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Enhancing Phase Stability of Ammonium Nitrate through Urea Nitrate Stabilization

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ABSTRACT

The present study has been aimed to investigate the stabilization effects provided by the addition of Urea Nitrate (UN) on the modification of phase (II) transition of Ammonium Nitrate (AN) and thus on its thermal decomposition behavior. Urea Nitrate was synthesized in the laboratory and was characterized to ascertain its structural ingenuity. Urea Nitrate was then co-crystallized with AN in three different weight percentages i.e. 3%, 6% and 10% for the preparation of Phase Stabilized Ammonium Nitrate (PSAN). The thermal decomposition patterns of virgin AN and prepared samples of PSAN were measured and compared using Differential Scanning Calorimetry (DSC) to detect the efficiency of UN as a potential stabilizer. The present study indicated that UN, in low weight percentages, was able to deliver a noteworthy postponement in the onset temperature range of near-room-temperature phase modification (III) of AN occurring at around 32°C–34°C. Also, co-crystallization of UN with AN significantly modified the hygroscopic tendency of the prepared co-crystals.

Keywords*: Urea Nitrate, Ammonium Nitrate, Phase Stabilized Ammonium Nitrate (PSAN), Phase Transitions, Co-crystallization, Differential Scanning Calorimetry (DSC).*

I. INTRODUCTION

The growing environmental awareness in recent years has led to the motivation and necessity of replacing Ammonium Perchlorate (AP) with more green propellants and considerable efforts toward this end have been pursued. The drawbacks associated with use of AP have led to a rejuvenated interest in Ammonium Nitrate (AN) based propellants, primarily because of the clean burning nature of AN, its low cost and easy availability[1]. Ammonium nitrate as a propellant ingredient may produce a propellant that does not produce primary or secondary smoke upon combustion[2]. However, although AN is well known as a low-energy oxidizer in gas generator compositions, its use in large motors is restricted as a result of several of its major adverse characteristics. Its hygroscopicity and near-room-temperature phase transformations resulting in volume expansion cause storage problems and lead to crack formation in the grain[3].

Ammonium Nitrate was considered early as an environment-friendly alternative to AP. The interest in understanding the physical and thermal properties of AN has a long history and is motivated by the wide use of this material as fertilizer and blasting agent. But inherent drawbacks like multiple crystal phase transitions occurring around 32°C onwards, extreme hygroscopicity, and low oxidizing potential precluded the possibility of its use[4]. The stumbling block for the application of AN, as solid propellant oxidizer, which is its dimensional instability is caused by polymorphic transitions near the propellant processing and storage temperatures. The transitions occurring at these temperatures cause destruction of AN crystal, which results in increase of volume and concomitant porosity of the propellant grain, as a result of non-alignment of the crystallographic axes of micro-crystallites in AN particles undergoing recrystallization. The permanent volume change due to growth of AN when it is thermally cycled, is undesirable because of loss in density and mechanical properties, unstable combustion, thermal expansion and structural instability[5].

Salts composed of an organic cation and an oxygen-rich anion comprise an important class of energetic materials with the attractive property that fuel and oxidizer components can be combined in a single stable compound. Thus, organic compounds, which are typically biodegradable, produce environmentally relatively-benign combustion products and have crystallographic likeness with AN crystalline structure, are of prime interest for the use as stabilizers for ammonium nitrate[6]. Hence, an attempt is made to study the results of AN lattice modification with addition of UN which contain both carbonyl (C=O) and amine (N–H) groups. Urea nitrate was selected to be studied as stabilizing compounds for phase stabilization of AN because on the one hand it is rather an effective acceptor of electrons while on the other hand it is also a good donor of electrons[7].

The main objectives of the present study are to: (a) synthesize UN under normal laboratory conditions, (b) characterization of the synthesized compound using different available techniques, and, (c) to prepare PSAN by adding the stabilizing compounds in different weight percentages by co-crystallization technique. Also, Differential

Scanning Calorimetry (DSC) for both prepared PSAN and virgin AN has been carried out and compared to understand the effect of addition of UN on the thermal decomposition behavior of AN.

