PREPARATION OF PHASE STABILIZED AMMONIUM NITRATE(PSAN) BY A SALTING OUT PROCESS

JUN-HYUNG KIM

Agency for Defense Development, P.O. Box 35-4, Yuseong, Taejeon, 305-600, Korea

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Introduction

Ammonium nitrate(AN) is a major oxidizing agent in many propellants and explosives. However, its use has been limited because of its solid state phase transition characteristics. There have been many studies in which the phase transitions among its polymorphs have been examined. The transition temperatures of the various phases are:

The phase transition $\text{AN}_{\text{IV}} \rightarrow \text{AN}_{\text{III}}$ can occur at temperatures of 32 – 55°C depending on the moisture content and thermal history of the sample. In addition, phase IV transforms directly to phase II at about 52°C when AN is exhaustively dried (Ingman *et al.*, 1982).

It is well known that the addition of potassium nitrate (KN) to AN to produce a solid solution improves the phase stability of AN (Coates and Woodard, 1963). By far, the phase stabilized AN(PSAN) has been mainly obtained by the melting method, where mixtures containing KN were formed by dissolving KN in the melt of AN, and quenching. Another preparation method includes the steps of evaporating AN-KN aqueous solutions saturated at about 90°C and drying the resulting precipitates.

In this paper, we describe a method for preparation of PSAN, where the process involves precipitation of AN with KN from the aqueous solutions of their salts by the addition of acetone. This kind of process is often referred to as "salting out" process (Murray and Larson, 1965).

1. Experimental Procedure

1.1 Salting out crystallization

A 300 ml cylindrical jacketed glass vessel ($\phi 60 \times 100$ mm) equipped with a teflon paddle impeller

of 40 mm diameter and 15 mm width was used as a crystallizer. AN was obtained from J.T. Baker Chemical Co. and KN was purchased from Fisher Scientific Co. These compounds were chemically pure, and were used without further treatment. In this work, we prepared six aqueous solutions of different compositions saturated at 25°C (Groups A-F, see Table 1). Equilibrium concentration data for the AN-KN-H₂O system were taken from the literature (Seidell, 1953). Acetone as the precipitant was rapidly added with agitation to the aqueous solutions. The adding process took about 2 seconds, and was followed by another 30 minutes of stirring. All experiments were carried out under the same condition of temperature (25°C) and agitation speed (600 rpm). The amount precipitated was measured by weighing after filtering the slurry through a 0.5 μm Millipore filter and drying of the precipitate.

1.2 Analyses of samples

Differential scanning calorimetry (DSC) was performed using a differential scanning calorimeter (DuPont Thermal Analyzer 1090) in order to examine the solid state phase transitions of the precipitated solids between 10 and 150°C with a heating rate of 5°C/min. The weight fraction of KN in the precipitate was determined by thermogravimetry (TG). The determination was easily carried out due to the large difference between the thermal decomposition temperatures of AN and KN, which are respectively 210 and 400°C (Weast, 1984). The TG analysis was carried out with a heating rate of 10°C/min up to 390°C in a nitrogen atmosphere. The nitrogen flow rate was kept at 80 ml/min. The sample sizes were about 5 mg for DSC and about 15 mg for TG experiments.

The X-ray powder diffraction analysis was also performed on a JEOL JDX8030 powder diffractometer with CuK α radiation in the angle range from $2\theta = 15^{\circ}$ to 60° .

2. Results and Discussion

Figure 1 shows measured precipitation curves. The x-coordinate of Fig. 1 is the mass ratio, R , defined as the added mass of acetone per unit mass of the

* Received on March 21, 1996. Correspondence concerning this article should be addressed to J.-H. Kim.

