The thermal decomposition of ammonium perchlorate (AP) containing a burning-rate modifier

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Abstract

The effect of the presence of a ferruginous compound on thermal decomposition of ammonium perchlorate (AP) was studied using a differential thermolanalysis (DTA) and a thermogravimetric analysis (TGA). It was found that the maximum decomposition reaction temperature (T_m) of AP is reduced in the presence of ferruginous compound, and is shifted to lower temperatures as the concentration of ferruginous compound is increased. The reducing ability of catocene on the thermal decomposition of AP is more efficient than that of two other ferruginous compounds investigated. The decomposition mechanism of AP powder of fine particle size differs from that of AP of larger particle size.

INTRODUCTION

Ammonium perchlorate (AP) is widely used as an oxidizer in energetic composites. Ammonium perchlorate is employed in most solid composite propellants, and various attempts to increase their burning rates have been made by many investigators [1–4]. The transition metal oxides, such as Fe_2O_3, CuO, $CuCr_2O_4$ and MnO_4 have proved to be effective catalysts for the burning-rate modifier. In recent years, in order to increase the burning rate and to address the problems of the processing and storage of composite propellants, the catalytic effect of organic compounds, such as the ferrocene series of compounds, on solid composite propellants has been studied [5–7].

Although it is well known that transition metal oxides affect the decomposition characteristics of polymers and oxidizers, such as ammonium perchlorate (AP), the exact mechanism of the effects on solid propellants is not yet clear. The object of this study is to elucidate the thermal decomposition of AP powder in the presence of various kinds of ferruginous compounds.

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EXPERIMENTAL

Sample preparation

All test samples were prepared as follows. The AP powder was dispersed in acetone; then Fe_2O_3, catocene or ferrocene-CHO was added. The composition of each formulation is listed in Table 1. The mixture of AP/ferruginous compound/acetone was mixed well and then the acetone

TABLE 1

DTA and TG results of AP/ferruginous compound formulations

No	AP particle size/μm			Catalyst [a]			Catalyst conc./wt.%			DTA/°C			TG Weight-loss ratio/wt.%	
	50	225	400	I	II	III	1	3	5	Endo.	Exo. 1st	2nd	1st	2nd
1	✓					✓	✓			245	316	388	13	83
2	✓					✓		✓		245	317	383	8	90
3	✓					✓			✓	245	317	285	11	81
4		✓				✓	✓			244	317	391	11	87
5		✓				✓		✓		245	317	379	12	85
6		✓				✓			✓	245	–	379	–	94
7			✓			✓	✓			243	318	380	16	83
8			✓			✓		✓		243	317	376	14	81
9			✓			✓			✓	243	317	381	15	81
10	✓				✓		✓			245	315	412	11	84
11	✓				✓			✓		245	150/316	401	3.4/11	85
12	✓				✓				✓	246	148/313	378	4.8/10	85
13		✓			✓		✓			244	318	388	13	85
14		✓			✓			✓		244	151/320	384	2/13	83
15		✓			✓				✓	244	148/323	378	3/10	83
16			✓		✓		✓			244	318	410	14	84
17			✓		✓			✓		244	148/322	406	3/11	84
18			✓		✓				✓	243	148/321	396	4/12	83
19	✓			✓			✓			246	310	373	–	99
20	✓			✓				✓		246	169/313	359	–	97
21	✓			✓					✓	246	171/313	351	4/12	85
22		✓		✓			✓			244	320	381	12	87
23		✓		✓				✓		245	320	371	12	87
24		✓		✓					✓	244	172/325	378	4/10	85
25			✓	✓			✓			244	325	365	15	83
26			✓	✓				✓		244	171/311	373	3/12	81
27			✓	✓					✓	243	171/318	368	3/11	81

[a] I, catocene; II, ferrocene-CHO; III, Fe_2O_3.

was removed under vacuum conditions. The mixture was dried in an oven at 50°C for 1 day.

