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PHASE TRANSFORMATION OF AMMONIUM NITRATE BY THERMAL FACTORS AND INOCULATION

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The reason for the special thermal behaviour of ammonium nitrate (AN) has been examined. Under certain experimental conditions more transition temperatures were obtained than hitherto found (37—42°, 50° and 86°). With Du Pont DSC curves several exothermic peaks or exothermic oscillations were shown after the endothermic peak at 51°, indicating that phase IV had been transformed to metastable phase III, as a consequence of which the III → II transformation at 86° also became possible. On repeated cycling the exothermic peak decreased or disappeared if the III → II transformation had developed to a greater extent. A successful IV → III transformation was induced by inoculation of AN with phase III, an unusual procedure in investigating the phase transformation of AN. The use of the method is obvious with regard to the fact that all transformations are controlled by the rate of nucleation.

Structural transition constitutes one of the most fundamental properties of many solid substances and has therefore been widely investigated. Presumably this is the reason for the great interest in polymorphic transitions of ammonium nitrate (AN), beginning with Tammann's studies in 1899 to mention only one of the earlier investigators [1]. For experiments the optical microscope equipped with a heating stage [2–6], the dilatometric method [7, 8] and recently DTA

Table 1

Phase transformation of ammonium nitrate

IV orthorhombic	$\xrightarrow[32.1^\circ]{\text{dilatation}}$	III orthorhombic	$\xrightarrow[84.2^\circ]{\text{contraction}}$
$a = 5.75$ Å $b = 5.45$ Å $c = 4.96$ Å		$a = 7.14$ Å $b = 7.65$ Å $c = 5.83$ Å	

II tetragonal	$\xrightarrow[125.2^\circ]{\text{dilatation}}$	I cubic	$\xrightarrow[169.6^\circ]{\text{MELT}}$
$a = 5.75$ Å $b = a$ $c = 5.00$ Å		$a = 4.40$ Å	

[6, 9, 10, 11] and micro-DTA measurements [12] have been used. In many cases the above-mentioned investigations are combined with other modern techniques, such as X-ray diffraction [6, 9] and electric conductance measurements [6].

From the literature data the steps of polymorphic crystalline modifications of AN and relevant temperatures may be given as shown in Table 1.

Most of the phase transformations of AN show a retarding effect: as a result, one can frequently observe the phenomena of superheating and supercooling. Among these transitions the IV → III is that mainly discussed because it does not appear regularly. Modification III may disappear and a direct transformation from phase IV to II may take place. Majumdar and Roy have dealt with the solid transition of AN and cited a number of valuable literature data [13], e.g. those of Bowen and Amoros et al. Bowen observed a metastable transition around 50°, and Amoros et al. confirmed this observation by suddenly heating the room-temperature phase of a single crystal above 55°.

According to these authors the metastable phase is tetragonal, but different in space group symmetry from the tetragonal modification stable above 84° [13]. Brown and McLaren have suggested that the IV → III transition takes place only in the presence of moisture by a dissolution and recrystallization mechanism involving drastic structural changes [6]. They also observed a very large increase in electric conductivity during the IV → III transition. Asadov et al. investigated the morphology of crystal growth during polymorphic transformations with optical microscopy and established the existence of a new phase between the well-known modifications IV and III [5]. According to Juopperi, the variable temperatures of phase transitions on heating may be explained as follows: when the II → III → IV transition has occurred in previous cooling, the IV → III transition will appear on subsequent heating at about 33°; in contrast, when a direct II → IV transition has taken place on cooling, modification IV will change on heating to modification II through a metastable transition at 50° [11a, b, c]. According to the investigations of Sowell et al., water is not the only foreign material which can promote the IV → III transition. They have shown that both the IV → III and the II → III transitions require drastic structural change. Both of these processes involve dilatation and therefore cannot take place in dry solid materials [9].

Experiments to influence the temperature and the rate of the phase transitions of AN with additives have long been performed. It has been shown that nitrates forming mixed crystals with AN are effective, in contrast to nitrates unable to produce mixed crystals [1].

On the basis of DTA measurements, the "classical" temperature value of the IV → III transformation, described as 32°, has been found significantly higher: scattered about 44°, sometimes with a maximum at 52°, e.g. 32 ± 10° [6], 43–51° [9], 44° [10], 32–62° [11a], 50° [12], etc. Sowell et al. [9], in agreement with Brown [6], attributed this change to the high purity of their sample. This finding was later confirmed by Juopperi [11].

Results and discussion

Our results were obtained in a differential-temperature-recording instrument (Du Pont Thermal Analyzer supplied with DSC module).

