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Investigations on Thermal Decomposition Behavior of Ammonium Nitrate Co-crystallized with Cadmium (II) Nitrate (Tetrahydrate)

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ABSTRACT

The present study investigates the influence of addition of Cadmium (II) Nitrate (Tetrahydrate) ($Cd(NO_3)_2.4H_2O$) on the thermal decomposition behavior of Ammonium Nitrate (AN) and on its various phase state transitions using Differential Scanning Calorimetry (DSC) analysis. Co-crystals of $Cd(NO_3)_2.4H_2O$ and AN were prepared by means of evaporation technique using a mixture of methanol and water as solvents and three samples were prepared. The quantity of $Cd(NO_3)_2.4H_2O$ was varied as 3, 6 and 10 percent of the total weight of the composition. DSC analysis of the samples was conducted in an inert isobaric atmosphere at a sample heating rate of 10 °C/min to assess their thermal decomposition behavior. A baseline, to facilitate comparison, was also obtained by analyzing untreated AN under same conditions. The present study established that $Cd(NO_3)_2.4H_2O$, when used in as low weight percentages as 3%, was capable of eliminating the phase state transition (II) along with a delay in the onset temperature of phase state transition (III) by a significant amount of ~20 °C. Addition of $Cd(NO_3)_2.4H_2O$ also lowered down the decomposition temperature range of the mixture which may enable faster liquefaction of the propellant ingredients leading to improved burn rates.

Keywords - Ammonium Nitrate, Cadmium (II) Nitrate (Tetrahydrate), Co-crystallization, Phase State Transitions, Differential Scanning Calorimetry, Thermal Decomposition Behavior.

1. INTRODUCTION

Solid propellants have been in existence since the invention of 'Black Powder' by Chinese around 9th century[1]. Owing to their peculiar inherent characteristics, solid propellants have been preferred over liquid propellants in certain applications. Their high lift-to-weight ratios, longer shelf life, ease of manufacturing, handling and storage, on-demand launch capabilities, high propellant densities and relatively simple motor design are few of the advantages associated with the use of solid propellant rockets[2].

A composite solid propellant (CSP) is a heterogeneous mixture of hydrocarbon/synthetic based fuel/binder, a crystalline oxidizer, metallic fuel, burn rate modifier/s and curing and plasticizing agent/s [3]. Crystalline oxidizer provides free oxygen upon its decomposition to enable self-sustaining combustion of the fuel in the absence of oxygenated environment. All of these ingredients are held together in a matrix provided by the binder which can also act as a fuel in certain conditions [4]. Metallic fuels like Aluminum (Al), Boron (B), Magnesium (Mg), Iron Oxide (Fe_2o_3), etc. assist in more energetic and aggressive combustion of the propellant [5]. Burn rate modifiers alter the burning rates and decomposition behavior of the propellant depending upon the requirement whereas curing and plasticizing agents are added to meet mission-specific physical and mechanical requirements [6-7].

Ammonium Perchlorate (AP, NH_4ClO_4) is a crystalline solid oxidizer which is currently being used in most of the CSP formulations, some of the notable examples being NASA's Space Shuttle solid rocket boosters (SRBs) and European Space Agency's (ESA) ARIANE-5 launcher. Extensive studies have been carried out by researchers all over the globe since last few decades to understand various aspects related to AP's decomposition and combustion mechanism [8-9]. Apart from vast available knowledge, AP delivers a superior ballistic performance, good thermal and shock stabilities and is safe to handle and store. But on the other hand, AP and AP-based composite solid propellants (APCPs) are not free from few of its inherent shortcomings. One major area of concern associated with the use of AP as a solid oxidizer is its chlorinated decomposition products. Production of HCl gas and inorganic chlorine compounds like Cl, Cl_2, ClO, ClOO, etc, in the exhaust of APCPs have raised environmental concerns and extensive theoretical and experimental research is being conducted worldwide to achieve a profound understanding of the same [10].

Detrimental effects to the environment and living organisms because of the use of APCPs have motivated the efforts of replacement of AP in the CSP formulation with green or clean-burning oxidizers [11, 12].

A green oxidizer or propellant is free of any halogenated and harmful exhaust products. Various green oxidizers are either already available or are being developed to serve as a replacement for AP to achieve more eco-friendly propellant formulations [13]. Such a green oxidizer which has been already in existence for a long time is Ammonium Nitrate (AN, NH_4NO_3) [14]. Ammonium nitrate is a crystalline nitrate salt of ammonium and is free of any kind of harmful halogens or toxic combustion emission products.