TG–DTG measurement

TG–DTG measurements were carried out using a Du Pont 2000 thermal analyzer. In the TG–DTG measurements, samples weighing about 5 mg were heated at a rate of $10°C\,min^{-1}$ from 30°C to 500°C under a static atmosphere of nitrogen. The results of the TG measurements are shown in Fig. 2 and Tables 1 and 2.

TABLE 2

DTA and TG results of the AP/catocene series

No	AP particle size/μm				Catalyst conc./wt.%		DTA/°C			TG Weight-loss ratio/wt.%	
	3	50	225	400	1	5	Endo.	Exo. 1st	2nd	1st	2nd
1	✓				✓		245	305	373	25	73
2	✓					✓	428	179/314	350	0.5/43	52
3		✓			✓		246	310	373	–	99
4		✓				✓	246	171/313	351	4/12	85
5			✓		✓		244	320	381	12	87
6			✓			✓	244	172/325	378	4/10	85
7					✓		244	325	390	15	83
8				✓		✓	243	171/318	368	3/11	81

DTA and DSC measurements

DTA and DSC measurements were performed using Du Pont 1090 and 2000 thermal analyzers. In the DTA (or DSC) measurements, samples weighing 2–4 mg were heated at a rate of $10°C\,min^{-1}$ in a crucible from 30°C to 500°C under a static atmosphere of nitrogen. The results of the DTA measurements are shown in Tables 1 and 2 and Figs. 1 and 3–5.

RESULTS AND DISCUSSION

The DSC and TG–DTG results of normal AP (without ferruginous compound) are shown in Fig. 1. Three typical features of TG curves of AP powder coated with different ratios of ferruginous compound are shown in Fig. 2. Typical DTA measurement results of AP coated with different ratios of ferruginous compound are shown in Fig. 3. The DTA results of different
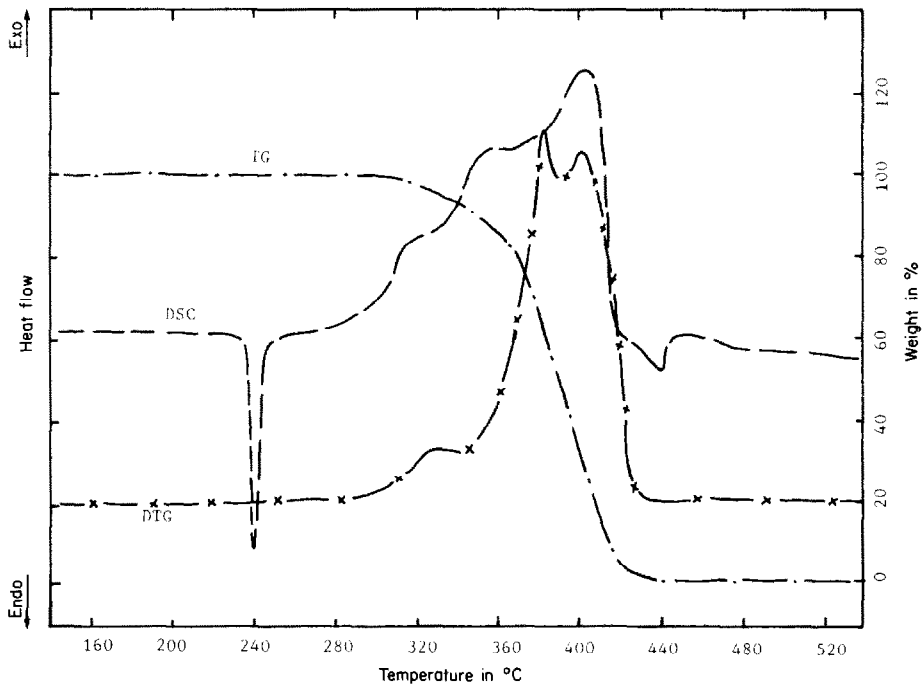
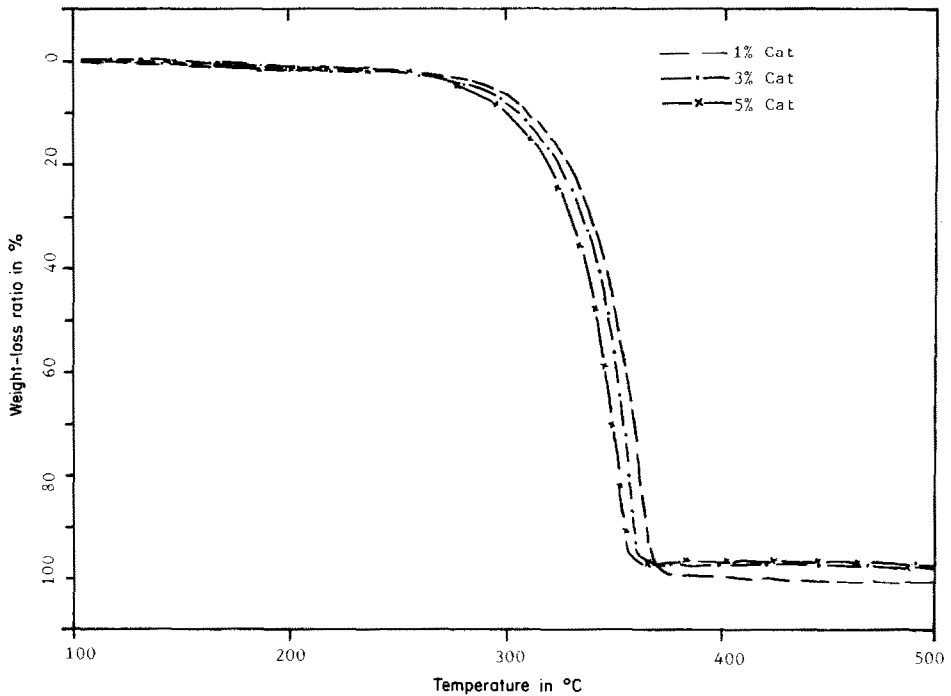Fig. 1. DSC and TG–DTG results for AP powder without catalyst.

