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ON THE CHEMICAL AND THERMAL STABILIZATION OF $NH_4NO_3(IV)$

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ABSTRACT

The authors present the results of a DTA and X-ray diffraction investigation of the changes induced in the phase transitions of ammonium nitrate by the addition of ammonium sulphate and water and by repeated heating and cooling through the $NH_4NO_3(IV) \rightleftharpoons NH_4NO_3(III)$ phase transition point.

INTRODUCTION

Ammonium nitrate phase transitions have been the object of much research [1–15]. The interest taken in such transitions is justified by the fact that the use of ammonium nitrate as a fertilizer involves high mechanical strength of the prills and a low caking tendency. Bulk storage, handling and drillability properties are strongly affected by the particles low mechanical strength. In turn, the mechanical strength of the prills depends on storage time, humidity and temperature fluctuations in the storage area. All these support the generally accepted idea that the mechanical strength of the prills should be related to the $NH_4NO_3(IV) \rightleftharpoons NH_4NO_3(III)$ polymorphic transition which is accompanied by sensible volume changes.

The ammonium nitrate prill is a polycrystalline aggregate. The volume changes of the elementary cell do not necessarily cause changes in the prill volume, but only changes in the volume of the crystallites. Under such conditions the crystal packing in the polycrystalline aggregate is changed and adherence between crystallites decreases. The product mechanical strength decreases after several thermal cycles through the transition temperature and after 20–30 cycles the granular product breaks down into dust or fine particles. This greatly increases the fertilizer caking tendency.

Many investigations, carried out in the laboratory and on industrial scale [16], have been aimed at reducing the effect of the $NH_4NO_3(IV) \rightleftharpoons$

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NH_4NO_3(III) transition upon the properties of prilled ammonium nitrate. They have been directed towards shifting the transition point above the usual storage temperature fluctuations and promoting the $NH_4NO_3(IV) \rightleftharpoons NH_4NO_3(II)$ transition which take place without substantial volume changes. Within certain limits the storage properties of ammonium nitrate have been controlled by means of reducing the water content below 0.1–0.2% and selecting conditioning additives which can change the prill microstructure [17]. The criteria for selecting such additives have not yet been made clear and the interaction mechanism between ammonium nitrate and the additives is not sufficiently understood.

This paper aims to investigate the modifications induced by ammonium sulphate in the ammonium nitrate crystal structure and its phase transitions. Although studies have been made concerning the thermal stabilization of ammonium nitrate [16–23], the mechanism of this process, the nature of ammonium nitrate–ammonium sulphate interactions and the destabilization effect of thermal cycling through the $NH_4NO_3(IV) \rightleftharpoons NH_4NO_3(III)$ transition point are not completely clear. Arguments have been proposed concerning an optimum concentration of water and its influence on the stabilizing effect of ammonium sulphate.

EXPERIMENTAL

In order to eliminate the effect of impurities, both salts (ammonium nitrate and ammonium sulphate) were purified by double recrystallization from hot, saturated, filtered solutions.

Samples were prepared by melting a mixture containing 0, 2, 4, 6, 8 and 10% ammonium sulphate at the minimum temperature required for a good homogenization. The fast cooling of the molten mixtures in a thin layer on a ceramic plate ensured the same cooling rate as in the prilling towers. The solid mixture, cooled at room temperature, was ground, dried in a drying cabinet under vacuum at 25°C and reground several times in order to eliminate the agglomerated particles formed through evaporation of the hygroscopic water. After 100–200 h drying at 400 mm Hg, the amount of moisture was 0.03–0.04%. Samples with variable water concentrations were similarly prepared by adding water before the melting of the mixture. Water concentration was adjusted by the duration in the drying cabinet. This way of preparing samples ensures pure NH_4NO_3(IV) phase crystallization and, thus, the effect of sample thermal history upon phase transitions is eliminated. The microstructure of the samples with the same thermal history depends only on water concentration, ammonium sulphate concentration and the number of cycles through the polymorphic transition temperature.

The DTA curves were obtained by heating pulverized samples in a Paulik–Paulik–Erdey type MOM derivatograph (Q.1500 M, Budapest), at a heating rate of 5 K min^{-1}. All recordings were made with the same amount of sample (0.7000 g). The X-ray diffractograms were obtained by means of a Philips diffractometer using Cr K_α radiation.

