate of burning may be increased as a result of an acceleration of PS degradation and/or an acceleration of AP decomposition by these additives. In order to find out which of the above processes is sensitized, TGA studies were performed on PS, AP and AP/PS propellants in the presence of additives. Table 2 clearly shows that the decomposition of PS is inhibited, whereas AP decomposition is considerably catalysed. The decomposition of AP/PS was slightly enhanced by CB and CS, whereas CM and CA lowered the decomposition rate (Table 2).

Table 1 Rate of burning of propellant (AP/PS = 3/1) plus additive (5 % by wt.) at ambient pressure

Additives	r_{add}/r
Copper benzoate	1.93
Copper salicylate	1.86
Copper malonate	1.62
Copper adipate	1.45

$$r_{add}/r = \frac{\text{Burning rate of propellants + additives}}{\text{Burning rate of propellats (without additive)}}$$

The PS degradation inhibition may be due to a decrease in the formation of peroxide linkages in the backbone of the PS chains, which is the first and foremost process in its oxidative degradation. However, these additives also form reducing species on decomposition, which may be responsible for the inhibition of oxidative degradation. It seems that the enhancement of the rate of burning of the propellants is due to the sensitization of AP decomposition. Further, it was found that AP and propellants in the presence of additives deflagrate at 518 K and 538 K, respectively. The TG data on AP + additives show that the decceleratory period of AP decomposition is catalysed considerably at 503 K, whereas the induction and acceleratory periods remain unaffected. Therefore, it was considered interesting to study the ignition delay for AP and AP plus additives in order to understand the role of additives in combustion.

Table 2 Effect of additives on thermal decomposition of PS, AP and AP/PS propellants

Temp., K	Sample	*Rate of decomposition min^{-1}			**Catalytic activity C_A		
549	PS	0.57	0.54	0.47	-	-	-
	PS + CB	0.22	0.21	0.20	0.39	0.39	0.42
	PS + CS	0.29	0.25	0.18	0.51	0.46	0.38
	PS + CM	0.35	0.32	0.29	0.61	0.59	0.61
	PS + CA	0.25	0.23	0.22	0.44	0.43	0.46
503	AP	0.57	0.52	0.11	-	-	-
	AP + CB	0.57	0.59	0.55	1.00	1.13	5.00
	AP + CS	0.57	0.57	0.45	1.00	1.10	4.00
	AP + CM	0.55	0.41	0.27	1.00	0.79	2.40
	AP + CA	0.70	0.59	0.41	1.22	1.13	3.70
533	AP/PS	0.48	0.53	0.50	-	-	-
	AP/PS plus CB	0.72	0.68	0.67	1.50	1.28	1.30
	AP/PS plus CS	0.67	0.80	0.83	1.40	1.51	1.60
	AP/PS plus CM	0.41	0.32	0.35	0.85	0.60	0.70
	AP/PS plus CA	0.30	0.29	0.41	0.63	0.55	0.80

*Rate of decomposition for PS & PS + additives was calculated at 30, 35 and 40% decomposition and for AP, AP/PS propellants with and without additives at 15, 20 and 25 % decomposition

$$^{**}C_A = \frac{\text{Rate of decomposition of AP or PS or AP/PS plus additives}}{\text{Rate of decomposition of AP or PS or AP/PS}}$$

The results reported in Table 3 clearly show that the ignition delay of AP is lowered to a great extent by these additives. The activation energy (or ignition energy) was also assessed by using the following equation, derived by Gordon *et al.* [13]:

$$t_{id} = B \exp (E_a / RT) \qquad (1)$$

where t_{id} is the ignition delay and B is a constant. Equation (1) leads to the conclusion that a plot of log (t_{id}) *vs.* $1/T$ should give a straight line. The data for AP and AP + additives were found to fit Eq. (1); plots are given in Figs 1 and 2. The calculated activation energy values (E_a) reported in Table 4 for AP + additives are lower than for AP with both techniques. It seems that the high-temperature decomposition of AP is enhanced enormously by these additives and consequently the rate of burning is increased.

The mechanism of action of these additives seems to be similar to that of carbonates of copper and chromium suggested in our earlier publications [6, 7]. These studies have also proved the contention that CuO is the real catalyst during the burning of propellants and the high-temperature decomposition of AP. CuO has also been proved to be the ultimate decomposition product of carboxylates of copper reported by Bassi *et al.* [14-16]. The freshly formed CuO would have a finer particle size and the large number of

