

PHASE MODIFICATION OF AMMONIUM NITRATE BY POTASSIUM SALTS

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Abstract

Modification of the room temperature phase (IV-III) of ammonium nitrate (AN) has been attempted using a variety of potassium salts namely, KF, KCl, KI, KNO₃, K₂CO₃, K₂SO₄, KSCN and K₂Cr₂O₇. No phase transition was observed when AN containing 1–2% by mass of these potassium salts is heated from room temperature (25°C) onwards in DTA and DSC scans, but the linear expansion due to phase transition was still observable in TMA measurements. Complete arrest of the linear expansion occurs only when a higher concentration of the additive is used. Similarly, in thermal cycling experiments, complete phase modification in the temperature range –80 to 100°C occurs only with a higher percentage of the potassium salt. The extent of modification, however, is found to be dependent both on the concentration, and the type of the anion. Potassium dichromate when used as an additive modifies the phase as well as the decomposition pattern of AN.

Keywords: ammonium nitrate, phase modification, potassium salts

Introduction

Ammonium nitrate (AN) is one of the most interesting substances from the allotropic point of view. Under ordinary pressures, it occurs in no fewer than five polymorphic forms and remarkably all of them are stable in their appropriate range of temperature [1]. Many negative features of AN, which is one of the most widely used nitrogenous fertilizer and a well known oxidizer in solid propellants and explosives, are attributed to these crystal transformations which behave unreliably. Predicting a reliable transition behavior of AN, especially that of the transition that occurs near room temperature and is accompanied by a sensible volume increase, is important because of the relation between this transition and the ultimate mechanical strength of the salt. Most of the studies aimed at investi-

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gating the mechanical strength of the AN prills support the generally accepted idea that the mechanical strength is related to the AN(IV)-AN(III) polymorphic transition.

The growing interest in this transition is further justified by the prominence that AN has gained as an environmental friendly chlorine free rocket propellant oxidizer. One of the major hurdles in replacing ammonium perchlorate, which is currently the most commonly used oxidizer in solid propellants, with AN is the aforementioned room temperature (32°C) phase transition. On storage or transportation, the processed propellant grain which contain AN upto 85% by mass could be subjected to temperature variation of this magnitude and thus could disintegrate or develop cracks, due to volume expansion during the phase change. The presence of cracks results in a totally unpredictable burning pattern, which could be disastrous. It is necessary, therefore, to extend the temperature region of the stable existence of phase IV much above 32°C , or stabilize the salt in one of the other safe structures.

Realizing the technical significance of the room temperature phase of AN, many attempts have been made in the past to develop phase stabilized ammonium nitrate (PSAN). The main difficulty in stabilizing the phase arises because of the sensitivity of the phase to a diverse range of variables [2–7] like, moisture content, grain size, mode of crystallization, thermal history of the sample, sample mass, number of previous transformations and heating mode, etc. The strategy frequently adopted to stabilize this phase involves incorporation of certain ions, in the AN crystal lattice. The earliest studies in this regard concern the use of potassium nitrate. The addition of KNO_3 has a remarkable effect on the properties of AN, and has been a subject of many investigations [8 and 9]. It is reported to decrease the density of AN slightly, lower the transition temperature and also the volume expansion on transition, reduce the hygroscopicity, and the number of contact points required for caking. Besides, potassium nitrate, the effects of other salts, such as, ammonium sulfate, sodium nitrate in presence of potassium nitrate, alkali metal nitrates, CuO , NiO , aluminum oxide, K_2O and ZnO have been examined [9–16]. It is cited that the most effective phase stabilizer shifts the low temperature phase transition from 32 to 118°C [10].

A recent observation of the stabilizing effect of KF is significant mainly because of the relatively small amount of KF compared to the other salts, required for phase modification [17–19]. It is suggested that a 2% by mass of KF can suppress the phase transition of AN completely as compared to around 4% for KNO_3 . It is apparent that KF is superior to KNO_3 in modifying the phase which otherwise is believed to be a result of replacement of ammonium ions by potassium ions. However, these results are not available in the open literature. Besides, the experimental techniques differ in different studies.

In the present study we report a systematic investigation of the IV-III room temperature phase transition of AN on cocrystallizing with a variety of potas-

sium salts with a view to ascertain the effect of the anions, if any, on the transition. An attempt has been made to minimize the volume change resulting from the transition. The effect of thermal cycling on the transition has also been determined. The transitions have been monitored by various experimental techniques, DTA, DSC, TMA and XRD.