Table 1 Composition of the aqueous solutions used in this work (weight %)

Designation	Composition			$XL_{KN}(i) = KN/(AN + KN)^*$
	AN	KN	H ₂ O	
Group A	67.7	0	32.3	0
Group B	0	27.86	72.14	100
Group C	54.8	13.95	31.25	20.291
Group D	59.93	8.62	31.45	12.574
Group E	61.41	7.26	31.33	10.572
Group F	65.63	2.71	31.66	3.965

* $i = A - F$ **Fig. 1** Precipitation ratio, f , as a function of mass ratio, R , for various aqueous solutions (○) Group A; (□) Group B; (●) Group C; (■) Group D; (▲) Group E; (▼) Group F

aqueous solution. The precipitation ratio, f , is defined as the ratio of the mass of the precipitated crystals by the addition of acetone to the mass of the salts in the original aqueous solution. It can be seen that on Group B (KN-H₂O-Acetone system), the values of f are somewhat higher than those of the other systems. At low R ratios, all the curves are almost directly proportional to R , whereas for R values which are greater than 10 (*i.e.* $R > 10$), no further significant change of precipitation ratio can be noticed.

Figure 2 shows the KN concentration in the precipitated crystals, XC_{KN} . At the lower R values, the more KN tends to precipitate simultaneously with AN (*i.e.* XC_{KN} increases). It can be also seen from Fig. 2 that the composition of the solid precipitated for large R (about $R > 10$) is nearly the same as that of the initial aqueous solution composition, $XL_{KN}(i)$ (see Table 1).

Cady (1981) published a phase diagram of the

Fig. 2 Change of composition of precipitates, XC_{KN} with mass ratio, R (●) Group C; (■) Group D; (▲) Group E; (▼) Group F; (—) $XL_{KN}(i)$; $i =$ Group C, D, E and F

AN-KN system, which was determined by means of hot- and cold-stage optical microscopy in conjunction with time-lapse photography. Cady prepared the solid samples of the AN-KN system by the melting method mentioned in "Introduction" part. Cady's results are shown in Fig. 3 together with data measured in this study. Phase boundaries between stable phases are indicated by solid lines. Dashed lines indicate boundaries between metastable phases. It is shown that samples with about 10–15 wt% KN show the transitions $AN_{III} \rightarrow AN_{II} + C_{II}$ at 110°C and $AN_{II} \rightarrow AN_I$ at 126°C, where C_{II} corresponds to the AN-KN addition compound of composition $KNO_3 \cdot 2NH_4NO_3$.

Figure 3 also shows measured phase transition temperatures of the precipitates obtained by the salting out method. It can be seen from Fig. 3 that our results are in fair agreement with those of Cady in the 0–30 wt% KN region. It is also shown that AN is stable over the temperature range from room temperature to about 80°C if XC_{KN} is greater than 10 wt%.

Fig. 3 Comparison of the phase transition temperatures measured in this work with the data of Cady (1981) for the AN-KN system

Figures 4(a) and (b) are the X-ray powder diffraction patterns of the crystals formed at $XC_{KN}=22.1$ by the conventional melting method and the salting out method, respectively. A comparison of the X-ray diffraction patterns between crystals obtained from these two methods indicates identical crystal structure. These results mean that the precipitates prepared by the salting out method are PSAN.

In conclusion, precipitation of AN with KN from the aqueous solutions of their salts using a salting out technique with acetone as the precipitant was investigated. The experimental DSC and X-ray diffraction results showed that the precipitates are PSAN. Therefore, it may be possible to make use of this technique for the preparation of PSAN as an alternative to the present processes.

Nomenclature

f	=	precipitation ratio	
R	=	added mass of acetone per unit mass of the aqueous solution	
T	=	temperature	[°C]
XC_{KN}	=	KN concentration in the solids	[wt%]

Fig. 4 X-ray powder diffraction patterns of crystals obtained at $XC_{KN}=22.1$ (a) by the melting method (b) by the salting out method

$XL_{KN}(i)$ = initial KN concentration in the solution of Group i , defined in Table 1 [wt%]

2θ = reflection angle of X-ray [°]

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