From the DTA curves, the ammonium nitrate polymorphic transition points were determined and some data concerning the thermal effects of these processes were obtained. Also, using DTA curves, the values of the non-isothermal kinetic parameters of $NH_4NO_3(IV) \rightarrow NH_4NO_3(III)$ and $NH_4NO_3(IV) \rightarrow NH_4NO_3(II)$ phase transitions were estimated.

RESULTS AND DISCUSSION

Mechanism of the phase transitions

Figure 1 shows the derivatogram with DTA, TG and *T* curves for pure ammonium nitrate (0.049% H_2O).

On the DTA curve before the endothermic effect corresponding to melting, which occurs with maximum rate at 184°C, there are four endothermic effects due to ammonium nitrate phase transitions located at 32, 50, 98 and 139°C. These results are in satisfactory agreement with the literature data, as follows

$$NH_4NO_3(IV)(\text{orthorhombic}) \overset{32°C}{\rightleftarrows} NH_4NO_3(III)(\text{orthorhombic}) \qquad (1)$$

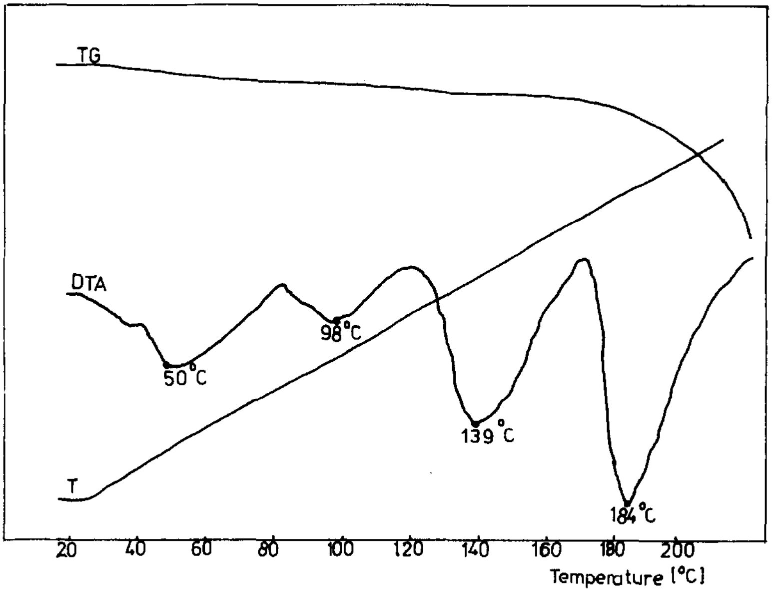

Fig. 1. TG, *T* and DTA curves for the pure ammonium nitrate with 0.049% water.

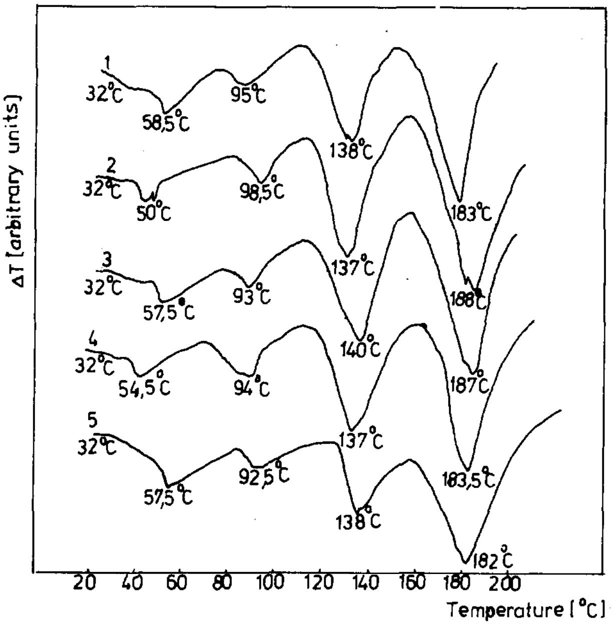

Fig. 2. DTA curves for ammonium nitrate with various contents of water: (1) 0.09%, (2) 0.13%, (3) 0.37%, (4) 0.63%, (5) 1.34%.

$$NH_4NO_3(III)(\text{orthorhombic}) \overset{84°C}{\rightleftarrows} NH_4NO_3(II)(\text{tetragonal}) \qquad (2)$$

$$NH_4NO_3(II)(\text{tetragonal}) \overset{125°C}{\rightleftarrows} NH_4NO_3(I)(\text{cubic}) \qquad (3)$$

