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Thermal decomposition of Ammonium per chlorate-PART-II: Effect of Source of Supply

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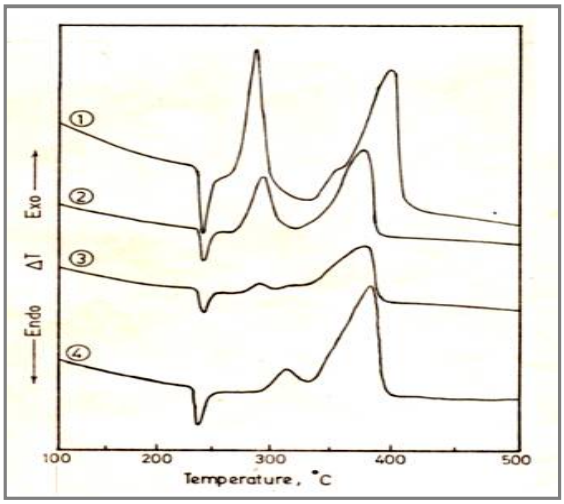
ABSTRACT

Thermal decomposition of ammonium per chlorate (AP) from different sources of supply is the subject matter of this research program. Both isothermal and non-isothermal studies have been reported. The AP samples from PEPCON, USA; MITSUBISHI, Japan: WIMCO, Mumbai; and APEP, VSSC, ISRO were employed in these studies. The low-temperature Isothermal experiments were conducted at 200℃, 210℃, and 220℃. Both, isothermal and non-isothermal experiments were conducted in an inert atmosphere of pure nitrogen, at controlled gas-flow, and at a sample heating rate of 10℃.min^{-1}. Induction periods reduced with increase in isothermal temperature. Sigmoid curves were observed under isothermal condition of 220℃ with progressive decomposition taking place. The order of thermal stabilities of these per chlorates are – PEPCON-AP > MITSUBISHI-AP > WIMCO = APEP.

Graphical Abstract:



DTA-Curves of AP from Different Sources of Supply.

Keywords: PEPCON-AP, MITSUBISHI – AP, WIMCO-AP, Uncoated APEP-AP, Coated APEPAP, Isothermal, Non-isothermal, decomposition.

INTRODUCTION

The thermal decomposition characteristics of ammonium per chlorate (AP) are known to influence the propulsion performance of solid rocket propellants [1]. During manufacture of composite solid rocket propellants, situations arise of using AP from different sources of supply to meet production demands or in contingency situations. In such cases, since the physical characteristics of AP vary from source to source, one need to understand the thermal behavior of AP from different sources for a given propellant formulation. The decomposition rate of AP and its kinetic parameters can be affected depending on the pre-history, pre-treatment, crystal dimensions, sample size etc [2]. Galwey *et al.*, [3] studied the decomposition of single crystals, powder and tablets of AP under identical conditions, and observed increasing activation energy values for these samples. In the present work, attention is focused on the thermal stability of AP from different sources of supply that can influence the combustion properties of composite solid rocket propellants based on these AP samples.

MATERIALS AND METHODS

Ammonium per chlorate samples employed in this study include those obtained from - Ammonium Per chlorate Experimental Plant (APEP), Vikram Sarabhai Space Centre, ISRO, Department of Space, Government of India; WIMCO, Mumbai, India; MITSUBISHI, Japan; and PEPCON, USA, Thermo-analytical techniques of Thermo gravimetric (TG), differential thermal analysis (DTA) were used employing DuPont-990 Thermal Analysis System, in an inert atmosphere of pure nitrogen, at a gas flow rate of 50 mL min^{-1},and a sample heating rate of 10°C min^{-1}. Particle-size distribution of AP samples was determined using BIS -Standard Sieves. The photomicrographs were produced using a high resolution microscope with photograph facility. The chemical composition of these AP samples was determined by employing the standard laid down procedures of ISRO.

RESULTS AND DISCUSSION

The chemical analysis of AP samples from these four sources of supply is summarized in table 1.

Table 1. Chemical properties of AP from Different Sources of Supply

Chemical Property	Different Sources of Ammonium per chlorate			
	ISRO, India	WIMCO, India	MITSUBISHI, Japan	PEPCON, USA
Purity as NH_4ClO_4 (%)	99.50	99.80	99.53	99.65
Total Ammonia (%)	14.40	14.44	14.40	14.42
Chloride as NH_4Cl (%)	Nil	0.013	Nil	0.019
Chlorate as NH_4ClO_3 (%)	0.024	0.023	0.012	0.005
Bromate as NH_4BrO_3 (%)	Nil	Nil	Nil	0.0003
Sulphate as $(NH_4)_2SO_4$ (%)	Traces	Nil	Traces	0.26
Sulphated ash (%)	0.33	0.06	0.05	0.26
Moisture (%0	0.02	0.04	0.025	0.024
pH of a 10 % Solution	4.50	4.50	4.71	6.40

The particle-size distribution of the four AP samples is shown in figure 1.