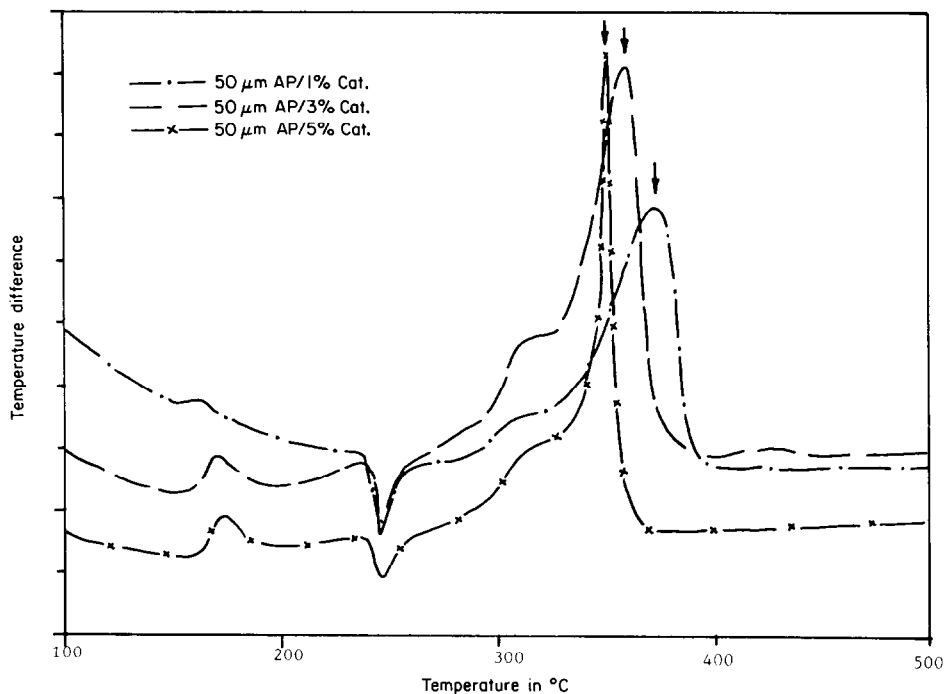Fig. 2. TG results for AP powder with different concentrations of catalyst.

