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Phase Stabilization of Ammonium Nitrate using Nitrourea

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ABSTRACT

The present study has been aimed to investigate the stabilization effects provided by the addition of Nitrourea on the alteration of various phase transitions of Ammonium Nitrate (AN). The investigation is done based on the comparison of thermal decomposition behavior of treated and untreated Ammonium Nitrate. Nitrourea was synthesized in the laboratory through the nitration process and was characterized using FT-IR to ascertain its chemical ingenuity. Co-crystallization technique was used treat AN when Nitrourea is used 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 untreated AN and prepared PSAN were obtained and compared using Differential Scanning Calorimetry (DSC) to identify the applicability of Nitrourea as a potential stabilizer. The present study led to the observation that all weight percentages of Nitrourea within AN decreased the decomposition temperature of the prepared co-crystals.

Keywords: Nitrourea, Ammonium Nitrate, Phase Stabilized Ammonium Nitrate (PSAN), Phase Transitions, Cocrystallization, Differential Scanning Calorimetry (DSC).

I. INTRODUCTION

The environmental effects of increased number of rocket launches pose a need of various approaches for developing eco-friendly solid composite propellants with an emphasis on using new energetic eco-friendly oxidizers or improving the existing eco-friendly oxidizers, i.e. Ammonium Nitrate. Numerous efforts have been initiated for the design and development of alternative propellants, which are environmentally benign as they contains either little or no HCl generating ingredients and are equally or more energetic, to cater the demands of future space and defense technology. Also numerous efforts have been made in improving the physical and mechanical properties as well as ballistic performance of the existing eco-friendly oxidizers¹.

Ammonium nitrate is the cheapest and one of the most commercially important ammonium compounds in terms of usage. It is known that AN was used in propellant formulation as early as late 19th century. Ammonium nitrate combines a favorable element composition (5% hydrogen, 60% oxygen, absence of halides), high thermal stability, and sufficient compatibility with a number of other constituents. However, its low enthalpy of formation (-4514 kJ/kg), relatively low density (1.725 g/cm³) and polymorphic phase transitions occurring near propellant processing and storage temperatures make AN uncompetitive in energy potential to a majority of other known oxidizers².

Considerable effort has been devoted to studies of the decomposition of AN. A Study conducted by Saunders has revealed that the pure AN decomposes at an easily detectable rate at temperatures only slightly greater than the melting point of 170° C and the products of decomposition are primarily N₂O and H₂O as shown in the equation below³:

$$NH_4 NO_3 \rightarrow N_2O + 2 H_2O \tag{1}$$

Bent has mentioned that in the absence of any acid added, the dissociation of $NH_4 NO_3$ to NH_3 and HNO_3 produces the acid required to initiate the decomposition reaction⁴. Generally NH_3 and HNO_3 escape from the melt but if the experimental conditions are such that the acid accumulates in the melt, the decomposition is autocatalytic. Hence, the thermal decomposition of AN is initiated by an endothermic proton transfer reaction as shown by the following reaction:

$$NH_4 NO_3 \rightarrow NH_3 + HNO_3$$
 (2)

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When the salt is heated from 200 to 230°C, exothermic decomposition occurs by the following reaction:

$$NH_4 NO_3 \rightarrow \frac{1}{2}N_2 + NO + 2H_2O$$
(3)

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The reaction is rapid but can be controlled and is the basis for commercial preparation of nitrous oxide. Above 230° C, the decomposition follows

$$NH_4 NO_3 \rightarrow \frac{3}{4}N_2 + \frac{1}{2}NO_2 + 2H_2O$$
(4)

And when AN undergoes explosion, the decomposition pathway followed is reported as follows

$$8 \text{ NH}_4 \text{ NO}_3 \rightarrow 5 \text{ N}_2 + 4 \text{ NO} + 2 \text{ NO}_2 + 16 \text{ H}_2 \text{O}$$
(5)

Rosser et al. have assumed the following known equilibrium reaction for HNO_3 that leads to the oxidizing species NO_2^+ and explained the formation of N_2O and water as the main products⁵.

$$2 \text{ HNO}_3 \iff \text{NO}_2^+ + \text{NO}_3^- + \text{H}_2\text{O}$$
(6)

$$NH_3 + NO_2^+ \rightarrow \text{products}(N_2O, H_2O)$$
 (7)

