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Thermo-Analytical Techniques as useful Quality Control Tools in the Manufacture of Ammonium Per chlorate

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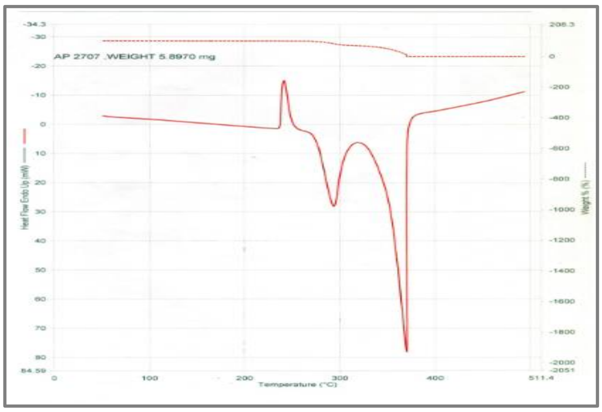
ABSTRACT

The utility of thermo-analytical techniques as production quality control tools in the manufacture of ammonium per chlorate is discussed. A random selection of three production batches (Batch capacity of 2 Tons batch^{-1}) were selected and studied employing thermo gravimetric (TG) and differential scanning calorimetric (DSC) methods. The endothermic enthalpies of crystallographic phase-transition from orthorhombic to cubic phase of three batches of ammonium per chlorate (AP) are in the range of 133.1 J g^{-1}-137.7 J g^{-1}, and the corresponding temperatures are in the range of 240.5℃ to 241.8℃. The peak temperatures of decomposition for the low-temperature decomposition (LTD) are in the range of 293.7℃ to 297℃; and high-temperature decomposition (HTD) are in the ranges of 370.3℃ to 376.1℃. The total exothermic enthalpies are in the range of 1655.6 J g^{-1} to 1668.4 J g^{-1}. The results are highly reproducible.

Graphical Abstract



TG – DSC Curves of AP Batch No. 2707.

Keywords: Ammonium Per chlorate, TG, DSC, Enthalpy, Phase-transition, Decomposition, Quality Control Tool.

INTRODUCTION

Ammonium per chlorate (AP), an inorganic white crystalline oxidizer, is extensively used as a part of the composite solid rocket propellant formulation across the globe. The combustion characteristics of a composite solid rocket propellant are highly dependent on the thermal and combustion characteristics of AP, may be due to its presence in larger quantity in comparison with the other constituents of the propellant composition [**1-14**].

Influence of various reaction parameters such as particle-size, aging of crystal etc., on thermal decomposition of AP was discussed by Keenan *et al* [**15**]. Heat released during the thermal decomposition of pure AP still remains a controversy. Hao *et al* [**16**] reported a value of 941 J g^{-1}; while Zhang *et al* [**17**] reported a value of 875 J g^{-1}; and Patil *et al* [**18**] reported a value of 834 J g^{-1}. A value of 590 J g^{-1} was reported by Hosseini *et al* [**19**] and Xu *et al* [**20**]. Yet, some other variation in values observed include, those by Wang *et al* [**21**] (576 J g^{-1}); and Eslami *et al* [**22**] (450 J g^{-1}); and Wang *et al* [**23**] (450.3 J g^{-1}).

Therefore, towards better understanding of these discripancies, simultaneous thermo gravimetric (TG), and differential scanning calorimetric (DSC) experiments were carried out on three regular production batches from the Ammonium Per chlorate Experimental Plant (APEP) of Vikram Sarabhai Space Centre, Indian Space Research Organization (ISRO), Department of Space, Government of India; and the results are discussed here under.

MATERIALS AND METHODS

Ammonium per chlorate samples considered in this study was procured from the Ammonium Per chlorate Experimental Plant (APEP) of Vikram Sarabhai Space Centre, Indian Space Research Organization, Department of Space and Government of India. The simultaneous thermo gravimetric (TG) and differential scanning calorimetric (DSC) experiments were conducted employing Perkin–Elmer –07 Model, at a sample heating rate of 10°C. min^{-1}, in an inert atmosphere of pure Argon, at a gas flow rate of 100 mL.min^{-1}.

