

Stabilization of Ammonium Nitrate for Phase Modification (II) by Co-crystallization with Copper (II) Nitrate (Trihydrate)

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Abstract– The present study has been aimed to investigate the stabilization effects imposed by the addition of Copper (II) Nitrate (Trihydrate) ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$) on the phase modification (II) of Ammonium Nitrate (AN) and eventually on its thermal decomposition behavior. $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ was co-crystallized with AN in weight percentages as 3%, 6% and 10% for the preparation of three samples of Phase Stabilized Ammonium Nitrate (PSAN). The thermal decomposition behaviors of untreated AN and prepared samples of PSAN were assessed and compared using Differential Scanning Calorimetry (DSC) to observe the effectiveness of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ as a potential stabilizer. The present study indicated that $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, in low weight percentages, was able to provide a significant delay in the onset temperature range of near-room-temperature phase modification (III) of AN occurring at around 32 °C– 34 °C. Also, increasing weight percentage of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in the composition resulted in the complete stabilization of phase modification (II) occurring at around 85 °C– 87 °C.

Keywords– Ammonium Nitrate, Copper (II) Nitrate (trihydrate), Phase Stabilized Ammonium Nitrate, Co-crystallization, Differential Scanning Calorimetry, Eco-friendly Solid Oxidizer.

INTRODUCTION

The unmatched and extensive use of Ammonium Perchlorate (AP) as an oxidizer in Composite Solid Propellant (CSP) rockets is the outcome of its superior ballistic performance and available thorough knowledge. But in spite of its unparalleled advantages, the use of AP in the formulation of CSP rockets comprises of some shortcomings as well. During the firing of large size boosters of launch vehicles such as Space Shuttle (containing around 503 tons of propellant), each of its Solid Rocket Boosters (SRBs) produces on an average of 100 tons of Hydrogen Chloride (HCl) gas which is let to the atmosphere. The resulting residue of the combustion of 503 tons of propellant in the initial 120 seconds of flight is 21% HCl and 30.2% Alumina (Al_2O_3) [1].

The aforementioned problem i.e. emission of HCl gas, associated with the use of AP as an oxidizer for solid propellant rockets, poses a crucial environmental concern. The emitted HCl gas lowers down the vapor pressure of water vapor in the air, and the HCl co-condenses with the water vapor to form aerosol by serving as a nucleation site for water vapors [2]. Thus formed aerosol creates a visible smoke signature which may eradicate the element of stealth and surprise in a combat. To overcome these problems, it is imperative to replace AP with a Green or Eco-friendly propellant that is free from any kind of toxic combustion products emission. Also, it is vital that the propellant composition is nearly free or completely smoke free during combustion to minimize the detectability of the trajectory of the missile and/ or the launching site during a combat. One such favorable green oxidizer is Ammonium Nitrate (AN) as it delivers HCl- free as well as almost smoke- free combustion. But in spite of being a benign eco-friendly solid oxidizer, AN suffers a very restricted use in CSP formulations. The key reasons behind this limited use of AN- based propellants is its two inherent and unfavorable characteristics, i.e. extensive hygroscopicity and five phase modifications occurring over a wide temperature range, i.e. –200 °C to 125 °C [3]. The transition temperature ranges of the various phase modifications of untreated AN are illustrated in Table 1.

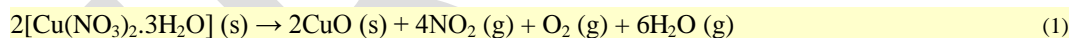
Table 1: Phase Modifications and associated temperature range

Phase Modifications	Temperature Range
Phase Modification V	-200 °C to -18 °C
Phase Modification IV	-18 °C to 32 °C
Phase Modification III	32 °C to 84 °C
Phase Modification II	84 °C to 125 °C
Phase Modification I	Above 125 °C

These phase modifications result in severe structural changes in the crystal lattice of AN leading to substantial volumetric and density variations [4], [5]. These volumetric changes decrease the adherence between the crystallites and thus the structural strength of the product decreases significantly during these thermal cycles [6]. The occurrence of such phase modifications near the propellant processing and storage temperatures, thus, prove to be a stumbling block for the application of AN as a solid oxidizer in the formulation of CSP grains. The structural instability of AN leads to the formation of cracks in the propellant grains which eventually result in unpredicted ballistic performance and/ or disastrous failure of the mission. In order to achieve stable and anticipated combustion of AN- based propellants, it is imperative to stabilize AN for one or more of its phase modifications, preferably those occurring around near- room and storage temperatures.