Keenan et al. have investigated the effect of synergistic catalysts on the decomposition of AN. Since AN does not burn easily and needs a catalyst to sustain combustion, compounds have been incorporated in AN based propellant formulations to catalyze the combustion reaction. Catalysts such as ammonium dichromate, copper chromate and chromium oxide are reported to increase the burning rate (BR) of AN propellants. Ammonium dichromate not only facilitates the decomposition of AN, but decomposes itself into water, nitrogen and chromium oxide, and thus is not solely catalytic in action. Chromium compounds in particular show a greater catalytic action than other cations. They have suggested that the NO_3^- in the acidic melt is deoxygenated to NO_2^+ by the dichromate ion. NO_2^+ further undergoes a number of reactions with NH_3 or NH_2^- forming intermediate nitramides or nitrosamines which are then decomposed to nitrogen or nitrous oxide and water⁶.

Kim has also reported that pure AN has at least five different crystal modifications depending on the temperature, i.e. cubical in the temperature interval between 125° C and its melting point 169.5° C (modification I), tetragonal in the temperature interval between 84° C and 125° C with a density of approximately 1.67 g/cm³ (modification II), orthorhombic in the temperature interval between 32° C and 84° C with a density of approximately 1.66 g/cm³ (modification III), also orthorhombic between -18° C and 32° C (modification IV), but with a density of approximately 1.73 g/cm³ which represents a density change of approximately 4% compared with the density of modification III, and orthorhombic pseudotetragonal (modification V) at temperatures below -18° C⁷. The transition temperatures of the various phases are,



An attempt is made to learn the consequences of AN lattice alteration with addition of Nitrouea which contain both carbonyl (C=O) and amine (N–H) groups. Nitrourea was selected to be studied as stabilizing compound for preparing PSAN because it is a moderately effective acceptor of electrons as well as it is also a decent donor of electrons⁷.

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





Also, Differential Scanning Calorimetry (DSC) for both untreated and treated AN has been conducted and compared to comprehend the outcome of addition of Nitrourea on the thermal decomposition performance of AN.

II. METHOD & MATERIAL

CHEMICAL'S SPECIFICATIONS

The chemicals utilized in the present study namely Ammonium Nitrate, Urea were purchased from Merck. Nitration process was used to prepare the Nitrourea from Urea. The acids and solvents for nitration and evaporation process namely, Nitric acid, Sulfuric acid and Acetone were also purchased from Merck. All of the utilized chemicals were of the purest form and were of Analytical Reagent grade. The specifications of the chemicals used for present investigation are represented in Table 1 and Table 2.

Table 1.	Specifications	of Chemicals	Used
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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

Chemical	Make	Molar mass (g/mol)	Boiling Point (in °C)	Density (g/ml)	Appearance
Nitric Acid	Merck	63.01	83	1.42	Colorless
Sulfuric Acid	Merck	98.079	337	1.83	Colorless to slightly yellow viscous liquid
Acetone	Merck	58.08	57	0.791	Colorless

SYNTHESIS OF NITROUREA

21.8 ml (40 g, 0.38 mol) of 98% Sulfuric acid was slowly added to 26.4 ml (34.85 g, 0.553 mol) of 70% Nitric acid in a 100 ml beaker. The mixture was cooled to around 0°C by keeping the beaker in a low temperature bath. 6 g (0.1 mol) of Urea was then added to the reaction mixture in small installments over a period of 30 minutes. After all of the urea had been added, the mixture was stirred for further an hour while maintaining the reaction mixture below 3°C. After that, the clear solution was dumped into 100 g of crushed ice/water in a 200 ml beaker which resulted in precipitation of white crystals. The milky solution was stirred by a clean glass rod till all ice had been melted and the mixture was then filtered using vacuum filtration. The filter cake was then washed twice with chilled water (5 ml) and dried over vacuum to yield 7.5 g of Nitrourea (melting point. of 157-159°C) (Fig. 1). The flow chart of the processes for the preparation of Nitrourea is represented in Figure 2.

CHARACTERIZATION OF SYNTHESIZED NITROUREA

The synthesized compounds were characterized through comparison of the data obtained from FT-IR spectroscopy with that of reported in the literatures for Nitrourea. A comparable range of absorption frequencies observed by the FT-IR spectroscopy permitted for positively characterizing the synthesized Nitrourea. 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.