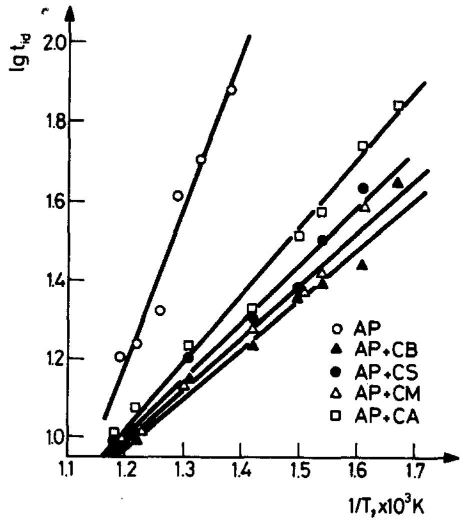

Fig. 1 Plots of log (t_{id}) *vs.* $1/T$ for AP and AP + additives (Hot plate technique)

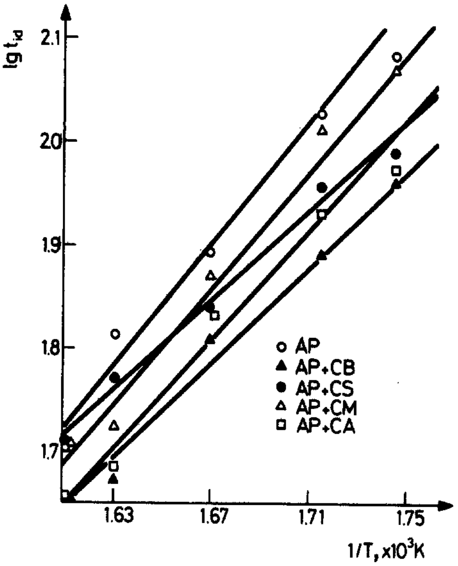

Fig. 2 Plots of log (t_{id}) *vs.* $1/T$ for AP and AP+additives (Tube furnace technique)

Table 3 Ignition delay (t_{id}) for AP and AP plus additives

Technique	AP		AP + additives				
	Temp.,	t_{id}	Temp.,	t_{id} (sec.)			
	K	sec.	K	AP+CB	AP+CS	AP+CM	AP+CA
Hot plate	596	-	596	45	-	-	70
	700	DNI	621	28	43	39	55
	723	76	646	25	32	26	38
	747	58	665	23	24	23	33
	770	41	703	17	20	19	21
	793	21	759	14	16	14	17
	815	17	814	10	12	10	12
	838	16	845	09	10	10	10
Tube furnace	573	122	573	92	97	120	93
	583	106	583	78	91	104	86
	598	78	598	65	68	74	69
	613	66	613	47	59	53	48
	623	58	623	45	52	51	45

DNI - did not ignite

defects and dislocations in its crystal lattice would provide active sites for the adsorption of the reactants. Consequently, the rate of burning would be increased. It may be concluded here that carboxylates of copper are better burning rate catalysts and act as sensitizers of AP decomposition. The catalytic activity of these additives was found to be inversely related with the activation energy, as shown in Fig. 3. It has also been observed that aromatic carboxylic salts of copper are better thermolysis catalysts than aliphatic copper salts (Table 1).

Table 4 Kinetic parameters for AP and AP plus additives

Sample	Activation Energy, kcal/mol	
	Hot plate (HP) technique	Tube furnace (TF) technique
AP	19.2	14.1
AP+CB	6.0	10.0
AP+CS	7.0	10.5
AP+CM	8.1	13.1
AP+CA	6.1	12.3

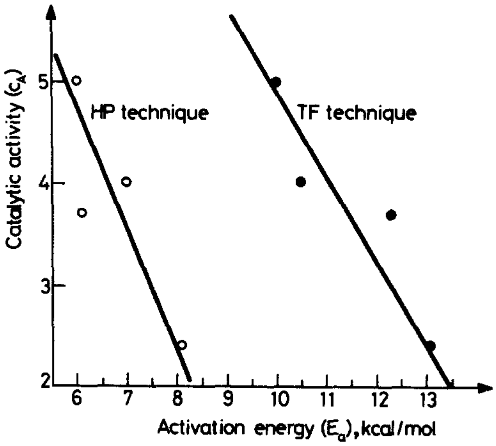

Fig. 3 Plots of catalytic activity (C_A) vs. activation energy (E_a) for AP+additives

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Zusammenfassung — Unter Zusatz von Kupfercarboxylaten wurde die Thermolyse von Ammoniumperchlorat- (AP) und AP/Polystyrol-Treibstoffen untersucht. Die Brenngeschwindigkeit wird erheblich erhöht. TG- und Zündverzugsuntersuchungen zeigen, daß die Zersetzung von AP durch Zusatz dieser Additive bei hohen Temperaturen enorm ansteigt, während sie bei niederen Temperaturen unverändert bleibt. Es wird darauf hingedeutet, daß die wichtigste Komponente zur Katalyse des Brennvorganges bzw. der Zersetzung von AP das Kupferoxid CuO ist. Eine Untersuchung zeigte, daß der Anstieg der Brenngeschwindigkeit durch die Katalyse der Zersetzung von AP bestimmt wird.