



## **Phase Stability of Ammonium Nitrate with Organic Potassium Salts**

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**Abstract:** A study has been undertaken on the effect of additives on the phase transition of ammonium nitrate(V) (AN). Results obtained using Differential Scanning Calorimetry (DSC) showed that organic compounds and potassium salts of organic compounds have an effect on the phase transition behavior of AN. The samples were further analyzed using infrared (IR) and powder X-ray diffraction (XRD). The mechanism of phase stabilization of AN by compounds of this kind was examined. The present study showed that the influence of additives on the phase transition of AN occurs through the polar groups that are involved in intermolecular interactions of orbital and electrostatic types that form new hydrogen bonds. AN exists in only one phase in the temperature range from 30 °C to +100 °C, when a potassium salt of organic compounds was added. However, with organic compounds, the III→II phase transition was changed. IR and XRD of composites are characterized by new intermolecular interactions. Compacted samples of AN containing potassium salts of organic compounds exhibited better stability than AN containing organic compounds to multiple cyclic changes within a temperature range. This we named ‘freezing and thawing analysis’. Additives have two functions on the AN phase transition. First, solid solutions of AN mixture were formed for K<sup>+</sup> replacement of NH<sub>4</sub><sup>+</sup>. Second, hydrogen bonds formed, which caused AN and salts of organic compounds to interact intimately

**Keywords:** ammonium nitrate(V), phase transition, organic compounds, differential scanning calorimetry

## 1 Introduction

The interest in understanding the physical and thermal properties of ammonium nitrate(V) (AN) has a long history and is motivated by the wide use of this chemical as fertilizer, blasting agent, gas generator and propellant. Recently, there has been new interest in AN in the propellant field because AN-based propellants produce eco-friendly plumes, are smokeless, are of low cost and have low sensitivity [1-3]. But the drawbacks in using AN in ANFO explosives, gas generators and propellants are its polymorphic phase transitions and hygroscopicity. Much research has been carried out to stabilize these phase transitions, most of the studies concentrating on the stabilization of the IV→III transition. The phase transitions of AN cause volume changes near the phase transition temperatures, which give rise to the caking together of AN mixtures, especially at room temperature. Hence for these reasons, applications of AN are limited in many conditions. A number of compounds have been found to phase stabilize AN. Examples include potassium nitrate, copper oxide and metal dinitramide salts [4, 5]. The disadvantage of this method is the amount of additive required to stabilize the phase transition, ranging from 2% to 10% by weight.

As has been known for a long time, potassium nitrate inhibits the IV→III phase transition of AN at room temperature. This is because the radius of the potassium and ammonium ions are almost equivalent, meaning that they may mutually replace each other to form solid solutions of AN/potassium nitrates [6]. Consistent with this theory, other potassium salts have been investigated and also found to have the same ability to stabilize AN against phase transition at room temperature [7, 8].

As well as potassium salts, metal oxides are also widely used as additives to inhibit the IV→III phase transition of AN at room temperature. Phase stabilization of AN with metal oxides is beneficial with respect to burning rate, ignition and other properties [9]. For example, copper oxide significantly influences the transition temperature of AN by the formation of a solid solution of copper(II) diammine dinitrate in the AN crystal lattice. The reaction proceeds as follows [10]:



Solid state reactions take place between CuO and AN, thereby shifting the temperature of the phase transitions. So it is abundantly clear that it is possible to prepare AN crystals that are stable at room temperature using small amounts of additives.

Recently several papers have been published showing that organic compounds can also affect the AN phase state and phase transitions [11-14]. This research shows that the effectiveness of these compounds in inhibiting the IV→III phase transition is due to them influencing the interaction of the ammonium ions and nitro groups. The amount of additive needed was also relatively large [15-18].

**Table 1.** Crystallographic phase information for ammonium nitrate

Phase	Structure	Crystal ordering	Stability range [°C]
V	tetragonal	ordered	below -17
IV	orthorhombic	ordered	-17 to 32.25
III	orthorhombic	disordered	32.25-84.2
II	tetragonal	disordered	84.2-125.5
I	cubic	disordered	125.5-169.6

Pradeep *et al.* [19] performed research into the mechanisms and found that hydrogen bonding is weaker in phase III of AN than in phases II and IV. Sorescu and Thompson [20] also found that weaker hydrogen bonding interactions in phase III permit large thermal vibration motions of the ammonium ions leading to the disordered character of this phase. According to these results, the selection of chemicals which could form new hydrogen bonding between additives and AN would allow us to change the AN crystallization so as to inhibit AN phase transitions.