The prepared Nitrourea was also tested using STA instrument to obtain DSC thermograms. The obtained DSC thermograms revealed the melting and decomposition temperatures of Nitrourea. The melting and



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decomposition temperatures obtained through these thermograms were also compared, for characterization and to validate the purity of the synthesized compound, with the temperatures reported in concerned literatures.



Figure 1: Synthesized Nitrourea

21.8 ml Sulfuric Acid + 26.4 ml Nitric Acid Cooling the mixture to 0° C Addition of 6.0 g Urea In small amounts over 30 minutes Stirring for further an hour Maintaining temperature below 3° C Dumping the solution over 100 g crushed ice/ water With Stirring till all ice melts Precipitation of white crystal mass Milky solution Filtration of precipitates Over vacuum filtration Washing with chilled water and drying Drying overnight Nitrourea (White Crystals)

Figure 2: Nitrourea Synthesis Flow Chart

PREPARATION OF PHASE STABILIZED AMMONIUM NITRATE

To prepare PSAN, the stabilizer is supposed to be introduced in the crystallographic structure of AN. For such fusion of two chemical ingredients at the molecular level, evaporation technique has been introduced and employed by various researchers all over the world.



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Vishweshwar et al. have reported that co-crystals can be synthesized by evaporation, sublimation, melting, sonication etc. A common way to synthesize co-crystals is through slow evaporation of a solution that contains stoichiometric amounts of the co-crystal components, or co-crystal formers. They have stated that the evaporation technique has been shown to work when different molecules of complimentary functional groups afford hydrogen bonds that are more favorable than each of the individual molecular components and in this case, the co-crystal is likely to be thermodynamically favored⁸.

Due to co-crystallization, one can expect changes in physico-chemical properties of the compounds such as chemical stability, hygroscopicity, dissolution rates, and solubility. The melting point of co-crystals, in general, differs from those of the individual components due to changes in molecular interactions, composition, and structure. Hence, it can be assumed that the change in melting point of the co-crystallized compound can prove to be beneficiary and can result in better ballistic performance in case of solid composite rocket propellants.

Three batches of co-crystallized AN were prepared for with varying weight percentages of Nitrourea and are represented below (Table 3):

S No	Datah	Weight Percentage (%)			
5. INO.	Datch	Ammonium Nitrate	Nitrourea		
1	Α	97	3		
2	В	94	6		
3	С	90	10		

Table 3. Prepared Batch's Compositions

THERMAL DECOMPOSITION STUDIES

Simultaneous Thermal Analyzer (STA) was used to obtain the thermal characterization of treated AN by Addition of Nitrourea. The instrument used for the present work was NETZSCH Simultaneous Thermal Analyzer (STA 409/PG) (Figure 3). Repeated runs of various prepared batches of treated AN 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 carried out in an atmosphere of ultrapure nitrogen, 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 sealed. The operating conditions like room temperature, end temperature, heating rate, etc. were furnished to the system by the attached computer.

The initial temperature for starting the experiment was set as 25°C. The final temperature is then assigned, which for this case, was varied around 330- 350°C. After the completion of analysis up to the furnished limits of temperature, DSC results were collected on the computer, installed with the software used to acquire and analyze the thermographs.



Figure 3: Simultaneous Thermal Analyzer 323





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GENERATION OF NITRONIUM IONS (NO₂⁺) IN MIXED ACIDS

Mixed acid was the mixture of nitric acid (HNO₃) and sulfuric acid (H₂SO₄). When the two acids were mixed, one hydrogen ion striped off from H₂SO₄ to protonate the HNO₃ and formed H₂NO₃.

$$HNO_3 + H_2SO_4 \rightleftharpoons H_2NO_3 + HSO_4^-$$
 (8)

Then, the protonated H_2NO_3 got decomposed to form two separate compounds where one was electrophile (Electron Deficient Compound) Nitronium ion (NO_2^+) and other was Water (H_2O)

$$H_2NO_3 \iff H_2O + NO_2^+$$
(9)