Ammonium Nitrate finds its application as an oxidizer in pyrotechnics, as a fertilizer in agriculture and as an explosive in form of Ammonium Nitrate Fuel Oil (ANFO). Instead of its clean burning exhaust, AN also suffers from a very limited use in the formulation of CSPs due to its own intrinsic shortcomings. Lower burning rates, inferior ballistic performance and its caking tendency makes it difficult for AN to be utilized as an oxidizer on a larger scale. One inherent characteristic of AN, which is considered to be one of the main reasons for its restricted use in the formulation of CSPs, is its five phase state transitions occurring between over a wide temperature range i.e. –200 °C to 125 °C [15]. Table 1 represents the temperature ranges for various phase state transitions of untreated AN.

Table 1 Phase State Transitions and Associated Temperature Ranges

Phase State Transition	Temperature Range
Phase State Transition (V)	–200 °C to –18 °C
Phase State Transition (IV)	–18 °C to 32 °C
Phase State Transition (III)	32 °C to 84 °C
Phase State Transition (II)	84 °C to 125 °C
Phase State Transition (I)	Above 125 °C

Severe structural changes in the AN's crystal lattice are experience due to these phase state transitions leading to extensive volumetric and density variations in the propellant formulations [16]. The adherence between the crystallites decreases due to volumetric changes thereby reducing the overall structural strength of the propellant grains during these thermal cycles [17]. The existence of such phase state transitions near the propellant processing and storage temperatures usually result in avoidance of application of AN as a solid oxidizer in CSP grains formulations [18].

Unpredicted cracks in the propellant grains can exist due to structural instability of AN-based composite solid propellants (ANCPs). The mass rate of generated combustion gases is directly dependent on burning surface area of the propellant. Formation of any cracks may open up new and unpredicted surfaces available for combustion which are likely to result in an unwanted rise in the operating pressure of the combustion chamber. High chamber pressures (P_c), beyond safety margins of the solid rocket motor (SRM) structures may lead to structural damages to the motor and failure of the mission. It is thus significant to stabilize AN for one or more of its phase state transitions, preferably those occurring around near-room and storage temperatures, to achieve stable and predicted combustion of ANCPs.

Various organic and inorganic additives, in significantly small quantities, have been suggested by researchers which may be employed for the preparation of Phase Stabilized Ammonium Nitrate (PSAN) [19-22]. In the case of inorganic stabilizers, the metal ion available from the metal salt, attaches itself to AN's crystal lattice thereby shifting the temperature ranges of phase state transition of AN crystals [23, 24].

Cadmium (II) Nitrate (tetrahydrate) (CdN, $Cd(NO_3)_2.4H_2O$) has been known to be utilized as flash powder for photographic applications in the past. It has been commonly used in theatrical pyrotechnics and fireworks and was selected for present investigation as a potential stabilizer because of its energetic combustion behavior. Also, CdN may dissociate into O_2 and NO_2 molecules during its thermal decomposition and such free oxygen may contribute in the combustion of fuel. The weak nature of N–O bond makes NO_2 a good oxidizer as at elevated temperatures (around 150 °C), NO_2 tends to decompose with release of free oxygen through an endothermic process ($\Delta H=114$ kJ/ mol) [25].

For the present study, three samples were prepared by co-crystallizing CdN with untreated AN using evaporation technique and weight percentage of CdN in the composition was varied as 3%, 6% and 10%. Differential Scanning Calorimetry (DSC) analysis of the co- crystals and that of untreated AN was carried out at a heating rate of 10 °C/min. DSC thermograms for all the analyzed samples were compared to evaluate the variations achieved in the onset temperature ranges and/or complete stabilization of any of the phase state transitions of AN resulting from the addition of CdN, at and above near-room temperatures.

2. EXPERIMENTAL PROCEDURES

2.1 PREPARATION OF CO- CRYSTALS

Various techniques have been reported and employed for synthesizing co-crystals [26]. Though respective technique has its own associated advantages and disadvantages, evaporation technique has been employed in this study owing to its minimum complexity and viability under standard laboratory conditions. Solvent plays an imperative part in evaporation techniques as it has considerable impact on intermolecular interactions and nucleation of co-crystals [27]. A solvent in such a process needs to be highly volatile in nature and thus methanol (CH_3OH) was selected for the co-crystallization process.