As well as all this, many studies have been performed on AN phase transitions using DSC [21], FTIR [22], XRD [23], Raman spectroscopy [24], NMR [25] and UV-spectroscopy [13]. These have shown that the phase behavior of AN strongly depends on the experimental conditions, such as humidity [26], crystallization method [7], thermal history of sample [7], sample size [27], pressure [28, 29], purity of sample [30], sample weight [31].

The aim of the present study was to identify new additives to inhibit the AN IV→III phase transition. Attention was given to compounds containing polar groups, in which the interactions of the polar groups with the AN and hence formation of hydrogen bonds would be expected. So, we selected for study organic chemicals as well as organic and inorganic potassium salts.

## 2 Chemicals and Methods

### 2.1 Chemicals

AN and organic chemicals, such as ammonium formate (AF), aminopropionic acid (AA), phthalimide (PA) and urea, were AR grade. 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) and 2,6-diamino-3,5-dinitropyridine (DADP) were industrial grade. Industrial grade AN was also used in some experiments. This was obtained from SINOPEC Nanjing Co., Ltd. Potassium carbonate (PC), potassium formate (PF), potassium persulfate (PP), potassium hexacyanoferrate ( $K_3[Fe(CN)_6]$ )(KFC), potassium acid phthalate (PAP), potassium dihydrogen phosphate (PDP) were also AR grade. The potassium salt of phthalimide (PPA) was made in-house by reacting phthalimide with potassium hydroxide.

### 2.2 Co-crystallization

A saturated solution of AN was prepared by dissolving 19.6 g AN in 10 mL of distilled water at 80 °C. The solution was heated using an oil bath and gently agitated (30 rpm) for 30 min. After the AN was completely dissolved, the required additive was added to the solution which was agitated for a further 30 min. The solution was then cooled to room temperature and then kept at -10 °C for 24 h. After 24 h, the crystals were collected by filtration and washed using isopropyl alcohol. Then the sample was kept at 50 °C for 48 h. When an organic compound was used as the additive, the AN was dissolved in methanol using the same procedure as outlined above.

### 2.3 IR observation

Solid phase transition measurements of the sample were performed using Fourier Transform Infrared microscopy (Bruker, 55FT-IR). The scanning range of the IR spectra was 525-4000  $cm^{-1}$ . Experiments were performed at room temperature.

### 2.4 DSC analysis

Differential Scanning Calorimetry (DSC) analyses of the dried samples were carried out using a METTLER (827e) instrument at a heating rate of 10 K/min. The samples were heated from 30 °C to 150 °C. The mass of the samples used was 1.500 mg. The system was in a nitrogen atmosphere.

### 2.5 XRD analysis

The AN samples were characterized by X-ray diffraction (XRD) using a Bruker D8 Advance XRD. Each sample was scanned over the  $2\theta$  angular range 5°-80°

with a sampling interval of 0.2°. The XRD reflections were obtained at room temperature (25 °C).

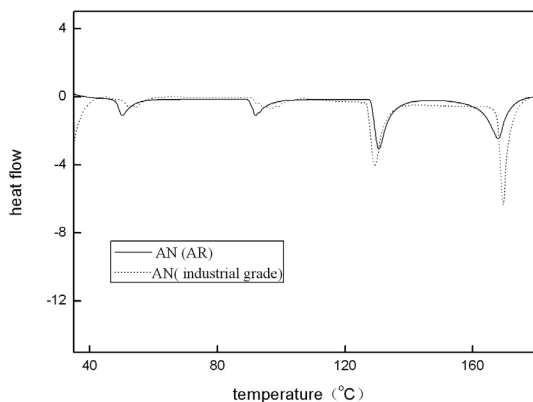
## 2.6 Freezing and thawing analysis

The freezing and thawing test was carried out in a box (EXCAL5423-H, Climates, France) to investigate the stability of AN at different temperatures. The temperature range was cycled from -10 °C to +50 °C. Each cycle consisted of storing the sample at -10 °C for 8 h, then bringing it up to 50 °C and storing it for 16 h at that temperature. The heating and cooling rates were 1.3 K/min. The sample was prepared by pouring the crystals into a mould ( $\phi=40$  mm) and then compacting them using a universal testing machine. The diameter  $\phi$  of the samples was 20 mm.

## 3 Results and Discussion

### 3.1 DSC analysis

First, the phase transitions of analysis grade and industrial grade AN were analyzed. The results are listed in Figure 1. It can be seen that purity has an effect since the transition temperatures of the two grades were slightly different, especially in the temperature range 30-100 °C. So, in the following experiments, analysis grade AN was used.