Experimental

Analar grade ammonium nitrate and the potassium salts, KF, KCl, KI, KNO₃, K₂CO₃, K₂SO₄, KSCN and K₂Cr₂O₇ were procured from commercial sources and used as such. PSAN samples were prepared by cocrystallizing AN with various amounts of potassium salts from aqueous solutions. In a typical experiment, AN (5 g) was dissolved in distilled water (100 ml). To this solution, a required amount of the potassium salt powder was added. The mixture was stirred to dissolve the salt completely. The solution volume was then reduced by evaporation on a water bath. The cocrystallized salt separated was dried in oven at 80°C and stored in a vacuum desiccator.

The DTA of the samples were carried out using a Shimadzu DT-40 simultaneous DTA-TG thermal analyzer in platinum cups employing a heating rate, 10°C min⁻¹, in flowing nitrogen. The sample size used was about 10 mg.

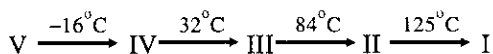
A Rheometric Scientific DSC was used to record the DSC profiles. The rate of heating or cooling used was 10°C min⁻¹. Measurements were made using about 5 mg samples in flowing nitrogen atmosphere.

The linear thermal expansion was followed by thermomechanical analysis, on a Shimadzu TMA-40 unit. The dried PSAN samples were powdered and made into cylindrical pellets (300 mg, 3–4 mm long and 6 mm dia) using a hydraulic press. Care was taken to maintain a uniform density, (~1.5 g cm⁻³), for all the pellets. Measurements were carried out in flowing nitrogen at a heating rate, 10°C min⁻¹, in the temperature range -100 to 160°C. The subambient cooling was monitored using a liquid nitrogen cryostat. The dimensional changes (either expansion or contraction) undergone by the sample pellet, under a specified load when subjected to heating or cooling was detected using a linear differential transformer. Absolute values of the dimensional changes were calculated from the initial dimension and the set amplifier output. In the thermal cycling studies, the samples were heated at a controlled rate followed by natural cooling.

X-ray powder diffraction studies for structural characterization were carried out on a Scintag diffractometer (USA), Model XDS-2000 using CuK_α radiation.

Results and discussion

The reported transition temperatures for various phases of AN are as follows [1].



Since the transition of interest depends on the purity of the sample, AN used was characterized each time using the same technique and experimental conditions, as that employed for characterizing the PSAN in the present study. The DTA of AN (Fig. 1) shows all the reported transitions from room temperature upwards as expected from an untreated sample. The IV-III transition occurs at 40°C instead of 32°C , which is not unusual since this transition is reported to take place anywhere between 31 and 55°C depending upon the source of the sample as mentioned earlier. The salt subsequently undergoes three more transitions, at 85 , 125 and 169°C (melting) before decomposing endothermically around 260°C .

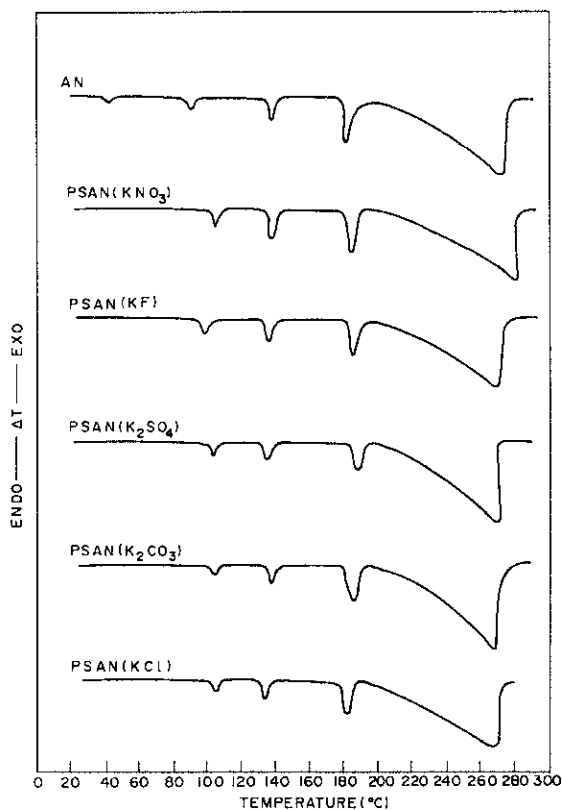


Fig. 1 DTA traces of AN ad PSAN samples

The DTA curves (Figs 1 and 2) of AN cocrystallized with the various potassium salts (1% by mass) show major changes in the phase transition temperatures. The peak at 40°C corresponding to the IV-III phase transition vanishes