RESULTS AND DISCUSSION

The particle-size distribution of three random batch samples of AP (Batch Nos. 2707, 2845, 2846) considered in this study is shown in figure 1. In the AP Batch No. 2845, the particle-size fraction corresponding to 300-250 μ range is slightly higher. In the case of Batch No. 2707, the particle –size range between 45-125 μ is relatively high. But for these small variations, all the three batches of

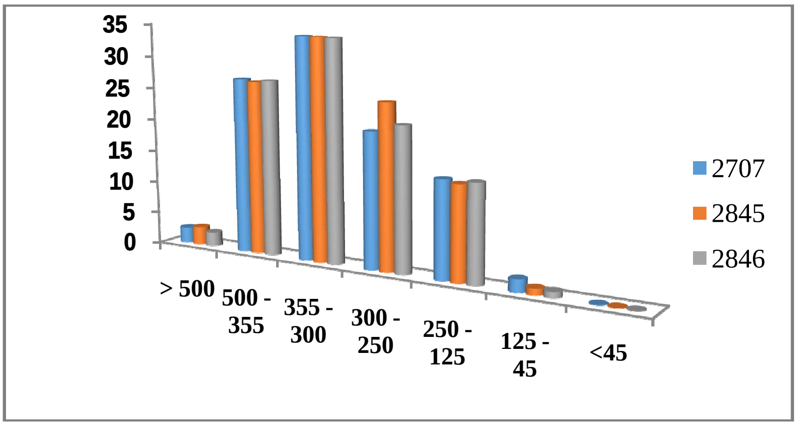


Figure 1. Particle–Size Distribution of Four Different Batches of Ammonium Per chlorate.

AP (each sample corresponds to 2 Tonnes /batch of production) are almost identical in terms of particle-size distribution. The chemical analysis of these three samples is presented in table1. From the chemical analysis of these three batches indicate that the production batches are highly reproducible. Thermal decomposition pattern of these three production batches as studied through simultaneous thermo-gravimetric (TG) and differential scanning calorimetric (DSC) techniques are presented through figure 2 to 4.

Table 1. Chemical Parameters Comparison for three Different Batches of Ammonium per chlorate

Chemical Parameter	Ammonium Per chlorate Batch Number		
	2707	2845	2846
Assay as NH_4ClO_4 (%)	99.35	99.28	99.30
Total Moisture (%)	0.19	0.20	0.20
Surface Moisture (%)	0.05	0.05	0.04
Sulphated Ash (%)	0.08	0.08	0.06
Water Insoluble's (%)	0.004	0.004	0.004
pH of 1M Solution	4.78	4.84	4.81
Chlorate as ClO_3 (%)	0.01	0.01	0.01
Chloride as Cl (%)	0.03	0.01	0.01
Sulphate as SO_4 (%)	0.003	0.003	0.001

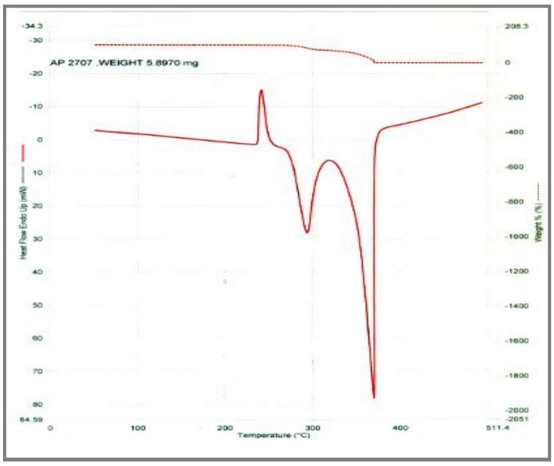


Figure 2. TG – DSC Curves of AP Batch No. 2707.

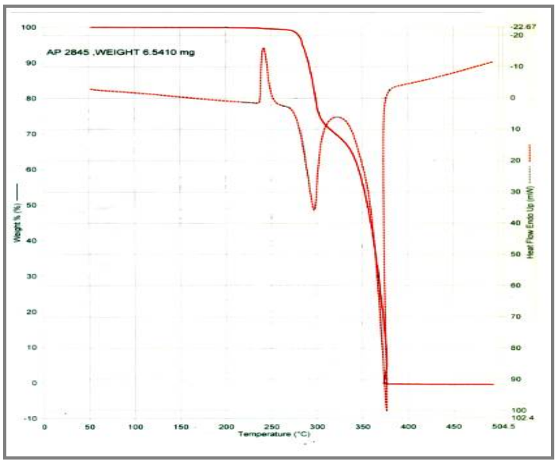


Figure 3. TG –DSC Curves of AP Batch No. 2845.