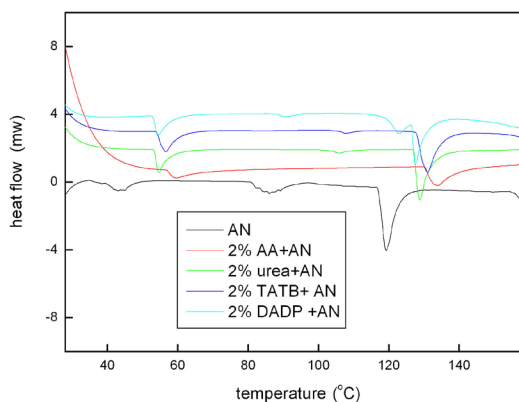


**Figure 1.** The typical DSC curve of AN.

In Figure 1, the first endothermic peak appeared at about 51 °C. According to previous studies [7, 32-36] and our experimental results, we believe that the endothermic peak at about 51 °C was the IV→II phase transition in AN co-crystallization samples.

Many researchers have found that hydrogen bonding of AN to additives affects the AN phase transitions [11-13]. So, we selected some organic and inorganic chemicals which contain polar groups. Our aim was to investigate whether hydrogen bonding of by additives to AN inhibits AN phase transitions. The DSC results are presented in Figures 2-8.

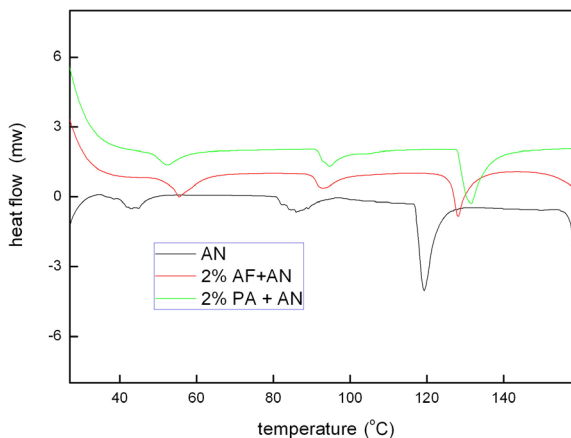
In Figure 2, we present the results for organic chemicals that contained carbonyl, carboxyl or nitro groups. The results show that the IV→II phase transition around 51 °C was still present but the IV→III phase transition at around 32 °C did not appear since the IV→II phase transition needs less energy. The III→II phase transition at around 84 °C did not appear, especially when urea or DADP was added. When urea was added to AN, the III→II phase transition shifted to 107 °C. And when DADP was added to AN, the III→II phase transition was almost unchanged. Hence, according to Figure 2, the addition of organic chemicals can influence the III→II phase transition of AN. This effect maybe due to hydrogen bonding or the structure of AN in a different phase. Two research teams have found structural differences of AN in different phases [37, 38].



**Figure 2.** The DSC curve of AN with added organic.

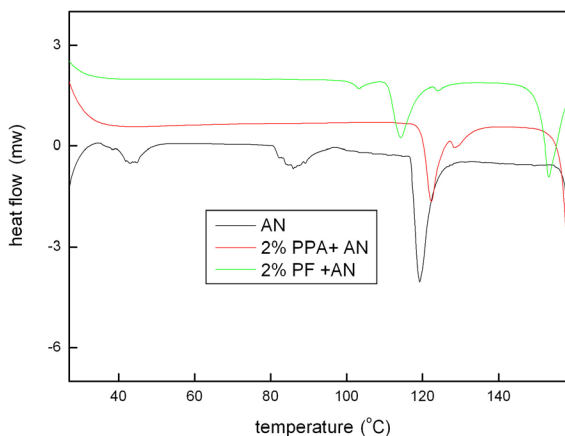
Maybe in the III structure there is hydrogen bonding formed by polar groups of the additive combined with free rotation of  $\text{NH}_4^+$ , and since other hydrogen bonds exist, the interaction of the  $\text{NH}_4^+$  and  $\text{NO}_3^-$  ions is inhibited, which causes the III→II phase transition to disappear. In order to further investigate the function of hydrogen bonding, other organic chemicals were also selected as additives. The results are shown in Figure 3. It was disappointing that the III→II phase transition still existed. The organic chemicals also contain carbonyl and carboxyl groups. Maybe the reason the phase transition still exists is due to the chemical structure. Another reason maybe was the amount of additive.

We added smaller amounts of additives than previous researchers [11-14]. It is possible that if the amount of additives is large, perhaps the effects of hydrogen bonding are increased. In support of this, Lang and Vyazovkin [39] found that the phase stability of AN remained when the amount of polymer additive was much larger. Hence we thought that hydrogen bonding may play an important role in the interaction of ammonium ion with the additive.