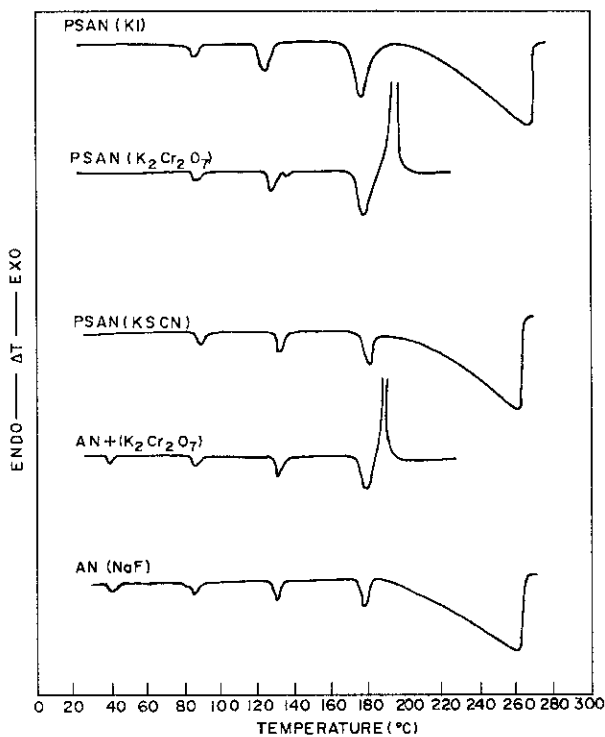


Fig. 2 DTA traces of various PSAN samples

when AN is cocrystallized with K_2SO_4 , K_2CO_3 , KSCN, KI, $K_2Cr_2O_7$ or KCl as observed in the case of the other two potassium salts namely, KNO_3 and KF, which are known to be phase modifiers [11, 17]. However, cocrystallization with other salts having similar anions, such as Na_2CO_3 , NaF, $NaNO_3$, $(NH_4)_2Cr_2O_7$ do not affect this phase transition. The vanishing of the transition at $40^\circ C$ also does not occur when a physical mixture of the salts (e.g. $AN+K_2Cr_2O_7$) is used instead, as is evident from the data listed in Table 1. This has been further confirmed by XRD data wherein no phase modified pattern was observed unless the additive is coprecipitated. The cocrystallization is believed to cause formation of solid solution of K^+ salts in AN [9]. It can also be seen that in most cases when the phase is stabilized, the transition temperature of III-II which occurs around $84^\circ C$ is shifted to a higher temperature. It is thus apparent that phase modification occurs with all the K^+ salts used irrespective of the anions. Another significant observation is the exothermic decomposition of AN when cocrystallized with $K_2Cr_2O_7$. While all the other cocrystallized samples decompose endothermically like AN, cocrystallization with $K_2Cr_2O_7$ results in exothermic decomposition. AN cocrystallized with ammonium dichromate (Table 1) does not show any phase modification though it decomposes exothermically. The exothermicity is attributed to

the catalytic reaction of dichromate ion in AN melt [20]. This observation could have a major implication in the use of AN as a propellant oxidizer since phase stabilization and additives like ammonium dichromate are reported to improve the combustion behaviour of AN based propellants. However, it is significant to note at this stage that the disappearance of endothermic peak at 40°C in the DTA curves indicates the stabilization of the phase by the use of just about 1% of the additive. This was apparently not found to be the case when the same samples were subjected to thermomechanical analysis.

Table 1 DTA data for various AN and PSAN systems

Sample	DTA peak temperatures/°C				
NH ₄ NO ₃	40	85	125	169	260
PSAN(KNO ₃)	100	125	169	270	
PSAN(KF)	90	125	168	265	
PSAN(K ₂ SO ₄)	103	125	168	265	
PSAN(K ₂ CO ₃)	103	125	168	265	
PSAN(KI)	90	125	168	265	
PSAN(K ₂ Cr ₂ O ₇)	90	125	168	200(+)	
PSAN(KSCN)	90	125	168	265	
PSAN(KCl)	100	125	168	265	
AN+K ₂ Cr ₂ O ₇	37	85	125	168	200(+)
AN(NaF)	38	85	125	169	260
AN((NH ₄) ₂ Cr ₂ O ₇)	38	85	125	169	200(+)