Fig. 3. DTA results for AP powder with different concentrations of catalyst.

particle-sized AP coated with same ratio of ferruginous compound are shown in Fig. 4.

From Fig. 1, it can be seen that two distinct weight-loss reactions occur at 316°C and 410°C for pure AP particles with weight losses of 17% and 80%, respectively. In addition, Fig. 1 shows that there is an endothermic peak at 240°C, without weight loss. This can be attributed to the phase transition of AP from the orthorhombic to cubic form [3]. These results agree with those reported earlier [3, 4].

The TG results for AP particles coated with ferruginous compound are shown in Fig. 2. The decomposition temperature of AP shifts to lower temperatures when ferruginous compound is added, and the shift increases as the concentration of ferruginous compound is increased. The TG test results of each formulation are shown in Table 1. It was revealed that the weight-loss ratios are of the same order for each formulation. In addition in the DTA results shown in Fig. 3, the maximum decomposition reaction temperature T_m decreases as the ferruginous compound concentration is increased. Therefore, it is concluded that the decomposition temperature T_m of AP is affected by the ferruginous compound, but that the weight-loss ratio is unchanged as it is added.

From Table 1, it can be seen that there is a 5% weight-loss reaction taking place for some AP/Cat (AP coated with catocene) and AP/FCHO
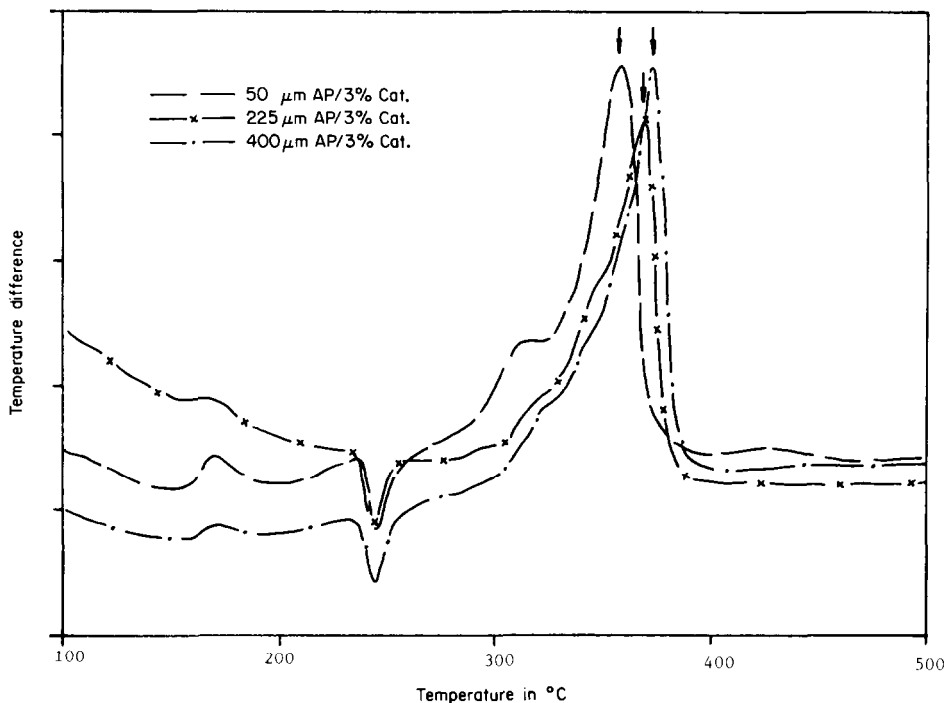
Fig. 4. DTA results for AP/catalyst systems with different particle sizes of AP.