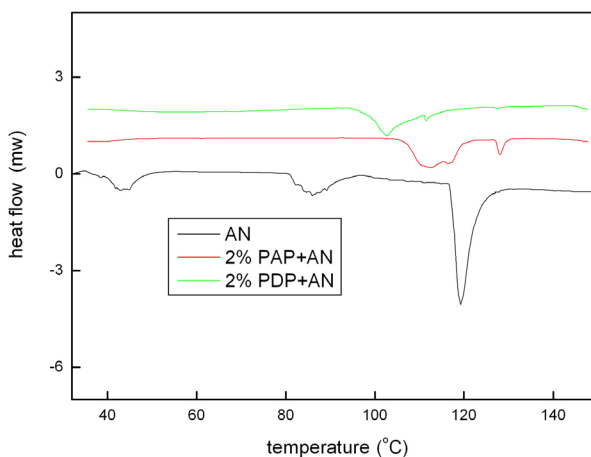
**Figure 3.** The DSC curve of AN with added organic.

We also investigated the effects of adding potassium salts of the same organic chemicals on the AN phase transitions. The results are shown in Figure 4. The results were very satisfactory. In the temperature range 30-100 °C, there was no endothermic peak. This means that the IV→III and III→II phase changes of AN were inhibited. So, potassium salts of organic chemicals are very effective on AN phase transitions in the temperature range 30-100 °C. We can therefore conclude that potassium salts of organic chemicals have two effects on the AN phase transition. First, when a potassium salt of an organic chemical is added, the change in the transition temperature can be explained based on the replacement of some ammonium ions by potassium ions, thus forming solid solutions of AN. Second, hydrogen bonds form, which causes the AN and the organic salt of organic to interact strongly. Thus the hydrogen bonding, which causes the III→II phase transition to disappear, notably increased. So the IV→III phase transition and the III→II phase transition of AN disappeared. In summary, the formation of a solid solution and changes in the hydrogen bonding function are key factors on phase changes of AN. However, the action of hydrogen bonding still needed to be demonstrated.



**Figure 4.** The DSC curve of AN with added organic salts.

In order to further investigate how potassium salts of organic chemicals affects the AN phase transition, other potassium salts of organic chemicals were also selected. The results are shown in Figure 5. The results were also very satisfactory. The phase changes of AN were also inhibited in the temperature range 30-100 °C. So, we can conclude that potassium salts of organic chemicals are very effective on the AN phase transition in the temperature range 30-100 °C.



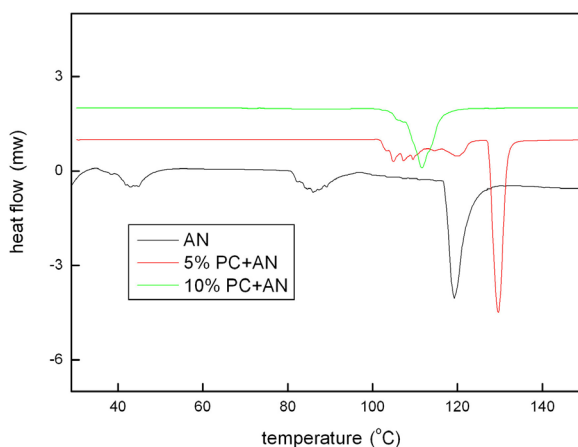
**Figure 5.** The DSC curve of AN with different amounts of added organic salts.

In order to investigate if other potassium salts inhibit AN phase transitions, some inorganic chemicals were selected, namely PP, PC and KFC. The results are shown in Figures 6, 7 and 8. These results also were satisfactory in that

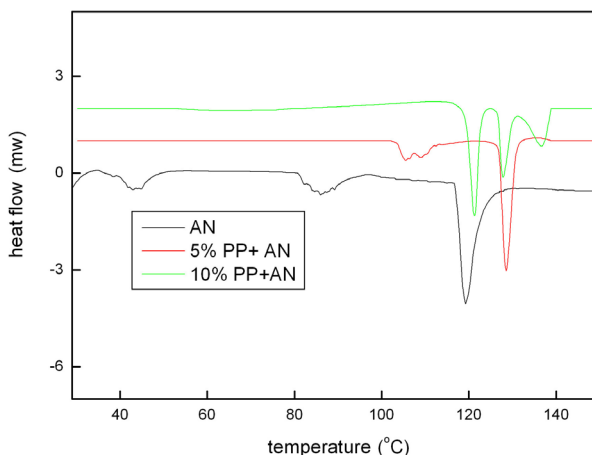


inorganic potassium salts are very effective on the AN phase transition in the temperature range 30-100 °C. However, Vargeese *et al.* [18] found that potassium ferrocyanide modifies the crystallization of AN but does not affect AN phase transitions. A possible reason for the difference between their results and ours is the amount of additive used. Vargeese *et al.* [18] added only 0.1-1% of additive. Therefore, we can further conclude that organic potassium salts, which contain polar groups, are very effective on the AN phase transition in the temperature range 30-100 °C. And also the amount of additive is an important factor.