The particle-size distribution of ISRO and WIMCO match very well with mean particle-size being 200µ; for MITSUBISHI, Japan is around 300µ, and that for PEPCON, USA being around 400µ. The typical particle shape of these four samples is depicted in figure 2.

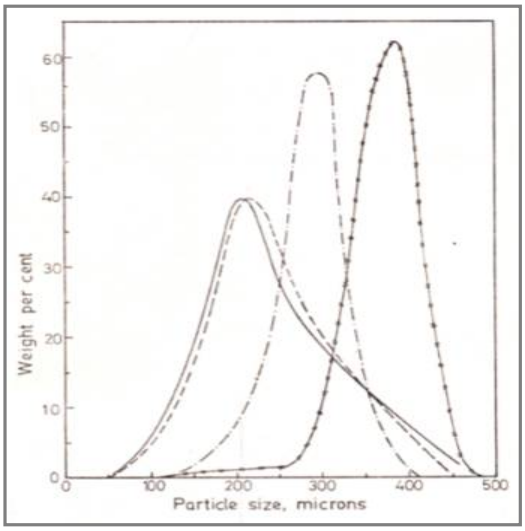


Figure 1. Particle-Size Distribution of AP from ISRO, WIMCO, MITSUBISHI, Japan; and PEPCON, USA (Particle –Size in Microns).

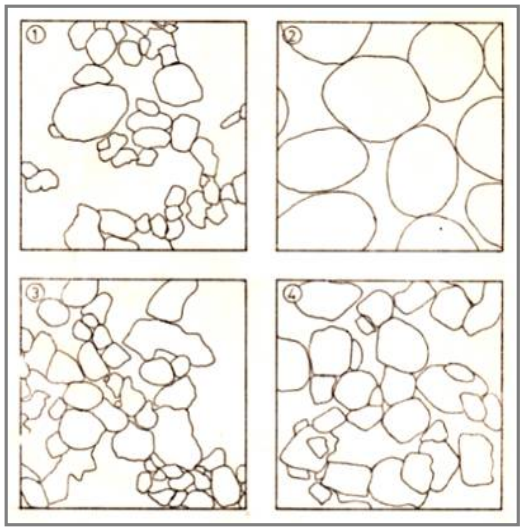


Figure 2. Particle shapes of AP particles from: (1). ISRO, India; (2). PEPCON, USA; (3).WIMCO, Mumbai, India; and (4). MITSUBISHI, Japan.

The AP particles from PEPCON are more spherical in nature and more uniform in size, while others contain particles of different shapes and sizes. These differences in particle-size distribution and particle-shape are expected to have profound influence on their thermal stability patterns. The thermal decomposition patterns of these samples as studied through thermo gravimetric (TG) method and are shown in figure 3.

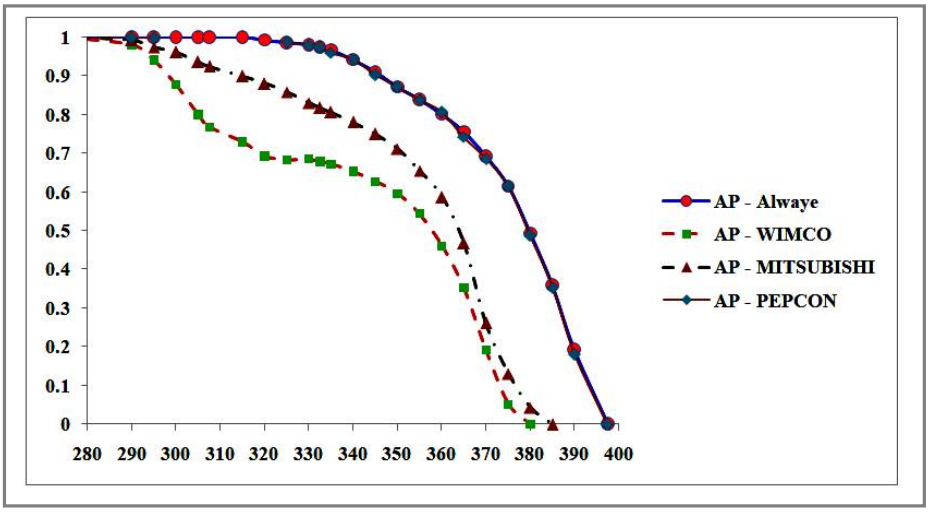


Figure 3. TG – Curves of AP from Different Sources of Supply.