(AP coated with ferrocene carboxaldehyde) formulations below 200°C. But there is no weight loss for the AP/Fe$_2$O$_3$ system. The difference can be explained as follows.

For the AP/FCHO system, there is a weight loss and an exothermic reaction at around 145°C. For the AP/Cat system, there is a weight-loss and an exothermic reaction at around 170°C. Referring to the TG measurement results and comparing the ingredient ratio of each formulation, it can be concluded that the exothermic, weight-loss reaction below 200°C is the decomposition reaction of catocene or FCHO. The catocene or FCHO is oxidized to Fe$_2$O$_3$ powder by the heating process. In the AP/Fe$_2$O$_3$ system, the Fe$_2$O$_3$ powder cannot be oxidized any more. Therefore, no oxidation reaction takes place for the AP/Fe$_2$O$_3$ system at around 200°C. In addition, in some AP/Cat and AP/FCHO systems, there is no reaction at around 200°C. This might be attributable to the lower concentration of catocene or FCHO in these AP/Cat and AP/FCHO systems. The weight-loss reaction of catocene or FCHO is small. Therefore, there is no remarkable change taking place. Furthermore, for AP powder the phase transition (from orthorhombic to cubic) takes place at around 240°C and the phase transition temperature is unchanged by the addition of ferruginous compound.

Two exothermic reactions take place for AP powder coated with

ferruginous compound. The first occurs at 317°C for most of AP/ferruginous compound formulations. But for the fine particle-size AP/Cat system, the first exothermic reaction occurs at around 310°C. There are no notable differences in the first exothermic reactions of pure AP and AP/ferruginous compound formulations.

The T_m value of the second exothermic reaction of AP coated with ferruginous compound shifts to lower temperatures when compared to pure AP powder. It was also found that the T_m of the second exothermic reaction is affected by AP particle size and by the nature of the ferruginous compound used. For example in Fig. 4 and Table 1, it can be seen that the T_m of the second exothermic reaction of the AP/Cat system shifts to lower temperatures when the AP particle size is reduced (in the presence of the same concentration of catocene). Likewise, with the same particle size of AP, the T_m value of the second exothermic reaction is shifted to lower temperatures when the concentration ferruginous compound is increased (Fig. 3). The same results were also found in the AP/FCHO and AP/Fe$_2$O$_3$ systems.

However some of the data do not agree with the majority of the experimental results. This may be attributed to experimental deviation, or be caused by non-uniform coating of the ferruginous compound.

In addition, it was found that the efficiency of catocene in reducing the T_m of the second exothermic reaction of AP is greater than that of the two other ferruginous compounds. The Fe$_2$O$_3$ powder is the least effective catalyst of the three. The reason may be as described below.

Catocene or FCHO catalysts are dispersed much better than normal Fe$_2$O$_3$ powder in AP/burning-rate modifier systems. The catocene or FCHO is oxidized to Fe$_2$O$_3$ compound when heated to 150–200°C. The particle size of the resulting Fe$_2$O$_3$ is smaller than that of the Fe$_2$O$_3$ catalyst powder. Therefore, although the percentage of Fe in Fe$_2$O$_3$ powder is higher than in catocene or FCHO, the reducing ability of catocene or FCHO on the T_m of the second exothermic reaction of AP is better than that of Fe$_2$O$_3$ powder.

Table 3 shows the autoignition temperature of mixtures of AP, burning-rate modifier and binder. The autoignition temperature of the AP/burning-rate modifier/binder system is lower than that of the AP/Burning-rate modifier system by about 10–40°C. It can be concluded that the binder and ferruginous compound form a synergistic function which enhances the decomposition reaction of AP. The reducing ability of a mixture of binder and burning-rate modifier on the autoignition temperature of AP is better than that of additive alone.