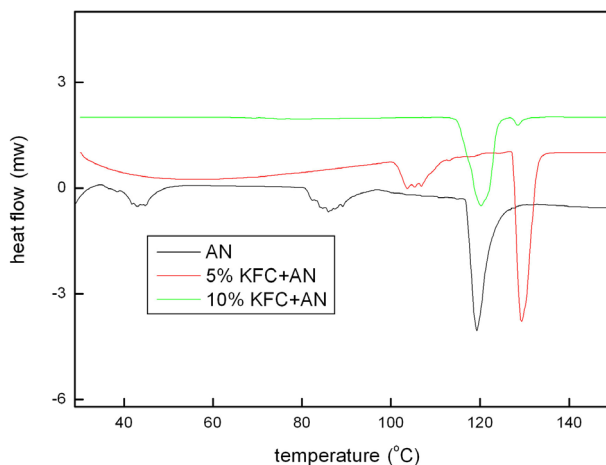
In order to demonstrate that hydrogen bonding is present in an AN mixture, an IR analysis was carried out.



**Figure 6.** The DSC curve of AN with different amounts of added inorganic salts.



**Figure 7.** The DSC curve of AN with different amounts of added inorganic salts.



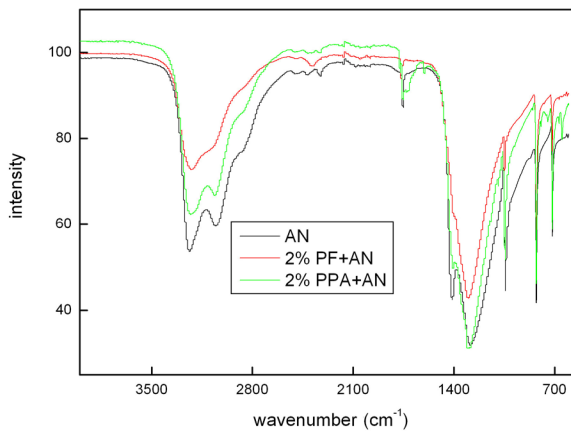
**Figure 8.** The DSC curve of AN with different amounts of added inorganic salts.

### 3.2 IR analysis

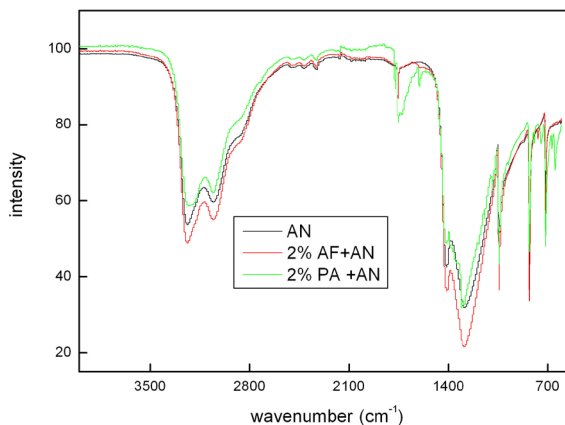
Many researchers have investigated the interaction of AN and additives, such as water [40] and organic compounds [41, 42]. We scanned mixtures of AN and additives using IR in the wavelength range  $525\text{--}4000\text{ cm}^{-1}$ . The results are shown in Figures 9-14.

There have been extensive studies on AN phase transitions using IR and Raman vibration spectroscopy. As can be seen in Figures 9 and 10, when AF, PF, PA or PPA was added, the IR spectra of the mixture exhibits remarkable differences. The main spectral distinction between these results lies in the wavelength ranges  $3000\text{--}3500\text{ cm}^{-1}$  and  $1500\text{--}1000\text{ cm}^{-1}$ . The absorption peaks around  $1800\text{ cm}^{-1}$  are assigned to  $\text{NO}_3^-$  vibrations. Those in the spectral range  $3000\text{--}3500\text{ cm}^{-1}$  are vibrations of  $\text{NH}_4^+$ . Those in the spectral ranges  $2500\text{--}1700\text{ cm}^{-1}$  and  $1050\text{--}750\text{ cm}^{-1}$  are vibrations of  $\text{NO}_3^-$ . According to these results, the vibrations of  $\text{NO}_3^-$  were not changed. Comparative analysis of the IR spectra shown in Figure 9 reveals the disappearance of the bands at  $3058\text{ cm}^{-1}$  associated with stretching vibrations of N–H bonds, suggesting that AN and PF maybe form a new system of hydrogen bonds in the mixture [12]. At the same time, the vibration frequencies of the ammonium ion at around  $3200\text{ cm}^{-1}$ , remain virtually unchanged in the mixture. Another remarkable change was the disappearance of the absorption peak at  $1411\text{ cm}^{-1}$ , which is the N–H asymmetric deformation [43]. Thus, from the changes at  $3058\text{ cm}^{-1}$  and  $1411\text{ cm}^{-1}$ , we can conclude that when PF and PPA are added to AN, a new system of hydrogen bonds is formed. Also we infer that hydrogen bonds form between ammonium ions with anions

rather than nitro groups with active hydrogen. Comparing Figure 10 to Figure 9, when AF or PA was added, the bands at  $3058\text{ cm}^{-1}$  and  $1411\text{ cm}^{-1}$  still appeared.