II. METHOD & MATERIAL

CHEMICAL'S SPECIFICATIONS

The chemicals used in the present study namely Ammonium Nitrate and Urea were purchased from Merck. Both the chemicals were of Analytical Reagent (AR) grade. The acids and solvents for nitration and evaporation process namely, Nitric acid and Acetone were also purchased from Merck and all were of AR grade as well. The specifications of the chemicals used for present investigation are represented in Table 1 and Table 2.

Table 1. Specifications of Chemicals Used

Chemical	Make	Molar mass (g/mol)	Melting Point (in °C)	Density (g/cm^3)	Solubility in water (g/100 ml at 10°C)	Appearance
Ammonium Nitrate	Merck	80.052	169.6	1.725	118	White crystals
Urea	Merck	60.06	135	1.32	107.9	solid, colorless crystals

Table 2. Specifications of Acids and Solvent Used

Chemical	Make	Molar mass (g/mol)	Boiling Point (in °C)	Density (g/ml)	Appearance
Nitric Acid	Merck	63.01	83	1.42	Colorless
Acetone	Merck	58.08	57	0.791	Colorless

SYNTHESIS OF UREA NITRATE

6 g (0.1 mol) of crystalline urea was dissolved in 8 ml of water. Endothermic nature of the dissolution process lowered down the temperature of the aqueous solution. Once the mixture warmed up to room temperature, 7 ml (9.94 g, 0.158 mol) of 70% concentrated nitric acid was added drop wise with stirring to the aqueous solution. The addition was an exothermic reaction which raised the reaction mixture temperature to around 40°C and resulted in precipitation of copious amount of white crystals. The solution was stirred for around 15- 20 minutes at room temperature. The white precipitated crystals were filtered over vacuum and washed with chilled water and Acetone (2 ml). The filter cake was kept overnight in a $CaCl_2$ desiccator to yield 10.795 g of Urea Nitrate (Fig. 1).

CHARACTERIZATION OF SYNTHESIZED UREA NITRATE

The synthesized compounds were characterized by comparing the data obtained from FT-IR spectroscopy with that of mentioned in the literatures for Urea Nitrate. A similar range of absorption frequencies observed by the FT-IR spectroscopy allowed for positively characterizing the synthesized compounds. For the analysis, KBr (SIGMA-ALDRICH, FT-IR GRADE) was used for obtaining the background spectrum which was used a reference for the analysis of the samples.

PREPARATION OF PHASE STABILIZED AMMONIUM NITRATE

To stabilize AN, the stabilizing compound is supposed to be introduced in the crystallographic structure of AN. For such interaction of two chemical entities, at the molecular level, some techniques have been introduced and employed by various researchers all over the world. The technique which is used for preparing the co-crystals for the present experimental work was the evaporation technique.

Three batches of co-crystallized AN were prepared for with varying weight percentages of Urea Nitrate and are represented below:

1. Ammonium Nitrate – 97 % : Urea Nitrate – 3%

2. Ammonium Nitrate – 94 % : Urea Nitrate – 6%

3. Ammonium Nitrate – 90 % : Urea Nitrate – 10%

Figure 1: Synthesized Urea Nitrate

THERMAL DECOMPOSITION STUDIES

Differential Scanning Calorimetry (DSC) is the most widely used technique of all the thermal analysis methods. In a heat flux DSC machine, the substance which shall be measured is placed in an aluminum pan whereas an empty aluminum pan serves as the reference. These two pans are put on an electrically heated plate in order to make sure that the temperature in the sample is the same as in the reference. Via those plates and the pans, heat is transferred to the sample and the reference with the use of a defined computer controlled heating program (the rates of the heating can be adjusted). The differential heat flux to the sample and the reference as well as the sample temperature are measured. The output of a DSC measurement, the so called thermogram is a plot of the difference of heat delivered to the sample and to the reference as a function of the sample temperature. If a physical or a chemical process which is endothermic (consuming energy as heat) is taking place, in order to maintain the same temperature of the two pans, more heat must be delivered to the sample pan than to the reference pan (where of course no transition occurs). The effect is a positive or negative peak in the thermogram (the sign of the peak is depending on the definition of the sign for the direction of the heat flow). The opposite is true for an endothermic process.