While the onset of decomposition for APEP (ISRO) Sample and PEPCON, USA samples are around 315°C; for MITSUBISHI, Japan and WIMCO, MUMBAI samples are around 285°C. Similarly, if we examine the end-set temperature of decomposition of these samples, their thermal stability of APEP (ISRO-Sample and PEPCON, USA samples have the same end-set of decomposition temperature of around 398°C, while that for MITSUBISHI, Japan is about 385°C, and that for APEP (ISRO) sample is 380°C.

The differential thermal analysis curves for these samples are shown in figure 4.

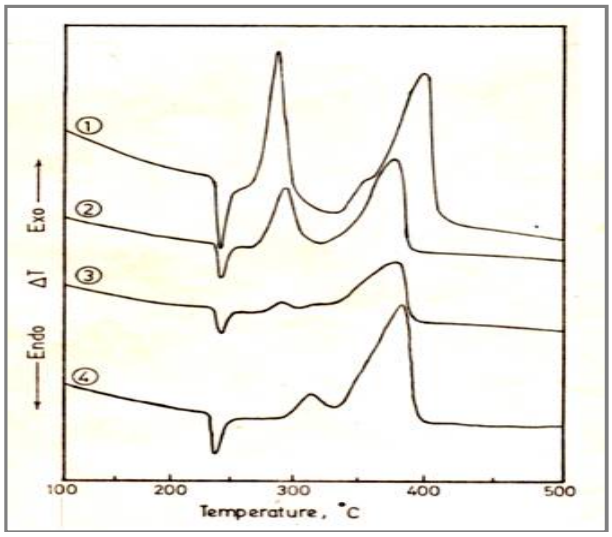


Figure 4. DTA – Curves of AP from Different Sources of Supply.

From the DTA thermograms it can be observed that, the crystallographic phase transition of AP, irrespective of the source of supply, remains the same at 238°C. The first exotherm is prominent in the order of APEP-AP > WIMCO–AP > PEPCON–AP > MITSUBISHI-AP. The low-temperature decomposition (LTD) peak for APEP-AP; WIMCO – AP; and MITSUBISHI-AP occurs almost at the same temperature (285°C). In the case of PEPCON-AP, it occurs at about 325°C. The high-temperature decomposition of AP occurs at about 398°C, 375°C, 375°C, and 385°C, for APEP-AP, WIMCO-AP, MITSIBISHI-AP and PEPCON-AP, respectively. Studies have been extended to low-temperature decomposition of these per chlorates under isothermal condition of 200°C, 210°C, and 220°C, to understand its thermal behavior. Figure 5 shows the isothermal behavior of these per chlorates at 200°C.

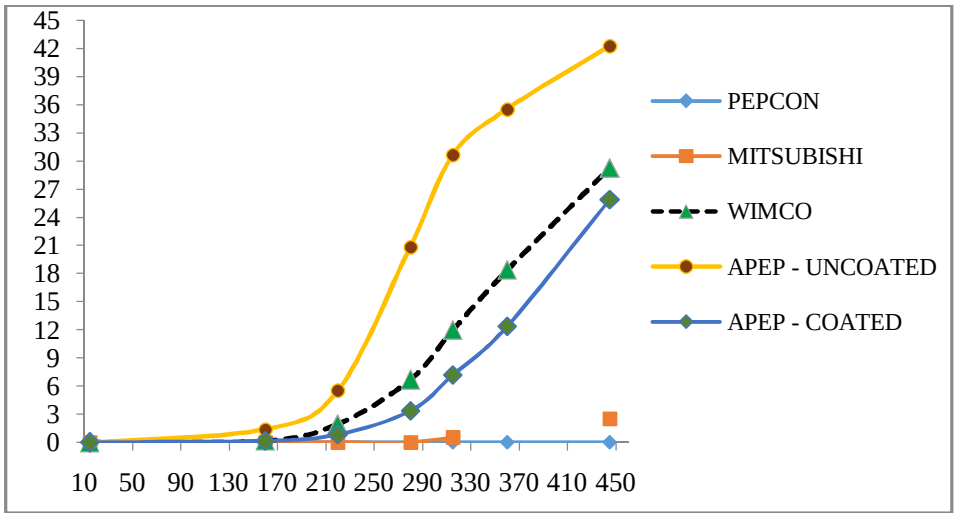


Figure 5. Isothermal Decomposition at 200°C of AP from different sources of supply
X-Axis: Time (t) in minutes Y-axis: Mass % loss.

At this isothermal temperature (200°C), induction periods are high, and PEPCON-AP does not decompose, while MITSUBISHI-AP has small decomposition. The other per- chlorates decompose considerably. The isothermal TG curves for these per chlorates at 210°C are presented in figure 6.