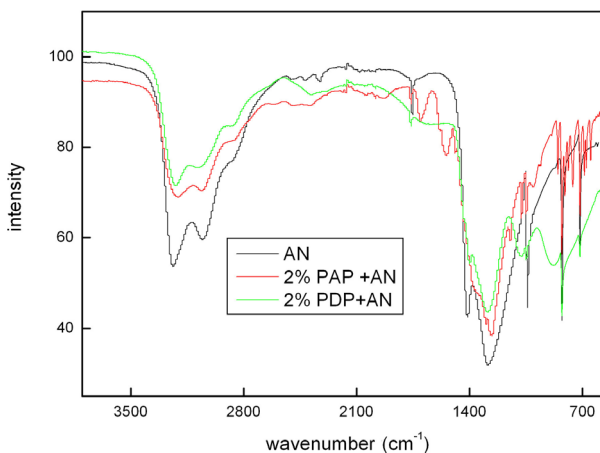
**Figure 9.** The IR curve of AN with added organic salts.



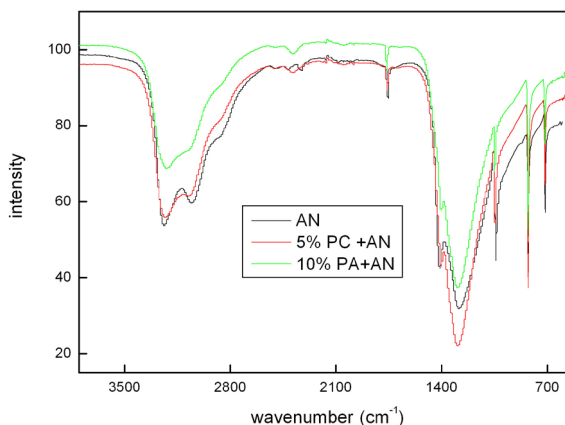
**Figure 10.** The IR curve of AN with added organic salts.

The other important question to be addressed is whether the crystal structure changes when additives are added to AN. When PF was added to AN, according to the bands at  $1040\text{ cm}^{-1}$ ,  $1047\text{ cm}^{-1}$  and  $712\text{ cm}^{-1}$  the AN structure was similar but not identical to phase II since the peak at  $711\text{ cm}^{-1}$  split into two with an additional peak at  $721\text{ cm}^{-1}$  [21]. The reason for this was that hydrogen bonding between PF and AN affected the AN crystal structure. The additives limited the free rotation of the ammonium ion in the AN mixture. And the IV–II phase transition needs less energy than the IV–III phase transition. The character of

phases II and IV are very similar [33]. Hence, the structure of the AN mixture was similar to phase II of AN when an additive was added to AN. However, it was not confirmed that the mixture of AN with an additive was phase II. When PPA was added to AN, the IR absorption peaks at  $1042\text{ cm}^{-1}$ ,  $1053\text{ cm}^{-1}$  and  $713\text{ cm}^{-1}$  were very similar to those for phase II. However, this observation does not confirm that the AN in the mixture was phase II.



