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THERMAL PROPERTIES OF AMMONIUM NITRATE
I. Study of the reproducibility of DTA curves in relation to modification transformation

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The reproducibility of the DTA curves of ammonium nitrate as functions of its grain size and the atmosphere during the measurements was studied with a derivatograph. The temperatures and the areas of the peaks assigned to the modification transitions IV → III (peak 1), III → II (peak 2) and II → I (peak 3) were evaluated. It was found that for some unground samples the area of peak 2 decreases markedly. It has been verified that in an atmosphere of moist air the temperature of peak 1 is lowered. The temperatures of lumpy and loose samples do not differ appreciably. Statistical methods evidenced the mutual dependence of the areas of peaks 1 and 2. The possible causes of this are discussed.

The sensitivity of ammonium nitrate (AN) crystals to modification transitions is a well-known and often studied problem [1]. From X-ray structure analysis results some authors [2–5] have reported that at normal pressure solid AN exhibits five different modifications. The transitions of AN from one modification to another are connected with temperature changes, and therefore the methods of DTA [1, 6, 7] and DSC [8, 9] are often used for their identification. In the temperature range 20–150° the DTA curves of AN are characterized by three endothermic peaks, assigned to the modification transitions IV → III (peak 1), III → II (peak 2) and II → I (peak 3).

The study of the reproducibility of the DTA curves of AN was stimulated by our previous study of the influence of various experimental conditions of the thermal properties of AN.

The present work investigated the question of the reproducibility of measured DTA curves of AN as functions of the grain size of the samples (ground, unground, and lumpy AN) and the atmosphere during measurements.

Experimental

For the measurement of the DTA curves, Lachema ammonium nitrate (p. a.) was used (0.15% H_2O). It was kept in a closed vessel in a drier at constant temperature (25°) for at least 7 days in order to eliminate the influence of the thermal history [10, 11]. The DTA curves of AN were measured with an OD 102 derivatograph (MOM,

Budapest); conditions: sample weight 100 mg, DTA sensitivity 1/1, rate of temperature increase 1.5 deg/min.

Three types of measurements were performed:

(a) Ground AN (samples 1–6) and unground AN (samples 7–12) were measured as a function of time (three measurements on each of two following days, at 3-hour intervals, under the same conditions in static air atmosphere).

(b) Ground AN was measured as a function of time (three measurements following each other under the same conditions) in a dynamic atmosphere of moist air (samples 13–15) or dried air (samples 16–18), or in static air atmosphere (samples 19–21).

(c) Lumpy AN was measured as a function of the place from which the sample was taken (lump surface-sample 22, lump inside-sample 23, lump remainder-samples 24, 25) and as a function of time (the remainder lump was measured on one day at 3-hour intervals, samples 26–28).

The ground samples were again pulverized with a ball mill before each measurements. Areas of peaks were limited by the tangent to the curves [12] and determined by the number of squares they covered.

Results and discussion

The thermodynamic (equilibrium) temperature of the modification transitions of AN may be affected by the addition of inorganic salts, the crystal structure changing due to the formation of solid solutions or chemical compounds [1]. In studying these processes by the DTA method, however, we obtain disequilibrium temperatures of the modification transitions, which depend on the experimental conditions (including the moisture content, which influences the transition kinetics).

The influence of the sample weight, the rate of temperature increase and the water content have not been considered, since all the samples were measured under the same conditions and the starting AN was tempered at a constant temperature and the same water vapour pressure. Under these defined conditions we directed our attention to the question of the reproducibility of the DTA curves with respect to the different grain sizes of the samples and the atmosphere of the measurements.

The results are listed in Table 1. Twenty-eight samples were measured altogether and the temperatures and the endothermic peak areas in the DTA curves were evaluated. From Table 1 it follows that:

1. Investigation of the effect of grinding on the DTA curves showed that:

   (a) For the ground samples (1–6) the temperatures of the peak maxima vary only within experimental error (peak 1: 50±1°, peak 2: 85±1°, peak 3: 120±1°). The area of peak 3 is comparatively constant, while the areas of peaks 1 and 2 vary considerably.