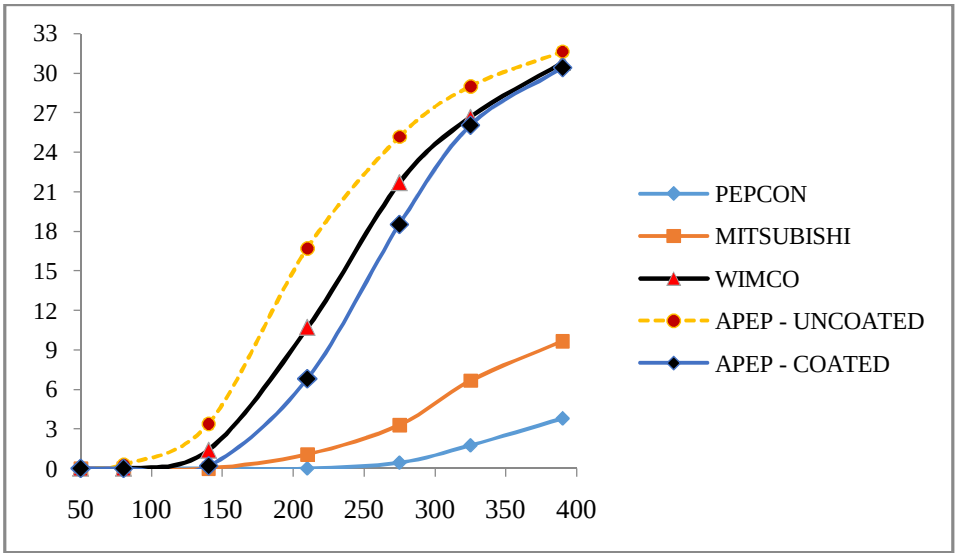


Figure 6. Isothermal TG Curves of per chlorates from different sources of supply at 210°C
X-axis: Time (t) in minutes, Y-axis: % mass loss.

From figure 6, it can be noticed that, the induction periods for PEPCON – AP and MITSUBISHI-AP are high relative to other per chlorates. Decomposition has begun in all the cases and is more prominent in the case of WIMCO-AP; APEP-AP (Uncoated); and Coated APEP- AP. Figure 7 shows the decomposition pattern of AP from different sources of supply under isothermal condition at 220°C.

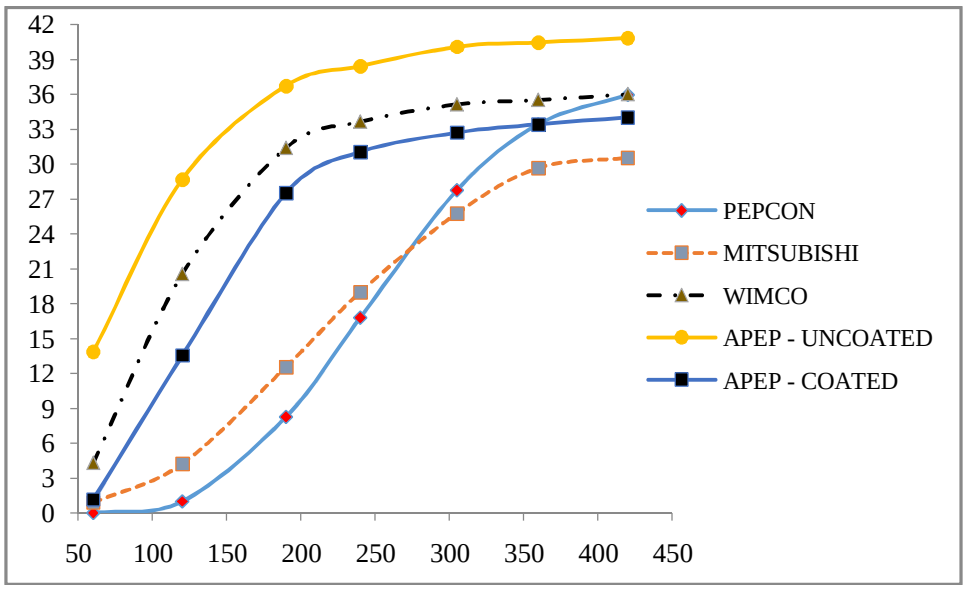


Figure 7. Isothermal Decomposition pattern of AP from different sources of supply at 220°C
X -axis: Time (t) in minutes, Y-axis: % mass loss.

From figure 7, it can be observed that, but for a small induction period in the case of PEPCON-AP, there is no induction period for other AP samples. Considerable reaction progresses in all cases. From the nature of the decomposition curve, we notice, both PEPCON-AP and MITSUBISHI-AP samples follow sigmoid curve. From the decomposition pattern the stabilities are in the order of (Uncoated) APEP-AP > WIMCO-AP > (Coated) APEP-AP > PEPCON-AP > MITSUBISHI-AP.

APPLICATION

These results are useful in understanding the behavior of propellant formulations when the source of supply of AP change and to fine tune the propellant formulation for reliable expected combustion performance.

CONCLUSION

The differences in thermal behavior of AP from different sources of supply are attributed to their particle-size distribution and shape of the particles.

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