Ammonium Nitrate and CdN were weighed as per required quantities using an electronic balance having accuracy up to a hundredth of a milligram. Minimum quantity of solvent, just to dissolve the chemicals completely, was taken in a 20ml glass beaker. A few drops of distilled water (~2ml) were also added in the beaker as AN tends to be slightly less soluble in methanol. The solvent mixture was preheated mildly and the temperature of the mixture was continuously monitored to keep it below the boiling point of methanol, i.e. 64.7 °C. Both AN and CdN were added into the solvent mixture in small installments and continuous stirring was done using a magnetic stirrer till complete dissolution of all of the chemicals was achieved. The mixture was then allowed to be heated at a mild rate with incessant stirring. Solvents started to evaporate under the application of heat till the mixture reached a saturated state. At saturation, a film was observed on the surface of the mixture and the heating was continued at a minimum rate to ensure absence of any water content in the mixture. Solidification of the mixture was accomplished when it was allowed to cool down to room temperature. The mixture was observed to be agglomerated and was thus treated with a small quantity of Acetone to re-crystallize the mixture and to remove any entrapped moisture. Co-crystals thus yielded were then vacuum-dried and stored in hermetic vials.

Table 2 and 3 represent specifications for the compounds used and yield information of co-crystals for the prepared samples, respectively.

Table 2 Specifications of Compounds Used

Chemical	**Make**	**Molar mass (g/ mol)**	**Melting Point (in °C)**	**Density (g/cm^3)**	**Solubility in water (g/100 ml at 10 °C)**
Ammonium Nitrate	Merck	80.052	169.6	1.725	118
Cadmium (II) Nitrate (Tetrahydrate)	Merck	308.47	59.5	2.45	122
Methanol	Merck	32.04	65	0.7918	--
Acetone	Merck	58.08	57	0.791	--

Table 3 Co-crystals Yield Information

Ammonium Nitrate (AN)		**Cadmium (II) Nitrate ($Cd(NO_3)_2).4H_2O$**		**Total Batch Weight (g)**	**Solvent/s**	**Yield (g)**
Weight (%)	**Weight (g)**	**Weight (%)**	**Weight (g)**			
97	2.91	3	0.09	3	$CH_3OH + H_2O$	2.87
94	2.88	6	0.18	3	$CH_3OH + H_2O$	2.74
90	2.7	10	0.3	3	$CH_3OH + H_2O$	2.66

2.2 DIFFERENTIAL SCANNING CALORIMETRY ANALYSIS

Simultaneous Thermal Analyzer (STA 409/ PC, NETZSCH make) was used to carry out the DSC analysis of the samples. Table 4 represents the various technical specifications of the STA machine used for the present study. Before proceeding with the analysis, the machine was conditioned to 25 °C for duration of three hours using a thermostat. Alumina crucibles and lids were used to hold the samples and sample's mass for each run was taken as 1.5mg which was ample to fully cover the base of the crucible. The DSC analysis was carried out in an ultrapure Nitrogen (N_2) atmosphere which was purged into the furnace at a rate of 60 ml/min. The temperature range for each of the analysis was fixed from 25 °C to 400 °C. All the prepared co-crystals and untreated AN were analyzed under isobaric conditions and at a heating rate of 10 °C/min. The output of DSC measurement, called as thermogram, reflected on the main features of the thermal decomposition behavior of samples, i.e., phase state transitions, melting, decomposition, etc. Thermograms for all of the samples were then compared to evaluate the net effect of addition of CdN on the thermal decomposition behavior of AN.

Table 4 NETZSCH STA 409/ PC Technical Specification Datasheet

Maximum Temperature Limit	1500 °C
Cooling Time (From 1500 °C to 25 °C)	45 min (Uncontrolled)
Maximum Heating Rate	50 °C/ min
Analysis Atmosphere	Air, N_2, CO_2, He, Ar
Furnace Material	Silicium Carbide
Thermocouple	Type S

3. RESULTS AND DISCUSSION

3.1 THERMAL DECOMPOSITION OF UNTREATED AMMONIUM NITRATE

The thermal decomposition behavior of untreated AN was obtained and has been shown in Fig. 1. The DSC thermogram of untreated AN depicted five endothermic peaks when AN was heated between the selected temperature range. The first three endothermic peaks with onset temperatures as 32.2 °C, 87.4 °C and 125.5 °C, respectively, verified three phase state transitions of untreated AN as is reported in literature. The fourth endothermic peak, having an onset temperature of around 167.7 °C, represented the absorption of heat for the melting of AN crystals and is in agreement with the melting point of AN as reported in literature [28]. The fifth endothermic peak presented the heat absorption for the final and complete decomposition of AN occurring with an onset temperature of 261.6 °C.