In addition, there are two different reaction patterns seen on Fig. 5. There are two indistinct peaks for fine particle sizes of AP, but for large particle sizes two overlapping reactions are found, resulting in shoulders on the peaks. In the TG–DTG measurement results, different weight-loss

TABLE 3

Autoignition temperature of AP powder with and without catalyst

No	Filler/wt.% AP			Binder [a]/wt.%		Catalyst [b] (8% of AP)					Autoignition temp./°C
	95	80	58.2	HTPB 38.7	HF 20	None	Cat	nBF	Ferr	Fe_2O_3	
1	✓						5%				315
2	✓								5%		337
3	✓									5%	354
4		✓			✓						212
5			✓	✓							325
6			✓	✓			3.1%				294
7			✓	✓				3.1%			297
8			✓	✓					3.1%		296
9			✓	✓						3.1%	320

[a] HTPB, hydroxyl-terminated polybutadiene; HF, hydroxyl-terminated polybutadiene-ferruginous compound. [b] Cat, catocene; nBF, n-butyl ferrocene; Ferr, ferrocene.
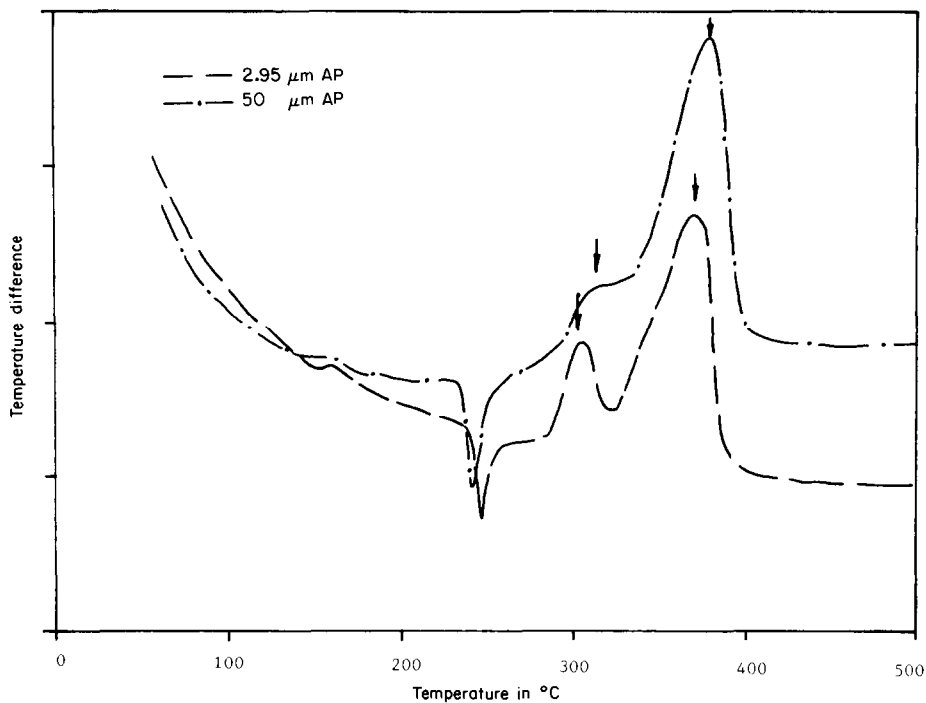

Fig. 5. DTA results for AP powder with different particle sizes.

ratios were found for fine or coarse particles of AP. Further investigation of the effect of particle size on the thermal decomposition of AP is required.

CONCLUSION

The maximum decomposition reaction temperature T_m of AP was shifted to lower temperatures when catocene, FCHO or Fe_2O_3 was added. The T_m of AP decreased as the concentration of catocene, FCHO or Fe_2O_3 increased. The ferruginous compound affects the second exothermic reaction temperature of AP. But there is no remarkable change for the first exothermic reaction when ferruginous compound is added. Furthermore, the reducing ability of catocene on AP decomposition is better than that of FCHO or Fe_2O_3. The decomposition mechanism for fine particle sizes of AP differs from that of AP with coarse particle sizes.

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