

PREPARATION AND DSC OF PHASE STABILIZED AMMONIUM NITRATE CRYSTALLIZED FROM ITS AQUEOUS SOLUTION CONTAINING POTASSIUM FLUORIDE

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Abstract

DSC of crystallized ammonium nitrate prepared from its aqueous solution containing 1 wt% potassium fluoride heated from room temperature to 300 °C showed the disappearance of phase transformation normally appears at 32 °C. Phases appeared only at 91.6 °C, 122.76 °C and 162.82 °C even when the nitrate was stored under natural conditions for 75 days or exposed to heating at elevated temperature and cooling to room temperature for several times. Acceleration of the decomposition of ammonium nitrate containing potassium fluoride was recorded at a temperature earlier than the decomposition temperature of pure ammonium nitrate and characterized by many calorimetric values.

Introduction

Ammonium nitrate is the most important commercial ammonium salt, with worldwide production on the order of tens million metric tons per year¹. Although used primarily as an agricultural fertilizer, a significant proportion is also used in the production of nonmilitary explosives used, for example, in coal and other mining and in quarrying and highway construction². In addition, ammonium nitrate has also received attention as a potentially effective oxidizer for rocket and missile propulsion systems^{3,4}. Despite the large-scale utilization of ammonium nitrate, this salt exhibits a number of undesirable properties. Most commercial processes resort to prilling⁵ or related granulation processes⁶⁻⁸, requiring subsequent drying and/or processing steps. Special vacuum crystallization process⁹ was not competitive with prilling techniques due to its formation of only small crystals. In addition, although no discrete hydrates of ammonium nitrate are known, the salt is highly hygroscopic, compromising its effectiveness as an explosive and leading to agglomeration of particles². It also suffers from the variable phase formation below or above room temperature. Thus five crystalline polymorphs of ammonium nitrate are known Table (1)¹⁰. The phase transition between phases IV and III is particularly problematic in that it occurs at close to ambient storage temperature (ca. 32°C). Because significant solid-state

reorganization occurs in the course of this phase transition, repeated cycling between phases IV and III leads to degradation of the physical state of ammonium nitrate, a process ultimately leading to powder formation^{1,2}.

Table (1)
The Phases of ammonium nitrate at variable temperatures^{1,2,11-13}

System	Temp. °C	State	Volume Change (%)
-	>169.6	Liquid	-
I	125.2 to 169.6	Cubic	+2.1
II	84.2 to 125.5	Tetragonal	-1.3
III	32.3 to 84.2	α-rhombic	+3.6
IV	-16.8 to 32.3	β-rhombic	-2.9
V	-16.8	Tetragonal	-

Behn¹⁴ discovered that when ammonium nitrate is exhaustively dried the transition at 32 °C disappears, and it is replaced by a transition at about 50 °C. Generally it is conceded the transition at 50 °C to 55 °C is a metastable transition between phases IV and II and therefore eliminates phase III from the ammonium nitrate phase diagram^{10, 14-16}. A

second method referred to lowering the temperature of the transition is, for example, by the addition of a soluble salt to the ammonium nitrate, potassium nitrate was found to lower the temperature of the IV - III transition about 6°C for each percent of added potassium nitrate¹⁷. However, small quantities (1% or less) of foreign salts also reported to stabilize ammonium nitrate crystals in a temperature range in which they are not normally stable e.g., phase II nitrate may be stabilized at room temperature by the addition of cesium nitrate to the ammonium nitrate¹⁸. Griffith¹⁹ stated that some salts overcome the influence of dehydrating the ammonium nitrate. When he added 0.1% sodium nitrate to molten ammonium nitrate and the mixture cooled to room temperature, the transition from phase IV to phase III occurred at 32 °C, even for the driest ammonium nitrate. However, the temperature of the IV - III transition could also be stabilized at 55 °C. by the addition of 1.84% magnesium nitrate to the system, while further addition of 0.1% sodium nitrate to the system was without detectable influence on the temperature of the transition at 55 °C¹⁹. Calcium nitrate also extends the stability of phase IV ammonium nitrate but the maximum temperature obtained for the IV -III transition was 50 °C. In addition to its influence on the temperature of transition between phase IV and phase III, magnesium nitrate has considerable influence on the temperature of phase III to phase II transition as it raised the temperature from 82°C to 90°C, in contrast to calcium nitrate which has very little influence on the temperature of the III - II transition¹⁹.

Mishra²⁰ treated ammonium nitrate with 0.5-2 wt% of potassium fluoride, considered the result to be true phase stabilization; the mixture was examined by DSC and thermo-mechanical analysis (TMA). Potassium fluoride was added to the fused ammonium nitrate phase and solid phase reported to form on cooling the liquid to below melting temperature. The normal endothermic transformations indicative of phase transitions at -18 °C and 32 °C were not observed during both heating and cooling cycle when sample tested by DSC in the temperature range of -55 °C to 80 °C. This was also confirmed by the linear expansion and

contraction of ammonium nitrate over the latter temperature range when was tested TMA²⁰.