   (b) For the unground samples (7–12) the temperatures of the peaks vary only within experimental error too (50±1°, 81±1° and 120±1°); however, the tem-

Table 1 Data of DTA curves of ammonium nitrate

No. of sample	Grain size	Atmosphere	Endothermic peak					
			1		2		3	
			temperature, °C	area, mm^2	temperature, °C	area, mm^2	temperature, °C	area, mm^2
1	ground	static air	50	186	85	186	120	662
2			51	240	86	47	121	639
3			50	205	84	126	120	662
4			49	178	84	181	119	631
5			51	242	85	81	121	649
6			50	207	86	159	120	626
7	unground	static air	50	191	81	142	120	595
8			51	208	82	54	121	615
9			51	235	–	–	121	596
10			49	245	80	18	119	640
11			50	246	80	7	120	589
12			51	260	–	–	121	606
13	ground	dynamic atmosphere of moist air	43	149	85	196	120	609
14			45	148	86	211	120	612
15			48	148	87	206	121	612
16	ground	dynamic atmosphere of dried air	49	173	83	181	117	647
17			51	171	86	175	119	598
18			50	225	85	148	119	729
19	ground	static air	49	191	84	179	120	637
20			50	176	86	177	119	629
21			49	177	86	194	120	603
22	lump not pulverized	static air	50	143	84	163	119	624
23			49	169	83	169	118	588
24	lump pulverized*		51	265	–	–	120	642
25			49	168	82	135	117	583
26	lump pulverized		45	166	86	216	119	627
27			42	166	84	192	118	600
28			48	150	85	221	120	643

*Samples pulverized in an agate dish

perature of peak 2 is 4° lower for unground samples. Peak 2 exhibits a marked change in area (for samples 9–12, peak 2 practically disappears).

2. Investigation of the influence of the atmosphere during measurement of the DTA curves yielded the following results (samples 13–21):

(a) The temperature of peak 1 changes somewhat more markedly in moist air. The temperatures of peaks 2 and 3 change only within experimental error.

(b) The area of peak 1 is appreciably lower in the atmosphere of moist air (samples 13–15), the values being very near. On the othet hand, the area of peak 2 is higher, showing their mutual relationship.

3. Investigation of the influence of the grain size (lump formation) of the samples on the shapes, temperatures and areas of the peaks in the DTA curves yielded the following results:

(a) The temperatures of peaks for lumpy and loose samples of AN do not differ markedly.

(b) For sample 24, endothermic peak 2 is appreciably decreased and split. Repeated measurement (sample 25) again shows an appreciable peak 2. This finding demonstrates that the area changes in peak 2 are connected with several factors.

(c) The temperature of peak 1 for the remaining lump undergoes marked changes as a function of time (samples 26–28), the changes being analogous to those for samples 13–15, measured in moist air atmosphere.

(d) The areas of peaks 1 and 2 change as a function of the site from which the samples were taken (surface, inside, remainder of the lump). The area of peak 3 remains comparatively constant.

As Table 1 and Figure 1 show, the areas of peaks 1 (P_1) and 2 (P_2) in the DTA curves are mutually related. In order to prove the mutual dependence of P_1 and P_2, statistical methods were used. From a more detailed analysis of the experimental data based on the significance of the correlation coefficients (R) at the significance levels of 0.05 and 0.01, the zero hypothesis of the mutual independence of parameters

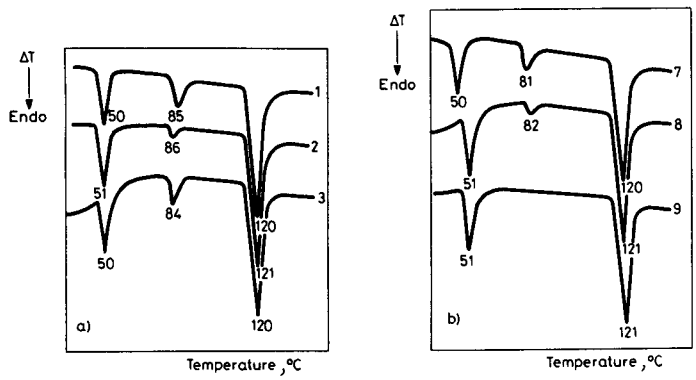

Fig. 1 DTA curves of AN: 1, 2, 3 – ground AN, 7, 8, 9 – unground AN

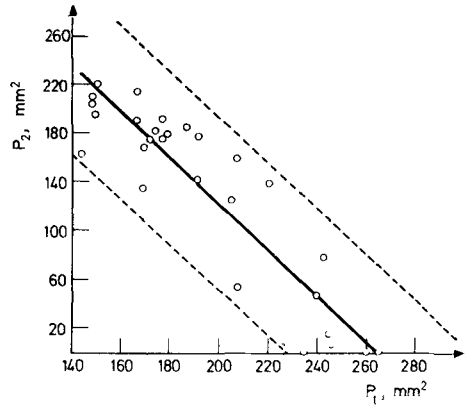

Fig. 2 Diagram of the dependence of the area of peak 1 (P_1) on that of peak 2 (P_2)

Table 2 Statistical data of the P_1 versus P_2 correlation

Correlation	R	$\nu = n - 2$	R_{crit}	
			0.05	0.01
P_1 versus P_2	0.900	26	0.381	0.487

P_1 and P_2 (Table 2) may be rejected. Since $|R| > R_{crit}$, a linear correlation may be considered as proved at the significance levels of 0.05 and 0.01 (the respective equation of the straight line has the form $P_2 = -1.8 P_1 + 483.8$).