We have confirmed that the polymorphic transformation of AN is very sensitive to thermal effects, foreign materials, or morphologic and crystallographic inhomogeneities influencing the thermal behaviour of the sample.

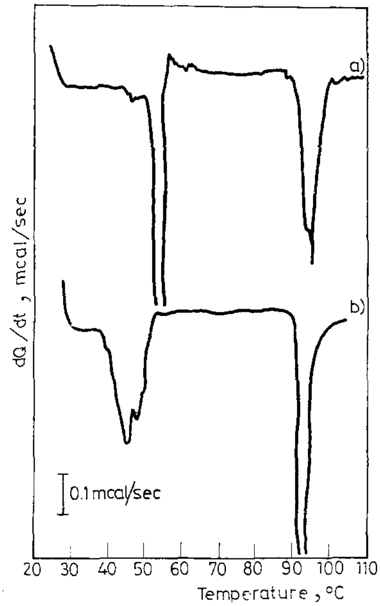

Fig. 1. DSC curves of AN a) after cooling very slowly in air; b) after standing 15 days in air. Sample weights: 6.97 mg. Heating rate: 5°/min, in air

On heating after very slow cooling in the presence of air, or after prolonged storage at room temperature, or after exposure to moisture, the transformation from phase IV into another phase occurs in more than one step and always under 51°, as evidenced usually by several endothermic peaks in the curves (Figs 1–3). On subsequent heating these peaks successively decreased and the temperature of the phase transition increased and approached 51°. The anomaly may be attributed to the hygroscopic nature of solid AN, because on repeated cycling the moisture content of the salt presumably decreased. It seems that this concept is also confirmed by the finding of Juopperi [11], according to which the above-mentioned phase transformation shifted from 33° (moist sample) to about 51° (sample dried in vacuo).

Using untreated AN, it was always doubtful whether the IV → III → II transformation or only the IV → II transformation would take place. Several times curves showed exothermic peaks, or more properly "exothermic oscillations", or at least the baseline shifted in the exothermic direction. This indicates that the specific heat of the sample changed after the endothermic peak at 51°. Accordingly, phase IV transforms to metastable phase III, as a consequence of which the III → II transformation at 86° also becomes possible (Fig. 4). On repeated cycling,

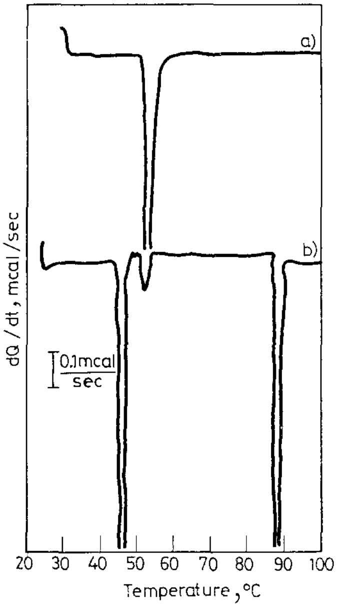

Fig. 2. DSC curves of AN a) immediately; b) after standing for 2 days in air; Sample weight: 9.41 mg. Heating rate: 2°/min, in air

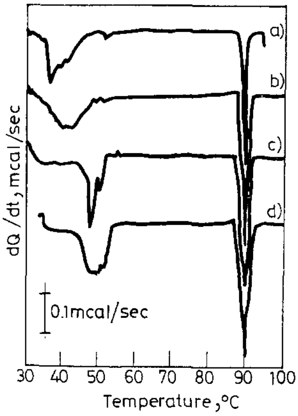

Fig. 3. Successive curves of AN after handling with moisture. Sample weight: 5.75 mg. Heating rate 2°/min, in air

however, the exothermic peak decreased or disappeared when the III → II transformation had developed to a greater extent (Fig. 5). The exothermic oscillations are apparently due to the fact that the sample heats itself and thus promotes the desired phase transformation.

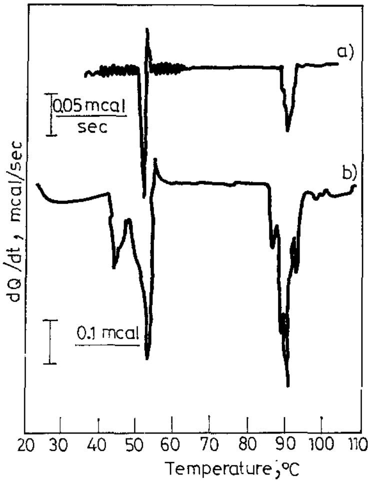

Fig. 4. DSC curves of AN with "exothermic phenomena" after the endothermic peak at 51°. a) Sample weight: 6.74 mg. Heating rate: 0.5°/min, in air; b) Sample weight: 3.00 mg. Heating rate: 5°/min, in air

From the appearance of more endothermic peaks than expected before 51° and from the exothermic oscillations after it, it may be concluded that in agreement with Asadov's morphological evidence, transient states do exist. The optical observations of Asadov et al. have unambiguously shown that the sudden transformation at about 50° is not a direct IV → III phase transition, but involves an intermediate phase [5]. Brown and McLaren have demonstrated with X-ray photographs that on the boundary of phases IV and III there is great disorder. It may be assumed that this finding was associated with the above-mentioned intermediate phase.