The aim of this paper is to prepare phase modified ammonium nitrate in an feasible and less expensive method. It was also intended to obtain modified ammonium nitrate that have stable phase around 32 °C thereby eliminating the volume changes of 3.6% which is implying a drawback on the stability of physical state of the solid ammonium nitrate. It was also intended to investigate the behavior of ammonium nitrate when exposed to natural storing conditions and its stability when heating to 80 °C and cooling to ambient temperature for several times.

Experimental Section

The preparation of modified ammonium nitrate containing 1wt% was carried out by completely dissolving 10 grams of ammonium nitrate in 50 ml of distilled water then 1wt% of potassium fluoride (0.1g) was added and stirred to achieve complete dissolution of the solid materials producing clear solution at room temperature. The clear solution was evaporated on hot plat at 90 °C until complete dryness was achieved. The white solid powder thus formed was crushed, filled in sample bottles and kept in dry condition by storing in desiccators.

The prepared solid powdered samples that were filled in sample bottles were exposed to natural storage conditions for 75 days as follow: 60 days at maximum of 45°C and minimum of 30°C; and for 15 days at maximum of 35 °C and minimum of 20°C. Another sample was cyclic heated to 80 °C and cooled to room temperature for (5) times DSC measurements was carried out for all samples using 10 mg at heating rate of 2 °C per minute from room temperature to 300 °C using Schimadzu DSC-60 thermal analyzer.

Results and discussion

Phase transformation of modified ammonium nitrate:

Dried, freshly prepared ammonium nitrate containing 1 wt% potassium fluoride from aqueous solution showed similar differential scanning calorimetric curves to those of samples exposed to natural storage conditions or the heating cooling cycles stated in experimental section above Fig. (1) shows the

DSC curve for modified ammonium nitrate heated to 300°C at heating rate of 2 °C per minute.

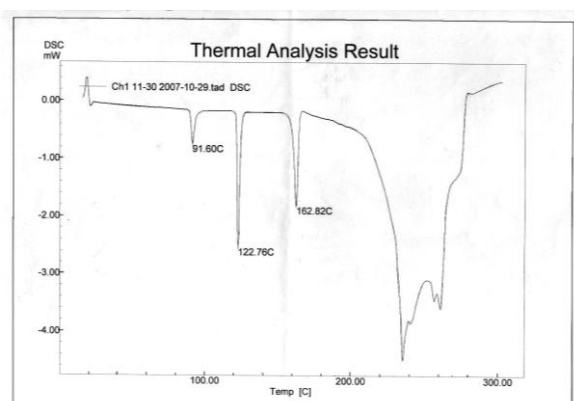


Fig.(1) : DSC heating thermogram illustrating the endothermic behavior of modified ammonium nitrate containing 1 wt% potassium fluoride.

The endothermic peaks of the thermal heating of ammonium nitrate from room temperature showed no endothermic changes up to the first recorded temperature of 91.6 °C. The closest temperature to the latter is the 84.2 °C of transformation to phase II of pure ammonium nitrate Table (1). The higher temperature of phase II formation observed in this work 91.6 °C may be related to new structure formation between ammonium nitrate and potassium fluoride. This high temperature stability is in agreement with other finding when foreign salt was added to ammonium nitrate. For example the temperature was lifted to 90 °C when magnesium nitrate was present; in contrast, calcium nitrate did not show a similar influence although it elevated the IV to III transformation to 50 °C²⁹.

The most significant finding of DSC of the modified ammonium nitrate prepared in this work was the disappearance of phase transformation of phase IV to phase III. This transformation is accepted to occur at 32 °C for pure non-dried solid ammonium nitrate. However, Behn¹⁴ stated, as outlined earlier, that this transformation disappeared and replaced by transformation at 50 °C when ammonium nitrate was exhaustive dried. It is conceded the transition at 50 °C to 55 °C as metastable transition between phase IV and II and therefore eliminating phase III from the ammonium nitrate diagram^{10, 14, 15, 21-23}. This as

reported by other worker, would implies that the transition from phase IV to phase III at 32°C and phase III to phase II at 82°C have been replaced by a single transformation near 50°C¹⁹.

In closely related results reported by Mishra²⁰ who prepared a modified ammonium nitrate also by adding potassium fluoride but to the melt phase of ammonium nitrate, showed similar stable behavior as observed for modified ammonium nitrate of this work. Unfortunately Mishra heated ammonium nitrate only to 80 °C (max. temperature required by the propellant industries) therefore no further heating changes reported above the later temperature in contrast to the changes observed up to 300 °C, the upper heating range applied in this work..

The influence of added salts on phase IV to phase III transformation of ammonium nitrate was also reported by other workers. Thus potassium nitrate which was gradually added to molten ammonium nitrated decreased the temperature of phase transition at 32 °C until transition disappeared when the wt% of added potassium nitrate was more than 15%^{17,24,25}.