(+) indicates exotherm

The linear expansion data from room temperature (25°C) upwards obtained from TMA studies on different PSAN pellets are given in Table 2. It is seen that a pure AN pellet undergoes a 6.6% linear expansion in the temperature range 40 to 75°C when heated at 10°C min⁻¹. This expansion is substantially reduced in the case of PSAN samples having 1% of the additive. However, a complete elimination of the expansion was found to be concentration dependent of the individual additive. Typical TMA curves for PSAN (K₂Cr₂O₇), PSAN(KI) and PSAN(KSCN) samples having different concentration of the potassium salts are given in Figs 3–4. It is seen that in most cases nearly 3 to 4% of the additive was required (Table 2) for overcoming the expansion. In the case of PSAN(K₂Cr₂O₇), however, the percentage of K₂Cr₂O₇ required was found to be 6%. In general the expansion data indicate that the behaviour is similar to that observed for the samples cocrystallized with KNO₃ and KF reported earlier [8, 9, 11, 17–19]. The amount of the potassium salts required for phase modification also matches well with the reported values [11, 18].

Table 2 Thermal expansion of AN and PSAN systems in the temperature range 25 to 100°C

Sample	Linear expansion/%	$T_{\text{range}}/^{\circ}\text{C}$
AN	6.6	44–76
PSAN 1% KNO ₃	6.03	42–76
PSAN 2% KNO ₃	5.3	39–52
PSAN 3% KNO ₃	1.3	40–50
PSAN 4% KNO ₃	0.09	
PSAN 1% KF	1.95	36–58
PSAN 2% KF	0.0	
PSAN 1% KI	5.09	44–76
PSAN 2% KI	3.40	36–55
PSAN 3% KI	0.13	35–46
PSAN 4% KI	0.0	
PSAN 1% K ₂ SO ₄	5.5	40–58
PSAN 2% K ₂ SO ₄	0.39	38–44
PSAN 3% K ₂ SO ₄	0.0	
PSAN 1% K ₂ CO ₃	5.01	40–62
PSAN 2% K ₂ CO ₃	2.13	40–60
PSAN 3% K ₂ CO ₃	0.44	40–58
PSAN 4% K ₂ CO ₃	0.0	
PSAN 1% KSCN	4.27	38–64
PSAN 2% KSCN	1.22	36–44
PSAN 3% KSCN	0.1	35–60
PSAN (4% KSCN)	0.0	
PSAN 1% K ₂ Cr ₂ O ₇	5.04	42–72
PSAN 2% K ₂ Cr ₂ O ₇	2.97	39–48
PSAN 3% K ₂ Cr ₂ O ₇	2.08	36–46
PSAN 4% K ₂ Cr ₂ O ₇	1.18	32–44
PSAN 5% K ₂ Cr ₂ O ₇	0.23	32–44
PSAN 6% K ₂ Cr ₂ O ₇	0.0	

X-ray powder diffraction data obtained at room temperature on AN and various PSAN samples are listed in Table 3. The XRD pattern of AN, PSAN(K₂CO₃) and PSAN(KI) illustrated in Fig. 5 show that the four prominent peaks at d , 2.72, 3.08, 3.95 and 4.92 Å corresponding to form IV of AN are missing in the PSAN samples. On the other hand, the presence of peaks at d , 2.61, 3.24, 3.37 Å, and the

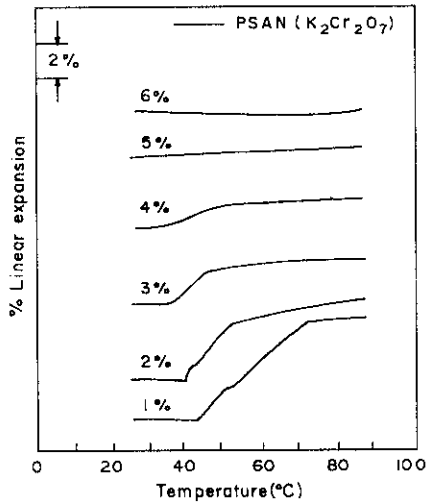


Fig. 3 TMA traces of PSAN($K_2Cr_2O_7$)

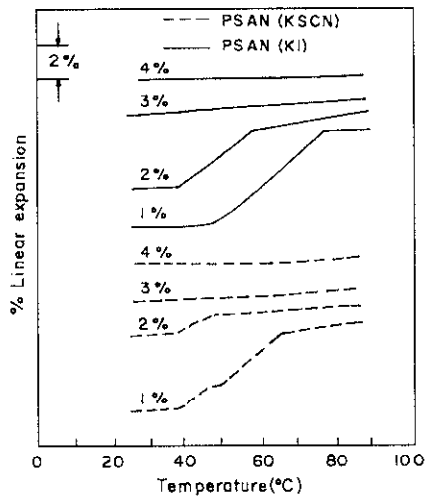


Fig. 4 TMA traces of PSAN(KSCN) and PSAN(KI)

corresponding hkl values (Fig. 5) are suggestive of the form III [21]. It can be inferred, therefore, that AN is stabilized by the potassium salts in phase III as observed earlier with KNO_3 [11].