The peak at 50°C has been assigned to the transition [2–4]

$$NH_4NO_3(IV) \rightarrow NH_4NO_3(II) \qquad (4)$$

It should be noted that the peak on the DTA curve at 50°C has not exclusively been found in all previous studies [24]. At present the conditions required for the occurrence of $NH_4NO_3(IV) \rightarrow NH_4NO_3(II)$ transition are not well known [24]. According to the explanation given in ref. 2, phase III and phase IV structures differ to such an extent that phase III cannot recrystallize but forms solutions. In the absence of water, phase IV changes directly into phase II. The water concentration for which transition (4) takes place ranges between 0.01% and 0.10% [17]. The derivatograms of pure ammonium nitrate samples containing from 0.049 to 1.360% of water show that, irrespective of water concentration, there are two distinct peaks at 32 and 50°C, i.e., the endothermic peak corresponding to transition (4) appears even in the presence of water (Fig. 2).

Considering that the endothermic peaks located between 84 and 98°C are certainly assigned to transition (2) and the high water concentration, the peak at 32°C should be assigned to a stable phase IV → metastable phase IV

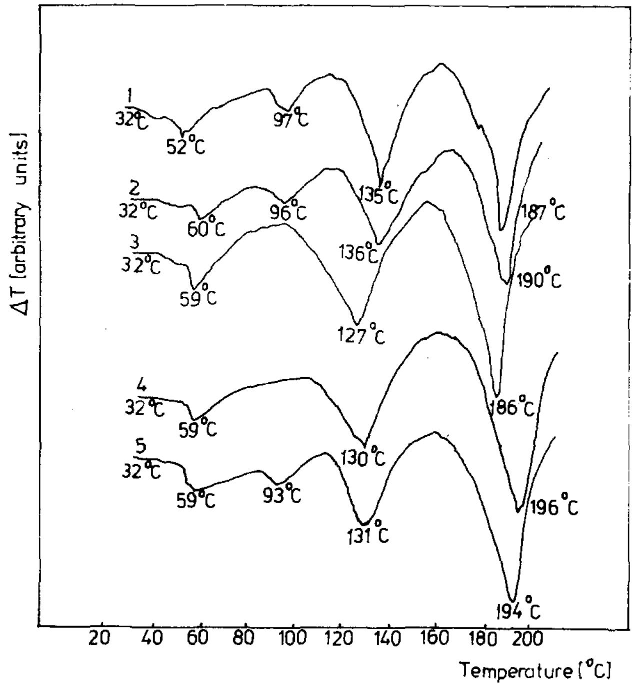

Fig. 3. DTA curves for ammonium nitrate with various contents of ammonium sulphate: (1) 2%, (2) 4%, (3) 6%, (4) 8%, (5) 10%.

transition. The metastable phase IV, depending on water concentration, changes at 50°C either into phase III or into phase II. The metastable phase IV is characterized by a tetragonal symmetry, with lattice parameter values different from those of stable phase II within the temperature range 98–139°C [1–6,8–11].

As the amount of ammonium sulphate gradually increases from 2 to 10% a decrease in the extent of the $NH_4NO_3(IV) \rightarrow NH_4NO_3(III)$ transition is noted and at 6% this transition does not take place (Fig. 3).

The peak at 32°C occurs with both 2 and 4% ammonium sulphate as well as with 6% ammonium sulphate samples. However, samples with a low additive concentration also exhibit a peak at 89°C which means that the NH_4NO_3(IV)(metastable) → NH_4NO_3(III) transition has certainly taken place and that at this temperature phase III changes into phase II. At a 6% ammonium sulphate concentration the peak at 89°C is absent from the DTA curve. All these confirm the hypothesis according to which the peak at 32°C cannot be assigned to the phase IV → phase III transition, but to phase IV (stable) → phase IV (metastable) transition. Ammonium sulphate promotes the transition of metastable ammonium nitrate phase IV into phase II. It should be noted that the amplitude of the peak at 32°C reduces as ammonium sulphate concentration increases. It is probable that above 6% ammonium sulphate the deformation of the crystalline phase IV cell may

TABLE 1

Shift of d_{111} of ammonium nitrate with ammonium sulphate and water concentration

Sample	$(NH_4)_2SO_4$ content	Water content	Number of thermal cycles		
			0	200	1000
1	0	0.047	3.080	3.082	–
2	4	0.14	3.094	3.060	–
3	6	0.13	3.090	3.060	–
4	8	0.10	3.075	3.079	–
5	10	0.14	3.078	3.074	–
6	6	0.73	3.056	3.072	3.084
7	8	0.74	3.077	–	–
8	10	0.51	3.055	3.069	3.077

occur in a way similar to that which takes place when stable phase IV changes into metastable phase IV. Therefore, the formation of the phase II structure occurs directly without an intermediate phase. One can also notice that, as a result of ammonium sulphate incorporation into ammonium nitrate, the temperature of this transition increases by approximately 5–10°C (Fig. 3).