Simultaneous Thermal Analyzer (STA) was used in the thermal characterization of stabilized AN by Addition of Urea Nitrate. The instrument used for the present work was NETZSCH Simultaneous Thermal Analyzer (STA 409/PG). Repeated runs of various prepared batches of prepared PSAN as well as virgin AN at a heating rate of 10°C/min allowed to observe on the good reproducibility of the main features of the thermal behavior of PSAN, i.e., two phase transitions, melting and decomposition.

The thermal analysis was done in ultrapure nitrogen atmosphere purged at a rate of 60 ml/min. The sample mass in the range of 1.5-2.5 mg was taken in an alumina crucible for each run. The sample and reference crucible were placed in the furnace and furnace was closed. The operating conditions like room temperature, end temperature, heating rate etc. were furnished to the system by the attached computer.

III. RESULT & DISCUSSION

The synthesis of Urea Nitrate yielded white, finely powdered, crystals with a strong odor of nitric acid. During synthesis, the dissolution process of urea in water was observed as an endothermic process which lowered down the temperature of the aqueous solution to around 8-10° C. The mixture had to be allowed to stand for some time, till the temperature of the solution had reached normal room temperature again, to carry out the rest of the synthesis procedure. Also, the synthesized Urea Nitrate was found to be minimally hygroscopic in nature.

While analyzing the spectra of Urea Nitrate as shown in Fig. 2 and comparing it with the spectrum for pure urea, it

indicated the existence of bonds between nitrogen of one of the amino groups. The absorption band with frequency 1466 cm^{-1} pertaining of the valence vibration of the bonds in pure urea, shifted to the side of lower frequencies to 1383 cm^{-1} in the spectrum of the compound by merging with the band of NO_3^- ion. The stretching frequency for NO_3^- was found to be 1311 cm^{-1}, which was consistent with that of mentioned in literatures. The sample also showed the other functional group assignments 3204 cm^{-1} (NH_2 symmetric stretch), 1703 cm^{-1} (C=O stretch), and 1568 cm^{-1} (N-H) consistent with the literature[7].