Generally, the reason for the crystal disorder was attributed to the hydrogen bonding which is believed to stabilize phase IV, hence replacing ammonium ion by K⁺ ion thereby reducing the extent of hydrogen bonding²⁶. Indeed the diffusion of K⁺ and fluoride ions into ammonium lattice might be favored due to their smaller ionic sizes compared with those of ammonium and nitrate ions (1.48 Å and 1.83 Å for NH₄⁺ and NO₃⁻ ions respectively compared with 1.33 for both K⁺ and F⁻ ions)²⁰. This possible diffusion could cause the disappearance of phase III and thereby the phase of modified ammonium nitrate prepared in this work was stable until it transformed to phase II at 91.6 °C.

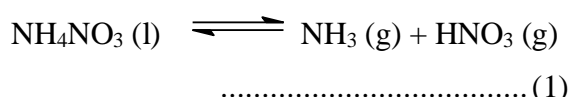
Phase II as stated in Table (1) is accepted to transform to phase I at 125 °C. The 122.76 °C found in this work was very close suggesting a little influence of potassium fluoride on phase II to phase I transformation. In addition, a similar small influence on the melting temperature was also observed when modified ammonium nitrate was transformed to melt phase at 162.82 °C compared with the reported temperature of 169.6 °C. This is not surprising

as influencing the melting point normally requires larger added salts than the 1% used in this work.

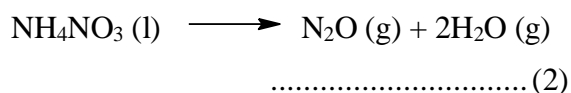
Decomposition of modified ammonium nitrate

The thermogram of modified ammonium nitrate with 1 wt% potassium fluoride started earlier than the reported decomposition temperature of pure ammonium nitrate of 210 °C²⁸. As indicated in Fig.(1) the endothermic peaks started at the melt phase at about 170 °C with slow rate until 205 °C when the rate accelerated and reached its maximum rate at 235 °C. Additional four thermal peaks were also recorded at 240 °C, 255 °C, 260 °C and 275 °C when the temperature finally ceased at 280 °C. These endothermic peaks may be related to intermediate products formation due the course of decomposition and also to endothermic nature of the volatilization into ammonia and nitric acid as opposed to the exothermic decomposition into nitrous oxide and water²⁹.

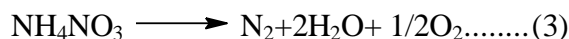
The metastable ammonium nitrate property might be related to the consistent of the reducing group (NH₄⁺) and the oxidizing group (NO₃⁻) in the same molecule. The kinetics of thermal decomposition of pure ammonium nitrate was studied by other researcher in a similar temperature range of the observed thermal changes in this work (i.e. 170 °C to 280 °C). Their results indicated that the degradation of ammonium nitrate is auto catalytic liquid phase reaction, the rate of which is proportional to the product of the mass of salt and the concentration of acid²⁷. The main reactions of heating of ammonium nitrate proposed to be dissociation at 170 °C (similar temperature of starting endothermic peak was recorded in this work) with enthalpy of 35.4 Kcal. according to the following^{30,31},



and decomposition at 290 °C with enthalpy of -16.4 Kcal. according to the following^{30,31}:



Moreover, a thermal decomposition of ammonium nitrate was also conducted but with the presence of sodium chloride by differential kinetic technique. The proposed radical mechanism of which indicated that the role of Cl⁻ is catalytic being oxidized by NO₂⁺ to Cl atoms, which recombined to give Cl₂ part of which reacting with NH₃ to provide a second sources of N₂³². The catalytic decomposition of ammonium nitrate



and those reported for pure ammonium nitrate or enhanced decomposition temperature in presence of magnesium nitrate¹⁹ all support the many decomposition peaks observed in this work as the presence of fluoride ions might also catalyze the decomposition in a similar manner as reported for chloride ions. That means, it is not an easy to elucidate the many peaks by only DSC tool, it is clearly requires additional studies such as at least thermogravimetric and kinetic investigations.

The modified ammonium nitrate was stable, in the sense of thermal and phase change, when exposed to natural storing or elevated (80 °C) temperatures as the DSC for these samples and that of the freshly prepared sample were almost identical.

Conclusion

In conclusion, the results clearly showed that modified ammonium nitrate crystallized by comparatively easy and less expensive method from aqueous solution containing 1wt% potassium fluoride was characterized by no phase changes from room temperature until 91.6 °C when first DSC endothermic peak of phase transformation appeared. This stabilization is strongly required by both the producers and the users of ammonium nitrate and offer good stability to the high standard required by propellant industry of 80 °C. The degradation, however, started earlier at 170 °C and characterized by many pathways probably producing many reaction products as indicated by DSC, yet the degradation ceased at 280 °C and the DSC was steady until 300°C. Furthermore, this ammonium nitrate showed good stability when exposed to natural storing condition under maximum temperature

of 45 °C and minimum of 30 °C for 60 days and maximum of 35 °C and minimum of 20 °C for 15 days, or 5 heating and cooling cycles to elevated temperatures of 80 °C.

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