Various attempts had been made to stabilize these phase modifications by addition of different inorganic as well as organic compounds [7], [8], [9]. Alkali metal nitrates, oxides and diamine complex of various metals had been studied extensively to evaluate their abilities to deliver any stabilization effects [10], [11].

For this study, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ was selected for investigation as a potential stabilizer because of the presence of O_2 and NO_2 molecules in its thermal decomposition products. The thermal decomposition reaction of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ is represented below as equation 1:



The presence of free oxygen molecules in the thermal decomposition products of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ is advantageous when used as a stabilizer for the modification of an oxidizer. Also, the weak nature of N-O bond makes NO_2 a good oxidizer as at elevated temperatures (around 150 °C) as NO_2 decomposes with release of free oxygen through an endothermic process ($\Delta H=114$ kJ/ mol) [12]. Such expedient properties make $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ a viable candidate for a potential stabilizing agent.

In the present study, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ was co-crystallized with pure or untreated AN in varying weight percentages and Differential Scanning Calorimetry (DSC) was carried out to investigate the modifications achieved on the onset temperature range and/ or complete stabilization of any of the phase modifications of AN, preferably those occurring at and above near- room temperatures.

EXPERIMENTAL WORK

CO-CRYSTALLIZATION

The stabilizing compound is supposed to be introduced in the crystallographic structure of AN to accomplish effective stabilization. Out of the available techniques for co-crystallization, evaporation technique was preferred owing to its feasibility and less complexity under normal laboratory conditions. Since the selection of the solvent is greatly influenced by its volatility, Methanol (CH_3OH) was preferred as a solvent to carry out the co-crystallization.

Required quantities of AN and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ were mixed with methanol in a 20ml beaker. The quantity of methanol was kept to a minimum and just enough to dissolve the chemicals completely. Since AN is less soluble in methanol under normal laboratory conditions, a few drops of distilled water were also added to ease and quicken the dissolution of both the chemicals. The solution was mildly heated and continuously stirred over a hot plate equipped with a magnetic stirrer till the complete dissolution of both the chemicals was achieved.

After dissolution, the heating rate was lowered and the stirring was done manually and occasionally till all of the solvent had evaporated. After saturation, a film was observed on the surface of the solution and the solution was allowed to cool down to room

temperature resulting in the solidification of the solution. Wet needle like co-crystals of PSAN were obtained to which a small quantity of acetone was added for re-crystallization and for removal of any moisture content present with the co-crystals. The co-crystals, thus yielded, were filtered and dried over vacuum and stored in air-tight vials.

The related product specifications for the chemicals used and co-crystallization yield data for the three prepared samples have been listed in Table 2 and 3, respectively.

Table 2: Specifications of chemicals used

Chemical	Make	Molar mass (g/ mol)	Melting/ Boiling Point (in °C)	Density (g/ ml)
Ammonium Nitrate	Merck	80.052	169.6	1.725
Copper (II) Nitrate (Trihydrate)	Merck	241.60	114.5	2.32
Methanol	Merck	32.04	65	0.7918
Acetone	Merck	58.08	57	0.791

Table 3: Co-crystallization yield data for the samples

Ammonium Nitrate		Copper (II) Nitrate (Trihydrate)		Total Batch Weight (g)	Solvent	Yield (g)
Weight (%)	Weight (g)	Weight (%)	Weight (g)			
97	1.455	3	0.045	1.5	CH₃OH + H₂O	1.32
94	1.41	6	0.09	1.5	CH₃OH + H₂O	1.23
90	1.35	10	0.15	1.5	CH₃OH + H₂O	1.28

DSC Analysis

After co-crystallization, the prepared samples were put to DSC analysis to assess the net effect of addition of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ on the thermal decomposition behavior of AN and thereby providing the information on its stabilizing potential. NETZSCH Simultaneous Thermal Analyzer (STA 409/ PG) was used to carry out the DSC analysis and the thermal analysis was done in ultrapure nitrogen atmosphere being purged into the furnace at a rate of 60 ml/min. The sample mass of 1.5mg was taken in an alumina crucible for each run. Repeated runs of prepared samples of PSAN as well as untreated AN were carried out at a heating rate of 10 °C/min and were compared.