The area of peak 1 in the DTA curves is thus connected with the area of peak 2. With an increased area of peak 1, a decrease in the area of peak 2 is found, and vice versa. Thus, the causes of the changes in peak 2 have to be sought for in the changes of peak 1, covering the total temperature effect of at least two processes in this temperature region.

Clearly, it is necessary to consider not only the modification transition IV → III, but also the formation of an amorphous product and the recrystallization processes connected with it, or the formation of the metastable phase III. The latter is usually shown as an exothermic peak in the DTA and DSC curves [8, 9]. However, since our experimental results showed the mutual dependence of the areas of endothermic peaks 1 and 2, and no exothermic peak was observed (except for sample 17) the possible explanation may rather be connected with an incomplete modification transition IV → III. This problem will be the subject of our further study.

References

1 M. E. Ivanov, V. M. Olevskij, N. N. Poljakov, I. I. Striževskij, M. L. Ferd and Ju. V. Cechanskaja, Technologija ammiacnoj selitry, Izdatelstvo "Chimija", Moskva, 1978.
2 R. N. Brown and A. C. McLaren, Proc. Roy Soc. London, Ser. A 266 (1962) 329.
3 B. W. Lucas, M. Ahtee and A. W. Hewat, Acta Cryst., B 35 (1979) 1038.
4 B. W. Lucas, M. Ahtee and A. W. Hewat, Acta Cryst., B 36 (1980) 2005.
5 C. S. Choi and J. E. Mapes, Acta Cryst., B 28 (1972) 1357.
6 R. R. Sowell, M. M. Karnowsky and L. C. Walters, J. Thermal Anal., 3 (1971) 119.
7 O. Juoperi, Thermochim. Acta, 9 (1974) 353.
8 I. Konkoly-Thege, J. Thermal Anal., 12 (1977) 197.
9 H. Langfelderová and P. Ambrovič, Thermochim. Acta, 56 (1982) 385.
10 S. B. Hendricks, E. Posnjak and F. C. Kracok, J. Am. Chem. Soc., 54 (1932) 2766.
11 M. Kabešová, J. Gažo, J. Jankovič and W. Waradzin, Chem. prumysl, 33 (1983) 121.
12 A. Blažek, Termická analýza (Thermal analysis), SNTL, Praha, 1972, p. 132.

Zusammenfassung – Die Reproduzierbarkeit der DTA-Kurven von Ammoniumnitrat in Abhängigkeit von der Korngrösse und der Art der Atmosphäre wurde mittels eines Derivatographen untersucht. Es wurden Temperaturen und Flächen der Peaks ausgewertet, die den Phasenübergängen IV → III (Peak 1), III → II (Peak 2) und II → I (Peak 3) zuzuordnen sind. Es wurde festgestellt, dass die Fläche des Peaks 2 bei einigen nicht zerkleinerten Proben wesentlich kleiner ist. Es wurde bestätigt, dass Peak 1 in einer Atmosphäre von mit Wasserdampf angereicherter Luft bei niedrigeren Temperaturen auftritt. Für klumpige und pulverförmige Proben wurden keine wesentlichen Unterschiede in den Temperaturen, bei denen die Peaks auftreten, gefunden. Statistische Methoden bestätigten den gegenseitigen Zusammenhang der Peakflächen von Peak 1 und 2. Die möglichen Ursachen für diesen Befund werden diskutiert.

Резюме – С помощью дериватографа была исследована воспроизводимость ДТА-кривых нитрата аммония в зависимости от размера гранул и атмосферы. Определены температуры и площади пиков для фазовых переходов IV → III /пик 1/, III → II /пик 2/ и II → I /пик 3/. Установлено, что для некоторых неразмолотых образцов площадь пиков 2 заметно уменьшалась. Подтверждено, что в атмосфере влажного воздуха, температуры пика 1 понижаются. Температуры кусковых и рыхлых образцов заметно не отличались. Показана взаимная зависимость площадей пиков 1 и 2. Обсуждены возможные причины этого факта.