**Figure 11.** The IR curve of AN with added organic salts.

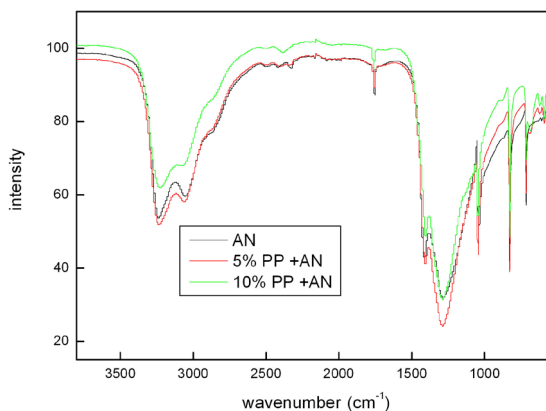


**Figure 12.** The IR curve of AN with different amounts of inorganic salts added.

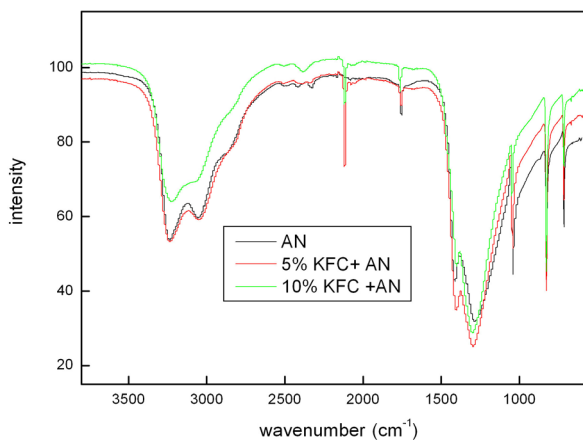
When AF or PA was added to AN, the only effect on featured IR absorption peaks was a slight change in their intensity. This is possibly because the AN crystallization was not changed (or only slightly changed) by the addition of

the AF or PA since it is difficult for these chemicals to enter the AN crystal lattice. By contrast, when potassium salts are added, potassium ions can enter the AN crystal lattice and replace ammonium ions. And the anions of organic potassium salts form stronger hydrogen bonds with ammonium ions than organic chemicals. Hence, when organic potassium salts are added to AN, the mixture has no endothermic peak in the temperature range 30-100 °C.

When PAP or PDP was added to AN, the results are as given in Figure 11. The results are the same as for PF and PPA. We also found that as the amount of these additives was increased, hydrogen bonding was increased (see Figures 12-14). This explains why the AN phase transition was still present when potassium hexacyanoferrate was added in concentrations in the range 0.1-1%.



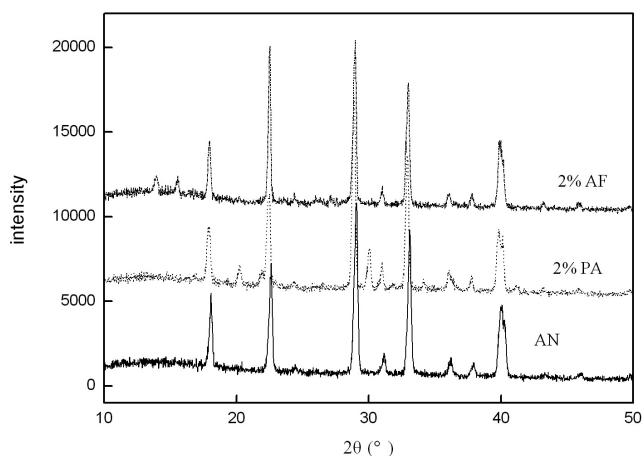
**Figure 13.** The IR curve of AN with different amounts of inorganic salts added.



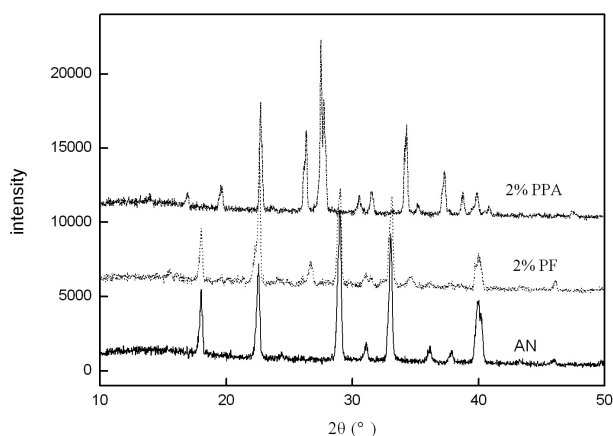
**Figure 14.** The IR curve of AN with different amounts of inorganic salts added.

### 3.3 XRD analysis

As previously discussed, when various potassium salts were added to AN, the hydrogen bonds formed by polar groups with ammonium ions inhibited the phase transition of AN in the temperature range 30-100 °C. Also the crystallization of AN was changed, but we were not able to confirm that the AN in the AN/additive mixture was in phase II. Therefore, XRD was used to analyze the AN crystals in the AN mixture. For this investigation, we selected PF and PPA as additives.



**Figure 15.** The typical XRD curve of AN with organic salts added.



**Figure 16.** The typical XRD curve of AN with organic salts added.

The XRD patterns obtained for both pure AN and mixtures are shown in Figures 15 and 16. For our pure AN sample, the main X-ray diffraction peaks

occurred at  $18.04^\circ$ ,  $22.58^\circ$ ,  $29.02^\circ$ ,  $33.04^\circ$  and  $40.04^\circ$ . Standard published XRD spectra of pure phase IV AN have X-ray diffraction peaks at  $17.9^\circ$ ,  $22.43^\circ$ ,  $28.9^\circ$ ,  $32.88^\circ$  and  $39.85^\circ$ . So we can conclude that at ambient temperature, our pure AN sample was in phase IV.