Asadov et al. remarked that their morphological examinations failed to reveal the mechanism by which the new phase was produced. The consideration that the IV → III phase transition requires drastic structural changes is founded only upon an indirect conclusion, drawn from a knowledge of the lattice parameters. In order to obtain direct experimental evidence for the mechanism of the IV → III phase transition, we examined whether addition of an AN sample "active" for the IV → III → II transition to an "inactive" sample will, on heating, "inoculate" the latter and induce a IV → III transformation (Fig. 6). The experiments show that the expected phases appeared one after the other IV → III → II.

As the growth of the nucleus could be followed in the successive curves, it is evident that a real inoculation had taken place. It seems that the process is localized on the boundary of the phases. From these experiments it is clear that in the above transformation of AN the rate of nucleation is hindered. The series of our experiments yielded convincing thermochemical evidence for the structural changes in the transformation of modification IV to III.

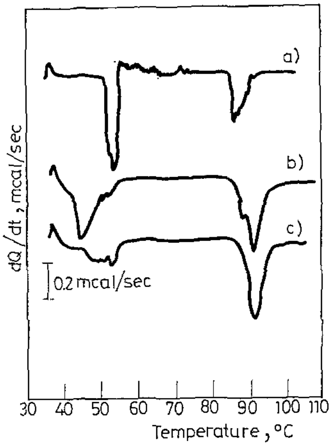

Fig. 5. Successive DSC curves of AN. Sample weight: 16.05 mg. Heating rate: 5°/min, in air; b) after standing for 15 hours in air

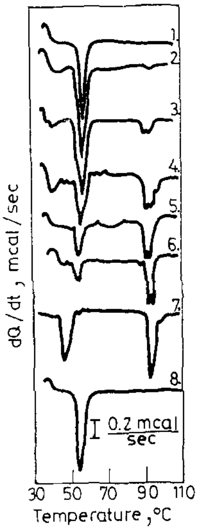

Fig. 6. Successive DSC curves of AN; inoculation with AN phase III. Sample weight: 6.93 mg. Heating rate: 5°/min, in air: 1, 2, 3 inoculation with AN modification III; 4, 5, 6 after cooling very slowly in air; 7 after standing for 20 hours in air; 8 after heating above 130°

Inoculation makes the transition process energetically easier by saving the energy of the nucleation. We have compared our inoculation procedure with a well-known method of inoculation. For the above-mentioned transformation of AN the use of KNO_3 is suitable, since it is isomorphic with AN phase III [1]. The corresponding curves (Fig. 7) are very similar to those obtained with AN inoculation in Fig. (6).

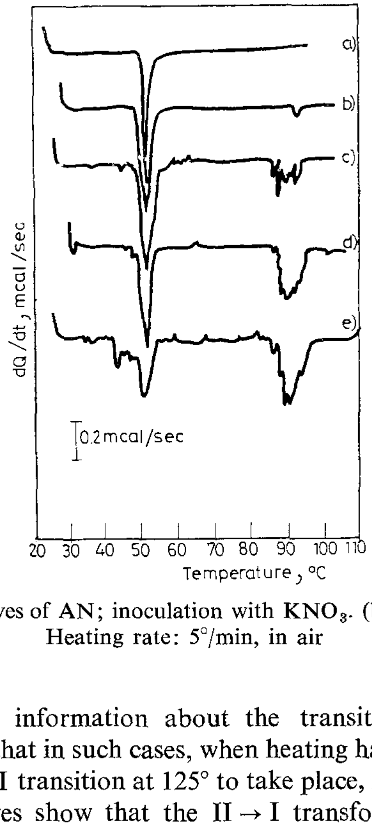

Fig. 7. Successive DSC curves of AN; inoculation with KNO_3. (b) Sample weight: 5.60 mg. Heating rate: 5°/min, in air

Figure 8 gives more information about the transitions IV → III → II → I. It is an old observation that in such cases, when heating has caused all transformations including the II → I transition at 125° to take place, in the next heating phase III disappears. The curves show that the II → I transformation occurs even at about 120°, and phase II slowly disappears.