RESULTS AND DISCUSSIONS

Thermal Decomposition of Untreated AN

The thermal decomposition behavior of untreated AN was observed and has been shown in fig. 1. The DSC thermogram of untreated AN revealed five endothermic peaks when the sample was heated from 25 °C to 350 °C. The first three endothermic peaks with the onset temperatures as 32.2 °C, 87.4 °C and 125.5 °C, respectively, were observed due to the three phase modifications of untreated AN. The fourth endothermic peak, having an onset temperature of around 167.7 °C, represented the absorption of heat for the melting of AN and the fifth endothermic peaks showed the heat absorption for the final and complete decomposition of AN.

Thermal Decomposition of Co-crystallized AN

The use of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ as a stabilizer proved to be effective in delaying the onset of the phase modification (III) by a range of 19.62 °C – 20.16 °C depending on its weight percentage in the co-crystals. A maximum delay of 20.16 °C was observed in the onset temperature of phase modification (III) when $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ was incorporated as 10% by weight.

The addition of 3% of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ delayed the onset temperature of the first endothermic peak but failed to provide any effect on the rest of the decomposition behavior of AN as shown in fig. 2. But when the weight percentage of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ was raised to 6%, it showed a successful stabilizing effect to the phase modification (II) along with a delay in the onset of phase modification (III) as can be seen in fig. 3. Similar effect was observed by incorporating 10% of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ by weight as represented in fig. 4. No

significant change was observed in the melting point temperature range of AN irrespective of the weight percentage of the stabilizing agent in the co-crystals. Although, all three weight percentages of the $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ provided an appreciable reduction of around $54^\circ\text{C} - 58^\circ\text{C}$ in the decomposition temperature range of untreated AN.

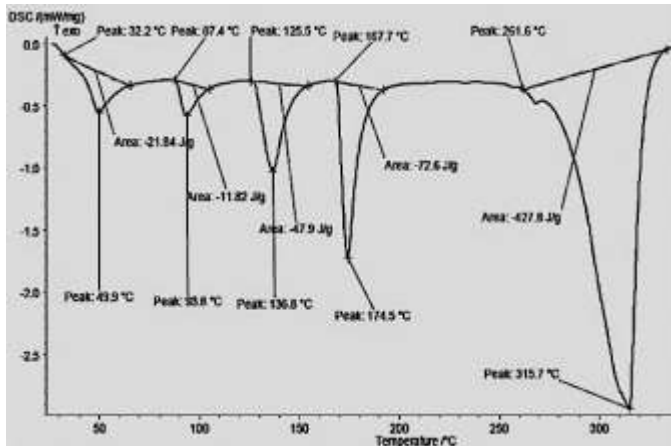


Fig 1: DSC Thermogram of the thermal decomposition behavior of untreated AN

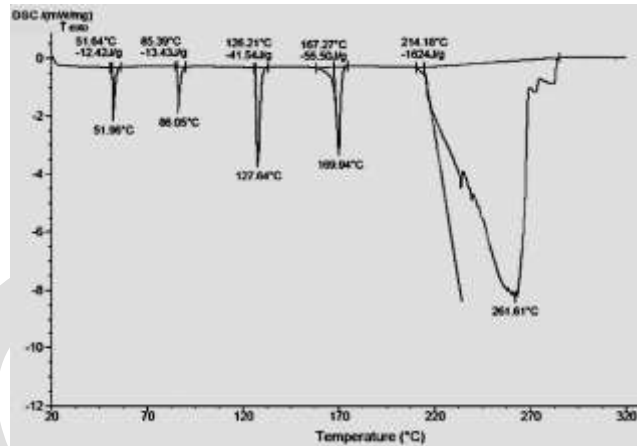


Fig. 2: DSC Thermogram of 97% AN Co-crystallized with 3% of Copper (II) Nitrate (Trihydrate)

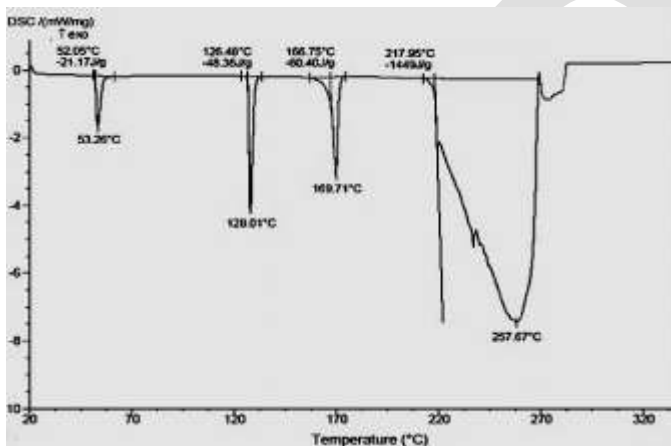


Fig. 3: DSC Thermogram of 94% AN Co-crystallized with 6% of Copper (II) Nitrate (Trihydrate)