The specificity of potassium ion in modifying the phase is further evident from the XRD pattern of the AN sample cocrystallized with Na_2CO_3 (Table 3) wherein AN continues to remain in phase IV.

Since AN or propellants based on AN could be subjected to both low and high temperatures on storage, the phase modification has to be realized in a broader

temperature range spanning low temperatures also. Typical TMA curves for PSAN(KSCN) samples having different amounts of KSCN in the temperature range -70 to 100°C are given in Fig. 6. It is seen that the expansion is restricted depending upon the concentration of the additive. Clearly, higher percentage of the salt is required to ensure complete phase modification when the sample is subjected to this temperature range. It is evident that AN containing 9% by mass KSCN does not show any expansion between -70 and 80°C . Identical studies carried out on K_2CO_3 based AN showed that about the same amount (9%) is required to completely restrict the expansion of a cooled sample (Table 4). In fact, metal oxides and potassium nitrate are reported to have been added to AN upto 12% prior to its use as a propellant oxidizer [13].

The effect of thermal cycling on the thermal expansion behaviour could also be important as strong hysteresis are reported to take place in ammonium nitrate [16]. This aspect has been studied earlier using DSC and XRD techniques [16]. However, the effect of thermal cycling on the actual expansion behaviour of AN and PSAN has not been reported. The effect of thermal cycling on the expansion of AN using TMA is depicted in Fig. 7. Run I (Fig. 7) shows the behaviour of AN pellet, which was heated from room temperature to 130°C , the expansion observed was around 6.6%.

Table 3 X-ray powder diffraction data

AN		PSAN(K_2CO_3)		K_2CO_3	
$d/\text{\AA}$	Intensity	$d/\text{\AA}$	Intensity	$d/\text{\AA}$	Intensity
2.7246	100	2.6176	100	6.9463	100
3.9596	94	3.2165	74	2.7480	90
3.0875	72	3.2418	52	2.7697	63
4.9252	45	1.4963	47	2.7829	56
2.3846	26	3.8981	46	4.8812	43
1.8402	23	3.3848	27	2.3405	42
2.2621	19	2.8357	19	6.4046	39
2.2482	18	2.4146	15	2.7404	35
6.8202	10	5.2508	14	2.4881	24
2.8789	8	2.2605	11	2.3208	19
2.4827	7	1.4923	10		
2.6996	6	2.3242	10		
1.6346	6	2.9222	8		
4.7311	5	4.5210	8		
5.4857	5	4.2397	7		
5.1669	3	1.7570	5		
		6.7275	5		
		5.1018	4		

Table 3 Continued

PSAN(KNO ₃)		PSAN(KI)		AN(Na ₂ CO ₃)	
<i>d</i> /Å	Intensity	<i>d</i> /Å	Intensity	<i>d</i> /Å	Intensity
3.8980	100	2.6133	100	3.0865	100
3.2435	92	3.3721	73	2.7263	68
2.6187	73	3.8865	41	4.9455	62
2.4145	56	3.2352	29	2.2653	47
3.3934	55	2.4097	29	3.9675	34
2.3470	51	3.2038	28	3.1155	22
3.2148	41	1.6248	28	2.2498	15
2.2588	32	2.8282	27	2.7434	13
4.5227	30	5.2063	22	3.0397	9
2.8350	29	3.6178	17	2.2555	9
1.8890	25	4.1805	17	6.6307	6
2.9295	24	2.2734	16	5.7008	6
5.2437	22	4.5107	14	6.8062	6
2.3247	20	2.2565	14	1.9808	6
2.0249	14	2.3995	12	1.8963	5
2.9183	8	2.5645	10	4.6381	4
2.2776	7	6.8330	10	3.0621	4
5.6416	6	4.1604	9	6.3355	4
4.1090	4	6.0866	8	5.5660	4

Table 4 Thermal expansion of PSAN(K₂CO₃) and PSAN(KSCN) in the temperature range -80 to 100°C