Our investigations gave further evidence for the frequently mentioned "hysteresis" effects, the "superheating" and "supercooling" phenomena. We attribute these phenomena to difficulties in nucleation. This assumption is supported by Staveley, who also emphasizes the difficulties in nucleus formation. In papers on the polymorphic phase transformation of AN one frequently encounters the terms "thermal history" and "sample history". In view of the above considerations, these "factors" represent temperature and crystallization problems.

Owing to its hygroscopic nature, AN can always adsorb moisture from the air, thus making easier the transition of phase IV to phase III, and as soon as this modification has been formed in small amounts it inoculates the other crystals.

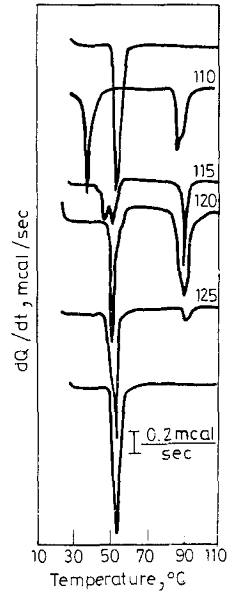

Fig. 8. Successive DSC curves of AN after heating at increasing temperature. Sample weight: unknown. Heating rate: 5°/min, in air

Since this process takes place on the boundary of the solid substance, and since AN is usually stored in large amounts and for a long time, this inoculation, i.e. recrystallization, may occur. For this reason, the main problem is not to hinder the transformation, which is almost impossible, but in some way to promote the reverse reaction.

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RÉSUMÉ — On a étudié les causes du comportement thermique spécial du nitrate d'ammonium. Dans certaines conditions d'expériences, on a obtenu des températures de transition en plus grand nombre qu'il n'avait été trouvé auparavant (37—42 °C, 51 °C et 86 °C). On a mis en évidence sur des enregistrements obtenus à l'aide d'un appareil d'analyse calorimétrique différentielle DSC Dupont, plusieurs pics exothermiques ou oscillations exothermiques après le pic endothermique à 51°C, ce qui indique que la phase IV a été transformée en phase métastable III. Par conséquent, la transformation III → II à 86 °C devient également possible. Lors du cyclage répété, le pic exothermique diminue ou disparaît si la transformation III → II s'est développée dans une plus grande mesure. On induit avec certitude une transformation IV → III en inoculant le nitrate d'ammonium avec la phase III, procédure insolite dans l'étude des transformations de phases du nitrate d'ammonium. L'avantage de la méthode est évident, puisque toutes les transformations sont contrôlées par la vitesse de nucléation.

ZUSAMMENFASSUNG — Die Ursachen des besonderen thermischen Verhaltens von Ammoniumnitrat (AN) wurden untersucht. Unter gewissen Versuchsbedingungen wurden mehrere Übergangstemperaturen erhalten als bisher gefunden wurden (37° — 42°, 51° und 86 °C). An Du Pont DSC Thermogrammen wurden mehrere exotherme Peaks oder exotherme Oszillationen nach dem endothermen Peak bei 51 °C nachgewiesen, welche zeigen, daß die Phase IV in die metastabile Phase III umgewandelt wurde. Infolgedessen wurde die Umwandlung III → II bei 86 °C ebenfalls möglich. Bei wiederholtem Meßzyklus nahm der exotherme Peak ab oder verschwand, wenn die Umwandlung III → II sich in größerem Maße entwickelte. Eine erfolgreiche IV → III Umwandlung wurde durch Inokulierung mit der Phase III von AN induziert, was ein ungewöhnliches Verfahren bei der Untersuchung der Phasenumwandlung von AN ist. Die Vorteile dieser Methode sind offensichtlich, da sämtliche Umwandlungen durch die Geschwindigkeit der Nuklierung geregelt werden.

Резюме — Были исследованы причины особого термического поведения нитрата аммония. При определенных экспериментальных условиях было получено больше температур переходов, чем до сих пор найдено (37—42°, 51° и 86 °C). На термограммах, полученных с помощью ДСК фирмы Дюпон, после эндотермического пика при 51°C, были видны несколько экзотермических пиков или экзотермических осцилляций, указывающих на превращение фазы IV до мета-стабильной фазы III, вследствие чего также становится возможным при 86 °C фазовый переход III→II. При повторном цикле экзотермический пик уменьшается или вовсе исчезает, если превращение III→II происходило в большей степени. Успешное превращение IV→III было вызвано, используя в качестве затравки фазу III, что является необычным методом в исследовании фазового превращения нитрата аммония. Использование этого метода согласуется с тем фактом, что все фазовые превращения контролируются скоростью образования центров кристаллизации.