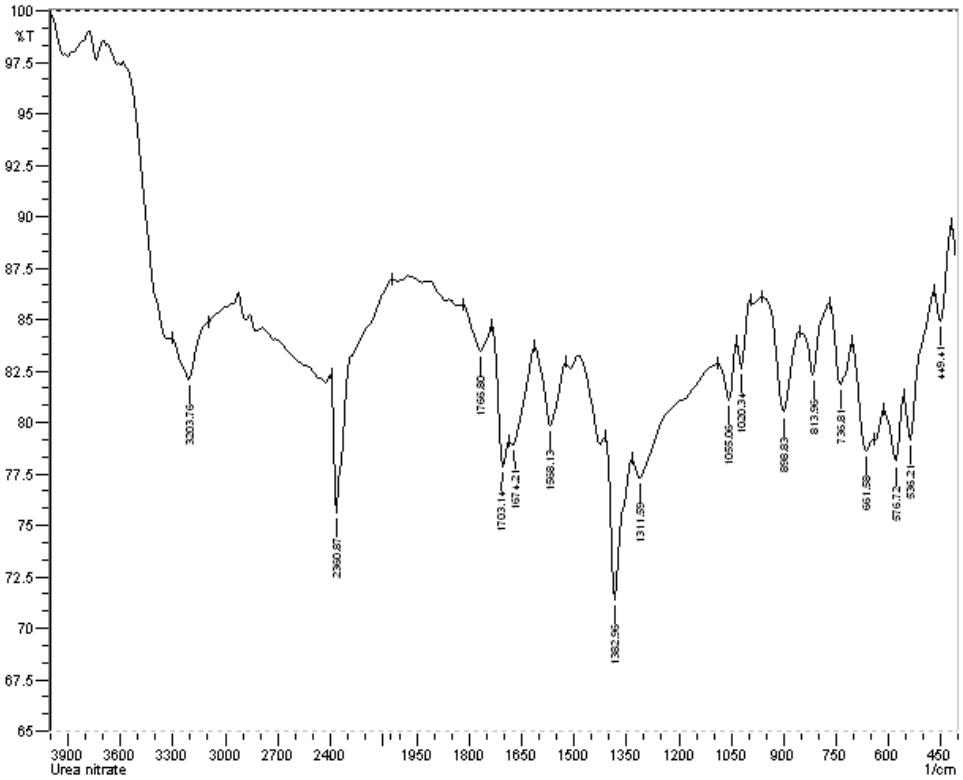

Figure 2: FT-IR spectrum of Urea Nitrate

To assess the net effect of Urea Nitrate on the phase stabilization of AN, a DSC thermogram of virgin AN was obtained and is shown in Fig. 3. The thermal decomposition behavior of virgin AN showed five endothermic peaks when heated from 25°C to 350°C at a heating rate of 10°C/min. The first three endothermic peaks, having an onset temperature of 32.2°C, 87.4°C and 125.5°C respectively, represent three phase transitions of AN. The fourth peak, having an onset temperature of around 167.7°C, represents the melting of AN and the fifth peaks shows the complete decomposition of AN.