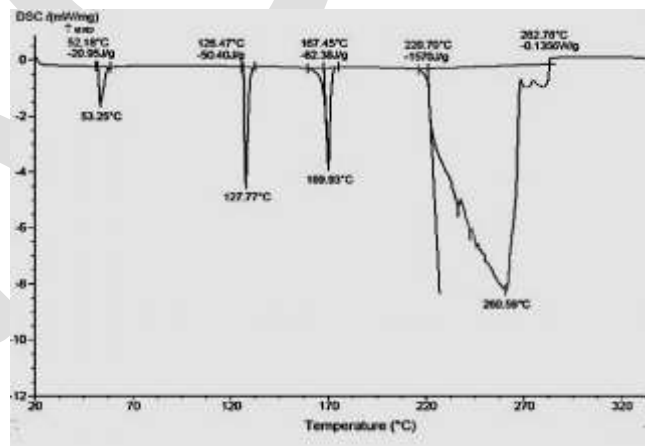


Fig. 4: DSC Thermogram of 90% AN Co-crystallized with 10% of Copper (II) Nitrate (Trihydrate)

CONCLUSION

The present experimental study indicated that $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, in as low weight percentage as 6%, can be utilized to completely stabilize the AN for the phase modification (II). The addition of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ also increased the onset temperature of phase modification (III) by a significant range of around 20°C . The stabilizing agent under investigation significantly lowered down the decomposition temperature range of the PSAN which may lead to enhanced burning rates of the AN- based propellant grains due to reduced amount of required heat for the combustion of the solid propellant.

REFERENCES:

[1] Fahey, D. W., "Scientific assessment of Ozone depletion", 2006 Update, Global Ozone Research and Monitoring Project Report No. 50, World Meteorological Organization, Geneva, Switzerland, pp. 572, 2007.

- [2] Korting, P. A. O. G., Zee, F. W. M. and Meulenbrugge, J. J., "Combustion characteristics of low flame temperature Chlorine-free composite solid propellants", AIAA, Vol. 6, Issue 3, pp. 1803- 1811, 1987.
- [3] Kim, J. H., "Preparation of Phase Stabilized Ammonium Nitrate (PSAN) by salting out process", Journal of Chemical Engineering, Japan, Vol. 30, Issue 2, pp. 336- 338, 1997.
- [4] Hendricks, S. B., Posnjak, E. and Kracek, F. C., "Molecular rotation in the solid state; the variation of the crystal structure of Ammonium Nitrate with temperature", Journal of American Chemical Society, Vol. 54, Issue 7, pp. 2766- 2786, 1932.
- [5] Brown, R. N. and McLaren, A. C., "On the mechanism of the thermal transformations in solid Ammonium Nitrate", Proceeding of the Royal Society, Vol. 266, pp. 329- 343, 1962.
- [6] Herrmann, M. J. and Engel, W., "Phase transitions and lattice dynamics of Ammonium Nitrate", Propellants, Explosives and Pyrotechnics, Vol. 22, Issue 3, pp. 143- 147, 1997.
- [7] Falck-Muss, R., Newman, D. J. and Atkin, S., "Stabilized Ammonium Nitrate", US Patent No. 3649173, 1972.
- [8] Mishra, I. B., "Phase Stabilization of Ammonium Nitrate with Potassium Fluoride", US Patent No. 4552736 A, 1986.
- [9] Campbell, A. N. and Campbell, A. J. R., "The effect of a foreign substance on the transition: AN (IV- III)", Canadian Journal of Research, Vol. 24 (b), Issue 4, pp. 93- 108, 1946.
- [10] Eisenreich, N., Deimling, A. and Engel, W., "Phase transitions of Ammonium Nitrate doped with alkali nitrates studied with fast X- Ray diffraction", Journal of Thermal Analysis and Calorimetry, Vol. 38, Issue 4, pp. 843- 853, 1992.
- [11] Engel, W. and Heinisch, H., "Process for producing Phase Stabilized Ammonium Nitrate", US Patent No. 6508995, 2003.
- [12] Rosser, W. A. and Wise, H., "Thermal decomposition of Nitrogen Dioxide", Journal of Chemical Physics, Vol. 24, pp. 493-494, 1956