The X-ray diffraction data confirm the formation of solid solutions between the two components of the mixture. As shown in Table 1 (samples 1–3), the position of the most intense diffraction line of ammonium nitrate tends towards smaller diffraction angles, confirming the incorporation of ammonium sulphate as a solid solution (the interplanar distance on the (111) face of NH_4NO_3(IV) crystals, d_{111}, increases from 3.080 to 3.090 Å). Thermal cycling of these samples produces decomposition of solid solutions with the probable formation of $3NH_4NO_3 \cdot (NH_4)_2SO_4$ and deformation of the NH_4NO_3(IV) lattice, noticed by a decrease in the interplanar distance on the (111) face from 3.080 to 3.060 Å. An increase in ammonium sulphate concentration from 6 to 8% leads directly to formation of the double salt with a deformation of the crystalline structure (identified by X-ray diffraction) and the recrystallization of NH_4NO_3(IV) into a modification different from the pure phase, i.e., metastable phase IV (Table 1, samples 4 and 5). Cycling these samples (Table 1) shows non-significant modifications of the metastable phase IV structure, thus showing the tendency of these samples towards thermal stabilization.

On the derivatogram of the sample with 10% ammonium sulphate, the peak at 32°C appears again. It occurs due to the complete destabilization of the solid solutions, $3NH_4NO_3 \cdot (NH_4)_2SO_4$, recrystallization and occurrence of non-deformed, pure NH_4NO_3(IV). Taking into account that on the diffractogram of the same sample one can clearly see the diffraction lines of the double salt, the modification of the mechanism phase IV → metastable phase IV → phase II appears as an effect of ammonium sulphate crystallization as a double salt with ammonium nitrate, as well as of the deformation of the phase IV lattice up to a limit favourable for transition into phase II.

Thermal cycling through the phase IV $\rightleftharpoons$ phase III transition point within the temperature range 20–60°C may have two effects. The first consists of recrystallization of solid solutions which are certainly in a metastable form after cooling the melt. Recrystallization of the solid solutions can stabilize the lattice of phase IV and, consequently, the thermal inertia of the system enables transition from metastable phase IV into stable phase II. This effect has not been observed experimentally. The second consists of the recrystallization of ammonium nitrate–ammonium sulphate double salts. In this case the stabilizing effect of ammonium sulphate due to metastable phase IV crystallization is maximum at a concentration of 6–8%. At higher concentrations the main components are probably the double salt and NH_4NO_3(IV), crystallized as pure phases. The diffractogram of the 10% ammonium sulphate sample shows a shift of both $3NH_4NO_3 \cdot (NH_4)_2SO_4$ and NH_4NO_3 diffraction lines, which indicates crystallization of the metastable phases. However, thermal cycling does not shift the main diffraction line of metastable phase (IV), i.e., a minimum concentration of 8% of ammonium sulphate is needed for ammonium nitrate stabilization. This conclusion is supported by the results of research concerning the conservation of the physical and mechanical properties of prilled ammonium nitrate [16].

On the basis of the above-mentioned facts one can consider that the formation of the metastable phases with NH_4NO_3(IV) structure promotes the transitions of this phase into stable phase II (or solid solutions with the structure of phase II). These facts are in agreement with the results obtained in the case of the derivatographic study of samples with 6–10% ammonium sulphate and 0.50–1.36% water.

Figure 4 shows that a water concentration of 0.50–0.70% does not change the mechanism of metastable phase transition, but this transition covers a wider temperature range, up to 100°C, i.e., the thermal inertia of the system increases. At a water concentration higher than 0.7%, the derivatograms in Fig. 4 show a peak characteristic of the transition of metastable phase IV into phase III. This is possible since phase III recrystallizes from aqueous solutions when the amount of water exceeds 0.70% of the total weight of the samples.