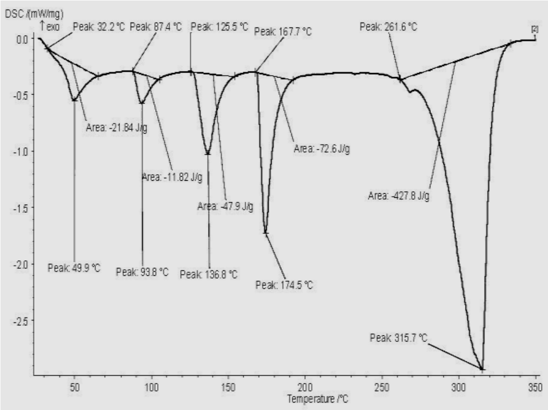

Fig. 1 DSC Thermogram of Untreated AN

3.2 THERMAL DECOMPOSITION OF CO-CRYSTALS

Addition of CdN with AN crystals delayed the onset of first endothermic peak by a range of 19.58-19.76 °C depending on its weight percentage in the composition. The maximum delay in the onset of the phase state transition (III) was found to be 19.76 °C and the weight percentage of CdN to deliver the same was 10%. When added as 3%, it only delayed the phase state transition (III) and no other significant change was observed in rest of the endothermic peaks as depicted in Fig. 2. When the weight percentage of CdN was raised to 6% and 10%, the phase state transition (II) was found to be completely stabilized and is represented in Fig. 3 and 4, respectively. The stabilizing effect and the delay in the onset temperature of phase state transition (III) was found to be increasing as weight percentage of the CdN was increased but the delay was almost negligible in comparison with the overall increment in weight percentage of the CdN in the composition.

No substantial change in the melting point temperature of AN was perceived, regardless of the amount of CdN in the composition. AN experienced an early onset of its decomposition process by an approximate range of 28.06 °C-35.76 °C due to addition of CdN in varying weight percentages.

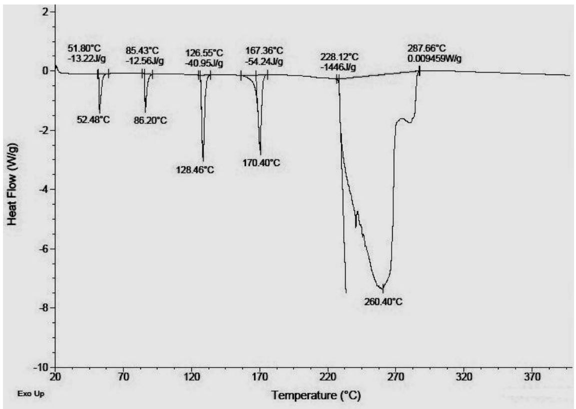

Fig. 2 DSC Thermogram of 3% CdN with 97% AN

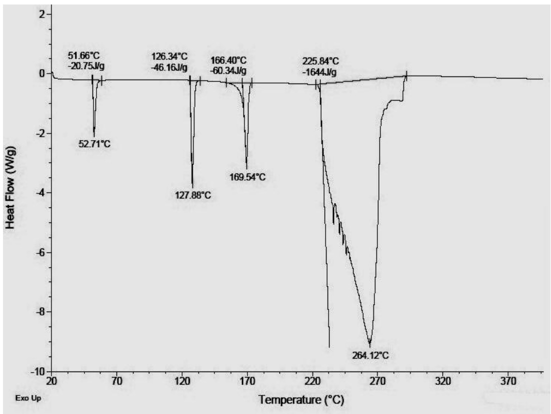

Fig. 3 DSC Thermogram of 6% CdN with 94% AN

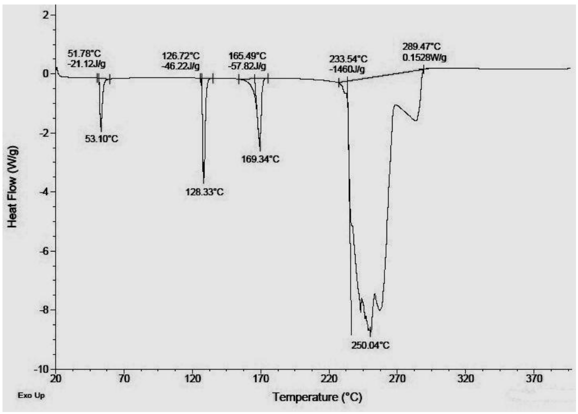

Fig. 4 DSC Thermogram of 10% CdN with 90% AN

4. CONCLUSION

The present investigational study established that CdN can be utilized, in as low weight percentage as 3%, to entirely stabilize the phase state transition (II) of Ammonium Nitrate. The addition of 3% of CdN deferred the onset temperature of phase state transition (III) by a significant range of around ~20 °C. Addition of CdN also dropped down the decomposition temperature range of AN by a considerable value. This advancement in decomposition temperature of the co-crystals makes it likely that dissociation and vaporization of propellant ingredients will require comparatively lesser amounts of heat energy. A reduction in the required quantities of heat energy may facilitate faster decomposition of the propellant resulting in improved burning rates of AN-based propellant grains and possibly leading to boosted use of AN in the formulation of CSPs in near future.

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