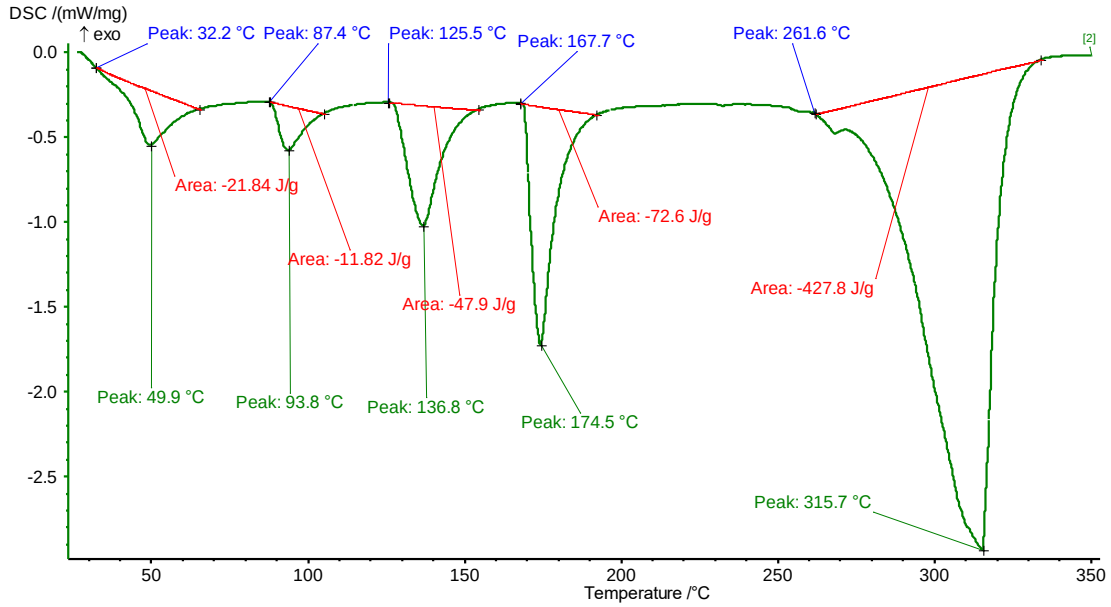

Figure 3: DSC Thermogram Showing Thermal Decomposition Behavior of Virgin AN

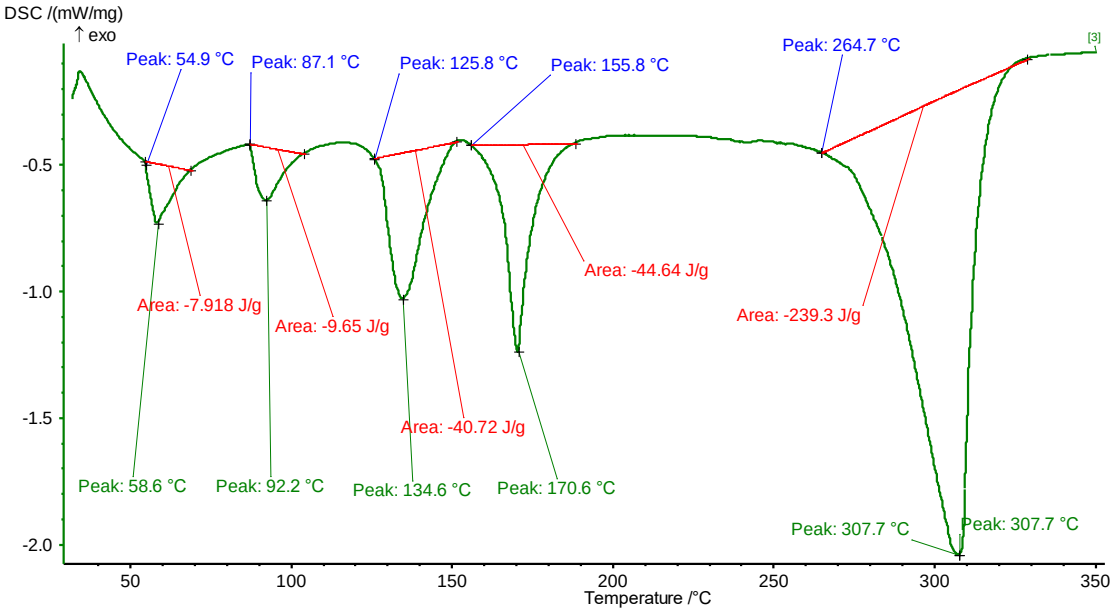

Figure 4: DSC Thermogram of 97% AN Co- crystallized with 3% Urea Nitrate

The use of Urea Nitrate as a stabilizing compound resulted in the delay of onset temperature for phase transition (III), occurring at ambient room temperature, by a considerable range, i.e. 18.5-22.7°C, depending upon the weight percentage of additive incorporated. The UN-PSAN was found to be phase stabilized for phase transition (III) up to a maximum temperature of 54.9°C when 3% UN was added. Figure 4 shows the thermogram of 3% UN added AN. The further increment in the weight percentage of the additive tend to lower down the onset temperature for the phase transition (III) and the delay was found to be minimum with the highest weight percentage experimented.

Also, the peak temperature for first endothermic peak was increased by a range of 4-8°C. The effect on the other two phase transitions as well as on the melting point of AN was found to be insignificant.