The thermal cycling of samples with a low water concentration, below 0.70%, does not alter the mechanism of ammonium nitrate polymorphic transition, but shifts the point of the metastable phase IV transition from 60–65°C to 55–60°C (Fig. 5). This phenomenon is related to the change in the crystalline structure of metastable phase IV in the presence of water.

As shown in Table 1 (samples 6–8), the diffraction lines of samples with 6 and 8% ammonium sulphate shift to higher diffraction angles, a fact which supports the rapid recrystallization of the $3NH_4NO_3 \cdot (NH_4)_2SO_4$ double salt, followed by the lattice deformation of phase IV.

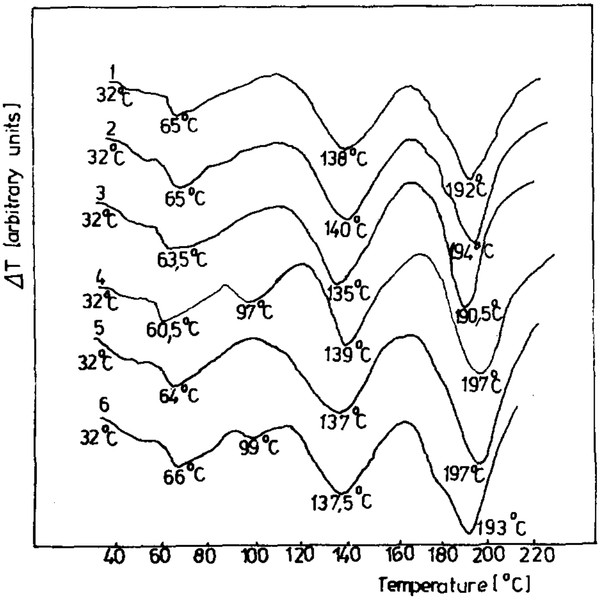

Fig. 4. DTA curves for ammonium nitrate with various contents of water and ammonium sulphate: (1) 0.73% water, 6% ammonium sulphate; (2) 0.83% water, 6% ammonium sulphate; (3) 0.74% water, 8% ammonium sulphate; (4) 1.60% water, 8% ammonium sulphate; (5) 0.51% water, 10% ammonium sulphate; (6) 0.78% water, 10% ammonium sulphate.

The thermal cycling of these samples leads to the recrystallization of pure NH_4NO_3(IV) (the interplanar distance corresponding to face (111) returns to a value of 3.080 Å, that of pure NH_4NO_4, i.e., thermal destabilization of the ammonium nitrate metastable phase. By comparing samples 3–5 with samples 6–8 (Table 1) one can note the negative effect of water upon the stability induced by the presence of $(NH_4)_2SO_4$ in ammonium nitrate.

Kinetic data

Phase transitions of crystalline solids occur through the processes of nucleation and growth of nuclei. The kinetics of these processes are satisfactorily described by the Johnson–Mehl–Avrami–Erofeev–Kolmogorov equation [26–28].

$$\ln(1-\alpha) = kt^m \tag{5}$$

where α represents the conversion degree, k the kinetic constant, t the time, and m is a constant, the value of which depends on the process mechanism.

From eqn. (5), taking the derivative with respect to time, one obtains

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = km(1-\alpha)t^{m-1} \tag{6}$$

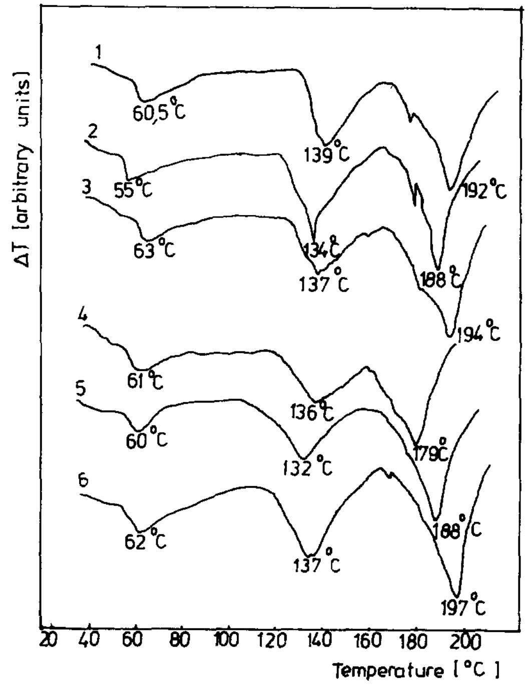

Fig. 5. DTA curves of thermally cycled ammonium nitrate: (1) 0.73% water, 6% ammonium sulphate, 1000 cycles; (2) 0.83% water, 6% ammonium sulphate, 200 cycles; (3) 0.74% water, 8% ammonium sulphate, 200 cycles; (4) 0.74% water, 8% ammonium sulphate, 1000 cycles; (5) 0.51% water, 10% ammonium sulphate, 1000 cycles; (6) 0.51% water, 10% ammonium sulphate, 200 cycles.