Sample (potassium salt/%)	Expansion/%	
	K ₂ CO ₃	KSCN
PSAN(4%)	2.9	2.77
PSAN(5%)	2.1	2.25
PSAN(6%)	1.5	1.8
PSAN(7%)	0.96	1.23
PSAN(8%)	0.1	0.6
PSAN(9%)	0.0	0.0

This expansion remained almost the same when the same sample was cycled 3 times thereafter in this temperature range, indicating that untreated AN re-

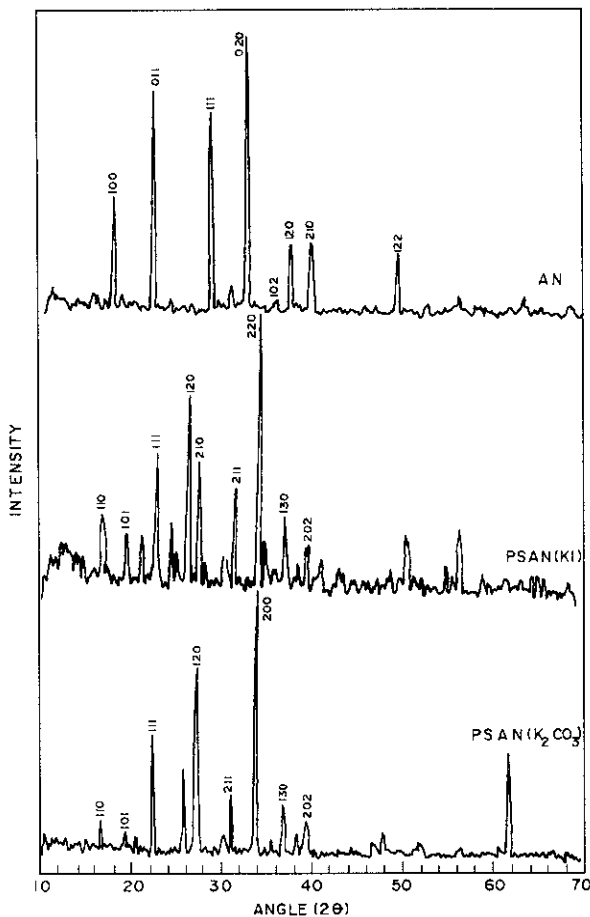


Fig. 5 XRD patterns of AN, PSAN(KI) and PSAN(K₂CO₃)

mains in phase IV at room temperature. The expansion curve appears to have a small shoulder, showing that perhaps a two-stage process is involved. Interestingly, similar pattern was observed for some of the PSAN samples also (Figs 3 and 4). On cooling to lower temperatures the AN sample shows (run II, Fig. 7) a significant expansion amounting to 3%, around -50°C . In run III where the sample was heated again from -100°C , no change was observed around -50°C but a contraction around 0°C was observed followed by expansion starting around 20°C which becomes considerable above 35°C .

Thermal cycling studies of the PSAN samples by TMA have brought about some interesting results. Typical TMA curves for PSAN(KSCN) with varying amount of KSCN, subjected to thermal cycling is given in Fig. 8. The samples (containing more than 3% KSCN) on heating from room temperature upwards (run I) does not show any expansion as mentioned earlier. When the sample was

cycled between room temperature and 140°C, the phase remained modified during the runs. On subsequent cooling, (run II) samples with low percentage of potassium salt (less than 5% KSCN) show an expansion around -50°C as in the case of pure AN. This however, vanishes at higher concentrations of the additive. On further heating, (run III) the linear expansion corresponding to IV-III transition was observed around 40°C, and was found to be concentration dependent. The samples containing 9% KSCN does not show any volume expansion at any temperature during the thermal cycling.

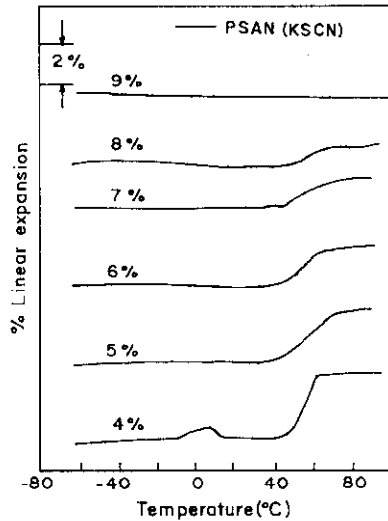


Fig. 6 TMA traces of PSAN(KSCN) in the temperature range (-80 to 100°C)