The formation of water can be disadvantageous as many compounds are soluble in water thus leading to lesser yields. Also, during the reactions employing extremely low temperatures, the water present in the nitrating mixture can get frozen forming ice thus resisting the efficient nitration of the given compound. This problem was overcomed by doubling the moles of sulfuric acid in the mixed acids. The solution of two moles of sulfuric acid with one mole of nitric acid resulted in the production of the required nitronium ions (NO₂⁺), Hydronium ion (H₃O⁻) and bisulfate anion (HSO₄⁻). The overall reaction can be represented as below:

$$HNO_3 + 2 H_2SO_4 \iff H_3O^- + NO_2^+ + 2 HSO_4^-$$
 (10)

In the absence of catalyst, nitric acid went appreciable self-dehydration to yield nitronium ions (NO_2^+) , nitrate ions (NO_3^-) and water. It can be represented by the following chemical reaction:

$$2 \text{ HNO}_3 \iff \text{NO}_2^+ + \text{NO}_3^- + \text{H}_2\text{O}$$
(11)

The nitrating power of solution of nitric acid in sulfuric acid depended on a balance of its acidity, leading to the formation of the nitronium ion, and its basicity which was considered to catalyze the reaction by aiding the loss of the proton.

SYNTHESIS OF NITROUREA

The product obtained from the synthesis of Nitrourea was found to be white colored lumpy crystals. The presence of lumps indicated towards the fact that Nitrourea was comparatively more hygroscopic than Urea Nitrate. No particular odor from the yield was observed. While carrying out the synthesis, the addition of Urea to the nitrating mixture resulted in an exothermic reaction which increased the temperature of mixture above the room temperature and to keep the temperature of the reaction mixture below 3°C, urea was added to the nitrating mixture in very small installments. The addition of Urea was done along with vigorous stirring so as to avoid increment of local temperature above the desired temperature during mixing time.

CHARACTERIZATION OF NITROUREA

While comparing the IR spectrum of pure urea with the IR spectrum of Nitrourea as shown in Fig. 4, the disappearance of urea band was observed. Also, a strong band frequency at 1381 cm⁻¹ was observed, which represents the absorption frequency range for NO₂ group. This validates the introduction of NO₂ group to the structure of pure urea and hence converting it to Nitrourea. The rest of the important functional groups assignments 3204 cm⁻¹ (NH₂ symmetric stretch), 1705 cm⁻¹ (C=O stretch), and 1571 cm⁻¹ (N-H) were found to be present as well⁹.







Figure 4: FT-IR spectrum of Nitrourea

THERMAL DECOMPOSITION STUDIES

To evaluate the net effect of Nitrourea on the phase stabilization of AN, a DSC thermogram of virgin AN was obtained and is shown in Fig. 5. The thermal decomposition behavior of virgin AN represented five endothermic peaks when the sample was heated from 25°C to 350°C at a heating rate of 10°C/min. The first three endothermic peaks, with an onset temperature of 32.2°C, 87.4°C and 125.5°C, respectively, represent three phase transitions of AN. The fourth peak, with an onset temperature of around 167.7°C, represents the melting of AN and the fifth peaks shows the complete decomposition of AN.

The effect of addition of Nitrourea as stabilizer was found to be different. Though the addition of Nitrourea also provided a delay in the onset of first endothermic peak by a range of around 20.13°C, the effects on any other peaks were almost negligible. An unexpected and little stabilizing effect was noticed when the Nitrourea was added in 3 % by weight and as can be seen in Fig. 6 but the effect vanished when the weight percentage was increased as shown in Fig. 7 and 8. Also, the maximum delay was provided by the addition of 6 % of Nitrourea by weight.

The melting point of AN was found to be unaffected by the addition of Nitrourea in any weight percentages but a significant decrease in decomposition onset and peak temperature was noticed which showed a pattern of decreasing with the increase in weight percentage of Nitrourea.



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Figure 5: DSC Thermogram Showing Thermal Decomposition Behavior of Virgin AN



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

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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



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

- 1. The synthesized Nitrourea 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 Nitrourea is found to be exact as that of reported in referred literatures and hence it is concluded that the synthesized compound is pure in nature.
- 3. The use of Nitrourea as stabilizer minimally delayed in the onset temperature of phase transition (III) of Ammonium Nitrate.
- 4. The addition of Nitrourea in AN significantly lowered down the decomposition temperature of AN.

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