Considering eqn. (5), eqn. (6) becomes

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = mk^{1/m}(1-\alpha)[-\ln(1-\alpha)]^{(m-1)/m} \tag{7}$$

Taking into account the Arrhenius equation

$$k = A\,\mathrm{e}^{-E/RT} \tag{8}$$

where A represents the pre-exponential factor, R the gas constant, T the temperature (K) and E the activation energy which, in the case of phase transition, consists of three terms corresponding to nucleation, E_n, nuclei growth E_g, and diffusion, E_d, and, introducing the notation

$$\begin{aligned} A' &= mA \\ n &= (m-1)/m \\ E' &= E/m \end{aligned} \tag{9}$$

eqn. (7) becomes

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = A'\,\mathrm{e}^{-E'/RT}(1-\alpha)[-\ln(1-\alpha)]^{n} \tag{10}$$

or

$$\frac{d\alpha}{dt} = A' \mathrm{e}^{-E'/RT} \mathrm{f}(1-\alpha) \tag{11}$$

where $\mathrm{f}(1-\alpha)$ stands for the conversion function.

The conversion function is complicated so that, in order to simplify calculations, the kinetic parameters had to be estimated from the initial portion of the DTA curve for which the condition $0 < \alpha \ll 1$ is considered to be valid. Within this range the argument $(1-\alpha)$ varies slowly so that, in a first approximation, the conversion function can be considered to be practically constant

$$\mathrm{f}(1-\alpha) = K \tag{12}$$

The reaction rate can be expressed by means of the ordinate, ΔT, of the DTA curve and the area, S, of the DTA peak by the relationship

$$\frac{d\alpha}{dt} \approx \frac{\Delta T}{S} \tag{13}$$

From eqns. (11), (12) and (13) it results that

$$\Delta T = A'' \mathrm{e}^{-E'/RT} \tag{14}$$

where

$$A'' = A'KS$$

Relation (14) is linearized by using logarithms as follows

$$\log \Delta T = \log A'' - \frac{E'}{2.303R} \frac{1}{T} \tag{15}$$

The apparent activation parameters, A'' and E', are determined from the intercept and slope, respectively, of the straight line resulting from the plot of $\log \Delta T$ vs. $\mathrm{f}(1/T)$.

Table 2 presents several results obtained in the non-isothermal kinetic study of the first two phase transitions of ammonium nitrate at 32 and 50°C.

In order to estimate the overall effect of the ammonium sulphate and water contents on the kinetic behaviour of the ammonium nitrate samples, the kinetic constants of the first two phase transitions, k_1 and k_2, at 298 and 323 K, respectively, were calculated. An examination of the data in Table 2 reveals that, for a constant water concentration, the doubling of ammonium sulphate concentration (experiments 2 and 3) causes a decrease by two orders of magnitude of the constant $k_1(298)$ and subsequently an increase in the kinetic stability of ammonium nitrate. The second phase transition (same experiments) seems to be accelerated by the increase in ammonium sulphate concentration. One can also note that an addition of ammonium sulphate above 6% does not cause a significant change in the rate of the phase transition. At these concentrations the solid solutions formed in the low-concentration range are destroyed.