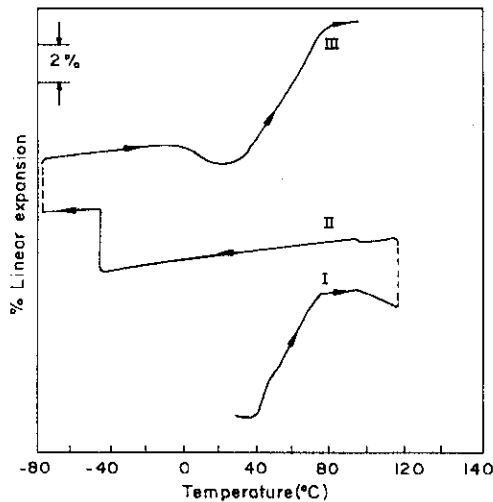


Fig. 7 TMA traces of AN on thermal cycling

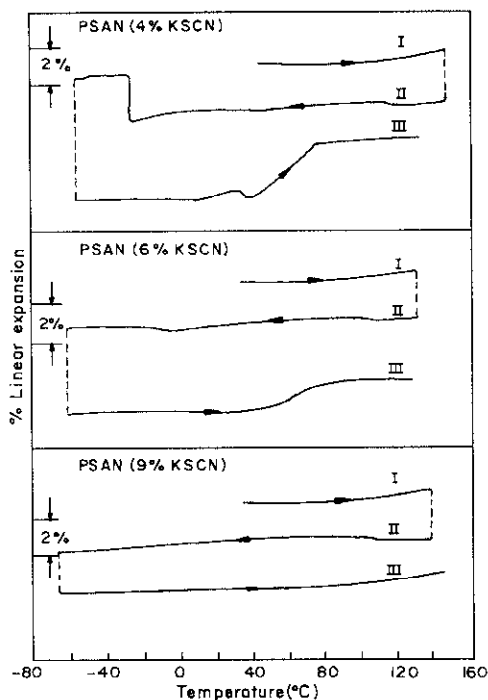


Fig. 8 TMA traces of PSAN(KSCN) on thermal cycling

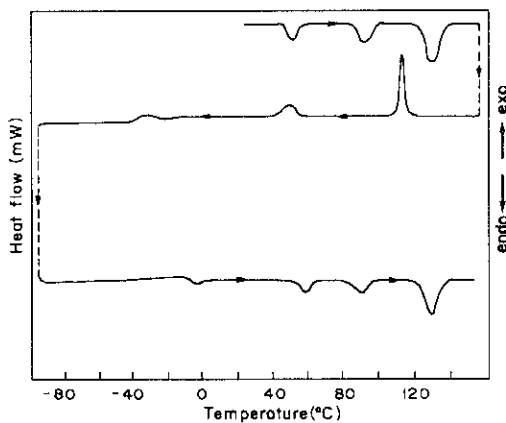


Fig. 9 DSC traces of AN on thermal cycling

The DSC results of AN (Fig. 9) match fairly well with the thermal expansion data. The temperature and the energies of transitions of AN subjected to thermal cycling is given in Table 5. The untreated salt when heated from room temperature undergoes various transitions (Fig. 9) in the order IV/III/II/I as reported earlier [13]. Minor differences in the temperatures of transitions observed between

DTA (Table 1) and DSC (Table 5) for the same sample of AN are not unusual [22]. The energy of these transitions matches closely with the reported values [14]. The sample on subsequent cooling shows transitions at 116, 44 and -36°C which correspond to the phases in the order I/II/IV/V without showing the phase III. It is reported [13] that if the temperature is allowed to rise above II-I inversion around 125°C , then on subsequent cooling the form II doesn't invert directly back to form III around 84°C , but it persists down to 48 or 45°C , when it reaches apparently form IV. The peak at -36 corresponds to IV-V transition as compared to -50°C in TMA measurements. On subsequent heating this transition reappears but only at -5°C as reported [16].

Table 5 Heats of transitions of AN and PSAN

Phase change	Peak temp./ $^{\circ}\text{C}$	$\Delta H/J\text{ g}^{-1}$
AN		
IV-III	49	15.43
III-II	92	16.15
II-I	129	49.8
I-II	116	44.39
II-IV	43.8	20.41
IV-V	-36.9	5.77
V-IV	-5	3.76
PSAN(K_2CO_3)		
III-II	112	19.79
II-I	129	51.25
I-II	120	49.9
II-III/IV	36	18.11
III/IV-V	-31	5.64
V-IV	0	3.59
IV-III	22	16.65

The heats of transitions for the thermally cycled sample were calculated. Only small differences in the enthalpy for the same transitions during cooling and heating cycles were observed. Based on the observations that these transitions are not changes from one pure crystalline form to another, but involves mixtures of phases coexisting, such differences could be expected [13].