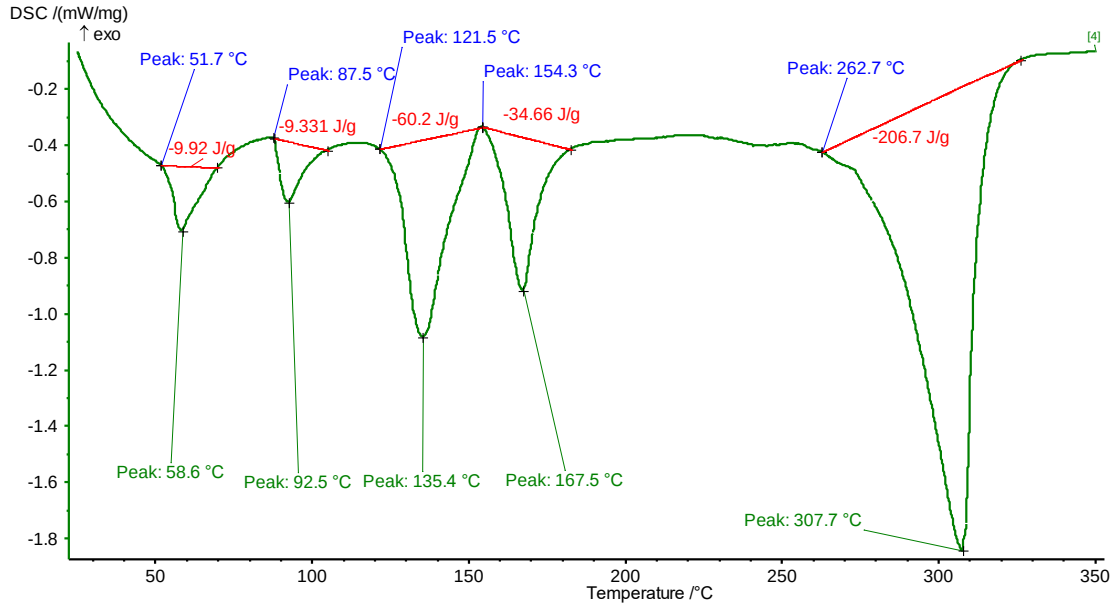

Figure 5: DSC Thermogram of 94% AN Co- crystallized with 6% Urea Nitrate

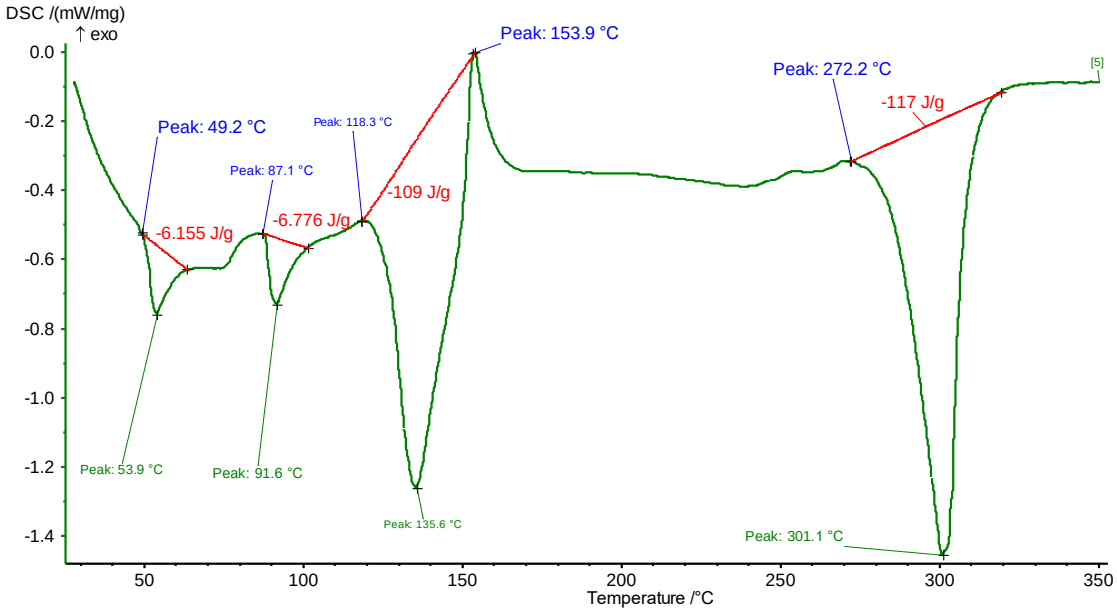

Figure 6: DSC Thermogram of 90% AN Co- crystallized with 10% Urea Nitrate

Figure 5 represents the thermogram obtained when the weight percentage of additive UN was 6%. No significant change was observed but a noteworthy change in the melting behavior of AN was observed when the weight percentage of UN was increased up to 10%. Instead of typical five endothermic peaks, only four endothermic peaks were observed as shown in Figure 6. The melting of AN, supposedly, occurred around 153.9°C followed by no

considerable change in heat flow till 272.2°C.

IV. CONCLUSION

The following conclusions can be drawn from the present study on the phase stabilization of AN by the addition of synthesized Urea Nitrate in three different weight percentages:

1. The synthesized urea nitrate exhibited the presence of almost similar functional groups as it is mentioned in literatures for the same compound when tested by using FT- IR spectroscopy. On this basis, it is concluded that the synthesized compound is structurally genuine.
2. The melting point range of the synthesized Urea Nitrate is found to be congruous with that of reported in referred literatures and hence it is concluded that the synthesized compound is pure in nature.
3. The use of Urea Nitrate as stabilizer delayed in the onset temperature of phase transition (III) of Ammonium Nitrate. Though, the maximum delay in the onset of phase transition (III) is provided, Urea nitrate, it is unsuccessful in altering the rest of the decomposition behavior of AN.
4. A noticeable change is observed in the heat flow during all of the endothermic peaks occurring during thermal decomposition of AN by the addition of stabilizing compounds.
5. The addition of Urea Nitrate does not affect that much on the hygroscopicity of Ammonium Nitrate.

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