TABLE 2

Kinetic data of the two-step polymorphic transition of $NH_4NO_3(IV)$

Sample No.	$(NH_4)_2SO_2$ conc. (%)	Water conc. (%)	No. of thermal cycles	A_1'' (s^{-1})	E_1' (kcal mol^{-1})	A_2'' (s^{-1})	E_2' (kcal mol^{-1})	Kinetic constants (s^{-1})	
								k_1 (298 K)	k_2 (323 K)
1	–	0.047	0	2.8×10^{3}	8.6	6.7×10^{8}	16.6	1.5×10^{-3}	3.1×10^{-3}
2	2.0	0.140		1.1×10^{8}	15.2	1.7×10^{12}	22.2	9.3×10^{-4}	1.8×10^{-4}
3	4.0	0.140		9.1×10^{3}	12.5	9.5×10^{7}	16.1	6.4×10^{-6}	1.4×10^{-3}
4	6.0	0.130		$3\ \times10^{1}$	6.1	2.9×10^{14}	25.0	1.1×10^{-3}	4.3×10^{-3}
5	8.0	0.100		–	–	1.8×10^{24}	41.8	–	1.3×10^{-4}
6	10.0	0.140		2.1×10^{3}	9.2	7.9×10^{27}	46.0	4.2×10^{-4}	8.9×10^{-4}
7	4.0	0.140	200	1.1×10^{3}	9.2	7.9×10^{27}	46	2.1×10^{-4}	4.2×10^{-4}
8	6.0	0.130		1.4×10	6.4	2.0×10^{31}	31.3	2.8×10^{-5}	4.3×10^{-4}
9	8.0	0.100		2.0×10^{2}	7.8	1.5×10^{12}	22.0	4.1×10^{-4}	2.1×10^{-3}
10	0.100	0.090	0	7.3×10^{-1}	4.0	1.0×10^{12}	22.0	9.1×10^{-1}	1.4×10^{-3}
11	–	0.130		2.0×10^{5}	12.0	2.5×10^{22}	36.8	3.9×10^{-4}	4.3×10^{-3}
12	–	0.370		1.5×10^{1}	6.0	9.8×10^{33}	55.2	6.4×10^{-4}	6.9×10^{-4}
13	–	0.630		3.7×10^{7}	15.2	2.0×10^{7}	14.7	3.2×10^{-4}	2.5×10^{-3}
14	–	1.340		4.3×10^{1}	6.7	4.3×10^{17}	30.7	5.9×10^{-4}	1.0×10^{-3}
15	6.0	0.730		1.7×10^{3}	9.2	2.1×10^{25}	45.0	4.1×10^{-4}	1.0×10^{-5}
16	6.0	0.825		5.9×10^{6}	14.5	3.5×10^{13}	27.9	1.6×10^{-4}	5.5×10^{-4}
17	6.0	0.730	1000	1	4.6	4.2×10^{8}	17.5	4.5×10^{-4}	7.2×10^{-4}
18	6.0	0.825	200	4.5×10^{8}	15.2	2.4×10^{35}	57.5	3.8×10^{-4}	4.8×10^{-4}
19	8.0	0.740	0	5.2	5.4	2.5×10^{11}	21.5	6.1×10^{-4}	8.5×10^{-4}
20	8.0	1.600		2.5×10^{3}	9.2	3.2×10^{9}	18.4	4.7×10^{-4}	1.3×10^{-3}
21	8.0	0.740	200	1.3×10^{10}	17.5	3.0×10^{5}	11.0	2.3×10^{-3}	1.1×10^{-2}
22	8.0	0.740	1000	7.5×10^{6}	17.5	6.9×10^{6}	14.6	1.2×10^{-6}	9.7×10^{-4}
23	10.0	0.51	0	5.2×10^{1}	6.9	2.3×10^{15}	27.6	4.8×10^{-4}	6.3×10^{-4}

According to the data given in Table 2 the increase in water concentration of pure ammonium nitrate does not change the values of the k_1 and k_2 kinetic constants. The thermal cycling decreases the rate of the first two NH_4NO_3 phase transitions.

The results of kinetic measurements lead to the conclusion that the thermal cycling of samples with an $(NH_4)_2SO_4$ concentration higher than 4%, if the water concentration is maintained at values below 0.70%, has a non-significant influence upon the rate of the two polymorphic transitions of ammonium nitrate and, consequently, the dimensional stability of the prills is ensured during storage of the industrial product only by inducing the NH_4NO_3(IV)(metastable) → NH_4NO_3(II) transition.

CONCLUSIONS

(1) The phase transitions of ammonium nitrate were reanalysed and certain specifications regarding the existence of some metastable phases were obtained

(2) The stabilizing effect of the addition of ammonium sulphate on the phase transition of ammonium nitrate at 32°C was analysed

(3) The kinetic parameters of the first two phase transformations of ammonium nitrate were determined and the effects of adding ammonium sulphate, water concentration and thermal cycling upon the thermal stability of ammonium nitrate were evaluated.

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