Our results for samples where AF or PA was added to AN showed no differences in the main features of the diffraction peaks (compare Figures 15 and 16). For samples where PF was added to AN, the main X-ray diffraction peaks occurred at  $18.03^\circ$ ,  $22.91^\circ$ ,  $26.68^\circ$ ,  $29.12^\circ$ ,  $33.06^\circ$  and  $40.11^\circ$ . And when PPA was added to AN, the main X-ray diffraction peaks were at  $19.52^\circ$ ,  $22.68^\circ$ ,  $26.38^\circ$ ,  $27.52^\circ$ ,  $34.32^\circ$  and  $37.32^\circ$ . The mixture results were thus different to phase IV at room temperature. When PPA was added, the X-ray diffraction peaks were similar but with some differences to phase III, especially at  $26.38^\circ$  and  $27.52^\circ$ . When PF was added to AN, the X-ray diffraction peak also showed a similar result, especially at  $26.68^\circ$ . A possible interpretation of these results is that hydrogen bonding was stronger with PF as an additive than when PPA was added because there are two carbonyl groups in PPA and only one carbonyl group in PF.

To summarise the X-ray results, the intensities and angular positions of the diffraction peaks of AN were changed by the addition of additives as may be seen by comparing our results with those published in Refs. [44, 45]. These results imply that the crystal structure of AN is changed by the addition of the additives we studied. The most likely cause of this is hydrogen bonding, which influences the interaction of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  ions.

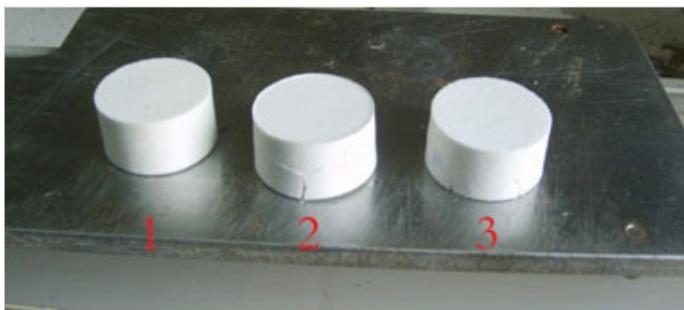
### 3.4 Freezing and thawing analysis

In order to investigate the AN mixture phase stability at room temperature, a freezing and thawing experiment was carried out. This method was an effective method of estimating AN phase changes through cracks produced in the sample surface [46, 47].

According to these experiments, PF was shown to be very effective in inhibiting AN phase transitions at room temperature. So in separate experiments we added PF and AF to AN. The AN/additive mixture was then compressed into a cylinder-shape. The cylindrical samples were then temperature-cycled between  $-10^\circ\text{C}$  and  $50^\circ\text{C}$ . When a phase transition happened, the change in volume was recorded. For example, in going from  $50^\circ\text{C}$  to  $-10^\circ\text{C}$ , the volume decreased when an AN phase transition occurred. Therefore, a crack appeared in the surface of the sample.

The effects of the fifth temperature cycle are shown in Figure 17. Cracks can clearly be seen to have formed in both pure AN and mixtures of AN with AF.

The crack in pure AN was very serious. No crack formed in mixtures of AN with PF. Therefore, we can assert that the freezing and thawing analysis method is viable for evaluating AN phase transitions. Also PF was a very effective additive for inhibiting the AN phase transition at room temperature.



1, 2% PF; 2, AN; 3, 2%AF

**Figure 17.** Results of freezing and thawing test.

## 4 Conclusions

Our paper describes an investigation of new additives for inhibiting AN phase transitions making use of DSC, IR, XRD and freezing and thawing experiments. The following conclusions can be drawn from our study:

1. Organic chemicals containing polar groups effectively inhibit the AN phase transition around 85 °C.
2. Potassium salts of organic and inorganic compounds were very effective at inhibiting AN phase transitions in the temperature range 30-100 °C.
3. The IR showed that hydrogen bonds formed between polar groups and ammonium ions.
4. Additives can affect the AN phase transitions in two ways. First, solid solutions of AN/additive mixes can form in which  $K^+$  replaces  $NH_4^+$ . Second, hydrogen bonds can form, causing AN and organic salts to interact intimately.
5. XRD experiments showed that the AN crystal structure was possibly changed.
6. Freezing and thawing analysis experiments showed that potassium salts, such as potassium formate, is a suitable compound to inhibit the AN phase transition at room temperature.



## Acknowledgements

This paper was supported by Inner Mogolia ShengAn Chemical Ltd. Co.

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