The DSC thermal cycling data of PSAN (4% K_2CO_3) showed marked changes in the transition behavior (Fig. 10). The transition IV-III does not appear as in the case of DTA when the sample is heated from room temperature upwards (Table 5). The III-II transition was found to take place at higher temperatures (112°C) as observed in the DTA while the transition II-I remains unchanged.

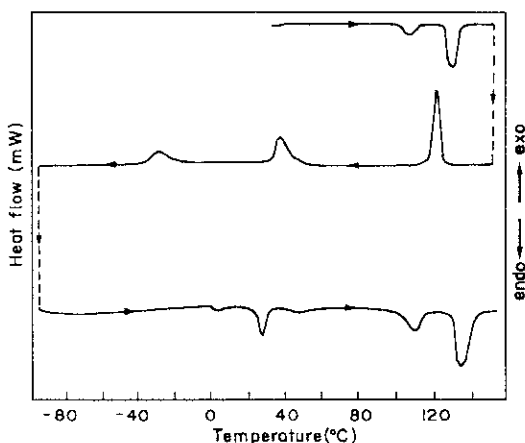


Fig. 10 DSC traces of PSAN(K_2CO_3) on thermal cycling

Similar observations have been reported for PSAN(KNO_3) systems [16]. However, the enthalpy change for III-II transition for PSAN samples was higher than that of untreated AN. A higher enthalpy was also observed for other PSAN samples (PSAN(KNO_3)) studied using DSC. The reason for high enthalpy is, however, not clear. On cooling the sample from $150^\circ C$, the peak at $120^\circ C$ corresponding to I-II inversion was followed by another peak at $36^\circ C$ (Fig. 10). This peak could be attributed to a II-III inversion unlike in AN where a II-IV transition takes place when cooled from $150^\circ C$. The transition to III instead of IV could be established by the observation that the salt remain modified (with 4% K_2CO_3) even after many thermal cycles above room temperature (25 – $100^\circ C$). XRD studies reported for PSAN(KNO_3) also support this argument [11]. Understandably, for samples which are not fully stabilized (less than 4% K_2CO_3) small percentages of form IV also could be expected to be present, as linear expansion depending upon the concentration of potassium salt, on heating from room temperature onwards, was observed. The peak at $-31^\circ C$ could be due to either a III-V or IV+III-V transition; the latter takes place in partially modified AN containing less amount of potassium salt as mentioned. The expansion observed around $-50^\circ C$ for PSAN samples with less amount of potassium salt, mentioned earlier (Fig. 8), could also be due to the presence of phase IV as in the case of AN. On subsequent heating from $-100^\circ C$, transitions were observed at 0 and $22^\circ C$. Based on the enthalpy change and TMA results, these endotherms could be attributed to the phase transformation V-IV and IV-III respectively. This shift in transition (IV-III) towards lower temperatures, has been observed in PSAN(KNO_3) systems also [11]. The most significant observation is, however, the reappearance of IV-III transition on thermal cycling which could be overcome by using a higher percentage of the potassium salt as evident from Fig. 8.

The phase modification of AN by K^+ and resulting changes in the transition temperature have been explained based on the replacement of some of the ammo-

nium ions by potassium ions [23]. The mechanism proposed explains the fall in the IV-III transition temperature with increasing concentration of potassium ion and shift in temperature of III-II transition to higher temperatures. Overall behaviour of the PSAN samples in this study appears to have been guided by the above mechanism. On the other hand, the effect of anions is not insignificant as the expansion behaviour is modified depending upon the type of anion. Furthermore, the nature of anion could also affect the decomposition characteristics of AN significantly. Potassium dichromate, for example, can stabilize the phase as well as make AN decompose exothermically. Another interesting result of the present study pertains to the extent of stabilization as revealed by various analytical techniques. Based on DTA or DSC data, one may conclude that 1% by mass of the additive is sufficient for complete stabilization of the phase III above room temperature. However, this could be misleading since the TMA measurements prove it to be not so. Presumably the higher amount of sample needed in these measurements, causes the effect to be seen more clearly. The effect of thermal cycling has to be further reckoned with. Thus, a much higher concentration of the additive is needed to ensure complete stabilization of the phase III than that shown by the DTA/DSC techniques.

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