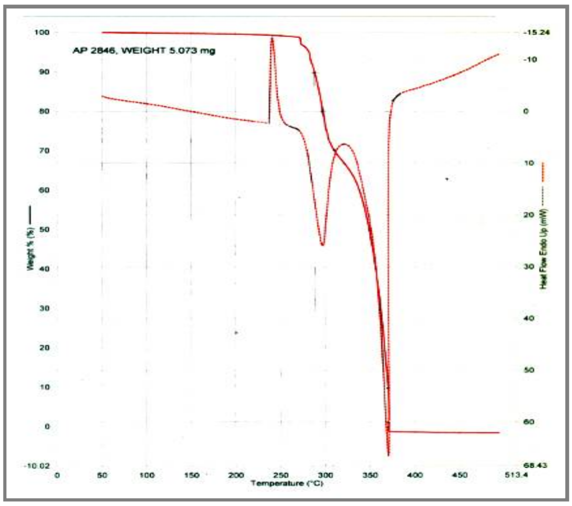


Figure 4. TG - DSC Curves of AP Batch No. 2846.

The heat involvement for the endothermic crystallographic phase-transition from orthorhombic to cubic phase for these three batches of AP samples is presented in table 2. Similar data for the low – temperature decomposition (LTD) and high-temperature decomposition (HTD) of AP for these three batches of AP is presented in table 3.

Table 2. Thermal Data for the Crystallographic Phase-transition of four batches of AP

AP Batch No.	Endothermic Phase-transition Temperature (°C)	Endothermic Enthalpy (J g^{-1})
2707	241.5	135.2
2845	241.8	137.7
2846	240.5	133.1

The endothermic phase-transition is not as simple as we normally state. In the initial phase, at low temperatures, the phase-transition of AP follows atom –by –atom process, and when the temperature approaches 243°C, the transition is martensite type. In either of the cases, the polymorphous transition proceeds through the formation and growth of the nuclei of the new phase; and the growth of the martensite nuclei occurs in a jump wise manner [24]. Another theory proposes that, based on single crystal X-ray diffraction data, the existence of a second order irreversible phase-transition takes place, besides the reversible first-order orthorhombic to cubic phase-transfer occurring slightly below the known transformation temperature [25]. While the first order transition which normally occurs rather suddenly, the second order transition occurs over a range of temperature and affects the decomposition of AP [26]. The crystallographic phase- transition temperatures are highly reproducible for all the three batches, and the endothermic enthalpy range between 133.1 J g^{-1} to 137.7 J g^{-1}. Similarly, the total exothermic enthalpy of both LTD and HTD put together are ranging between 1655.6 J $g^{-1}$and 1668.4 J g^{-1}.

Table 3. Thermal Data for the LTD and HTD of AP

AP Batch No.	Exothermic Low-temperature Decomposition of AP		Exothermic High-temperature Decomposition of AP		Total Exothermic Enthalpy (J g^{-1})
	Peak Temperature (°C)	Enthalpy (J g^{-1})	Peak Temperature (°C)	Enthalpy (J g^{-1})	
2707	293.7	431.5	370.3	1236.9	1668.4
2845	297.0	463.2	376.1	1192.4	1655.6
2846	296.7	446.8	370.3	1218.2	1664.2

APPLICATION

Thermo-analytical techniques as useful quality control tools for the production of ammonium per chlorate manufacture. Observed parameters are reproducible and within the acceptable range. When used in composite solid rocket propellant formulations, are expected to give reproducible combustion rates avoiding trial mixing.

CONCLUSION

Under the given set of production parametric conditions, the three batches are highly reproducible. Endothermic phase-transition enthalpy, and the total exothermic enthalpies indicate that there is a good reproducibility of production batches and are expected to give same order of combustion rate performance when used in the propellant formulation.

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