# Thermoanalytical Investigation of Stored Ammonium Nitrate Doped with Diammine Copper-(II)

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#### Thermoanalytische Untersuchung von gelagertem Ammoniumnitrat, das mit Kupfer(II)diamminsalz phasenstabilisiert worden war

Ammoniumnitrat, phasenstabilisiert mit Kupfer-diammindinitrat, wurde nach 10jähriger Lagerung mittels DTA and TMA erneut untersucht. Die Phasenumwandlungen IV/II und IV/III, die für den Einsatz des Materials von Interesse sind, liegen immer noch oberhalb 50°C. Trotz eines Wassergehaltes zwischen 0,4% und 1,4% wurde kein Zusammenbacken beobachtet.

# Examen par thermoanalyse, après stockage de longue durée, de nitrate d'ammonium, stabilisé par une diammine de cuivre (II)

A l'issue d'une période de stockage de 10 ans, des échantillons de nitrate d'ammonium stabilisé par l'addition de diammine-dinitrate de cuivre, ont été soumis à des analyses thermiques différentielles et des analyses thermogravimétriques. Les changements de phases IV/II et IV/III, qui sont importants pour l'emploi de cette substance, se situent toujours encore à des températures supérieures à 50 °C. Malgré une teneur en eau entre 0,4% et 1,4% on n'observe aucune formation d'agglomérats.

## Summary

Ammonium nitrate doped with diammine copper dinitrate and stored for 10 years was reinvestigated by DTA and TMA. The phase transitions IV/II and IV/III, which are of interest for the practical use, still occur above 50 °C. In spite of moisture contents between 0.4% and 1.4% no caking was observed.

# 1. Introduction

In the propellant and explosives field ammonium nitrate has been always attractive as it is cheap and readily available. Its use was restricted due to its phase change IV/III, which normally takes place at 32 °C in humide material. This phase change causes a volume change creating the known difficulties. These difficulties and scientific interest stimulated the interest into the unique compound resulting in many papers dealing with thermal analysis of ammonium nitrate<sup>(1-5)</sup>.

The stability regions of the different phases are therefore well established. They differ for humid and absolutely dry ammonium nitrate (see Table 1).

The difficulties in the use of the compound are frequently met by incorporating  $KNO_3$  into the lattice stabilizing<sup>(6, 7)</sup> therewith phase III.

We developed a different way of influencing the phase behaviour doping the nitrate with diammine copper-(II), avoiding the occurrence<sup>(8)</sup> of phase III. After having stored the resulting products for ten years no caking was observed. All samples were free-flowing. Therefore it was decided to reinvestigate the materials by thermal analysis to see, if the additives are still influencing the phase properties.

# 2. Experimental

#### 2.1. Materials

Ammonium nitrate in quantities of 10 kg to 50 kg was melted together with different quantities of copper oxide and atomized. The reaction between the two compounds yields diammine copper dinitrate, which is incorporated into the ammonium nitrate lattice.

For the reason of convenience the samples are characterized by the weight percent of copper oxide, with which ammonium nitrate was melted together.

The materials were stored in the laboratory in plastic bottles, which were opened frequently. No attempt was made to exclude moisture. The temperatures ranged from  $5 \,^{\circ}$ C to  $35 \,^{\circ}$ C.

# 2.2. Thermal analysis

A Dupont 990 thermal analyzer was used together with a DTA and TMA cell. In the DTA experiments about 4 mg were cooled without control with liquid nitrogen to about -60 °C and heated up to the melting point with a rate of 10 °C/min.

In the TMA experiments 500 mg-600 mg in a small quartz tube were cooled with liquid nitrogen to about -60 °C and heated with 5 °C/min.

#### 2.3. Water analysis

The water content was determined by the Karl-Fischermethod. As with the Karl-Fischer-method an interference is

Table 1. Phases of Ammonium Nitra
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Phases	v	IV	III	II	I
Stability [°C]	dry – 18 humid	-18  to  +55 -18  to  +32	- 32 to 84	55 to 125 84 to 125	125 to m.p.

CuO [wt.%]	DTA-Pea Tempera	aks ture [°C]								H <sub>2</sub> O [wt.%] B.H.	K.F.
1	(-18)		54		((90))		127	170		0.45	0.35
			54				127	170-2	2		
	(-18)	((46, 48, 50))	53	>	86-9	0	127	169			
		44-50	= 53	<	88	(119)	127	170			
		(48–50)	54	>	88	(124)	126	168			
2	(-20)(0)		54	≥	87		127	170		0.60	0.60
	,	49–54			86		126	170			
		47-51	≪ 54	=	87		129				
	(-18)	48-50	≪ 54	>	88		127	171			
3	(-15)	51	≤ 54	=	86	(119, 126)	129	170		0.80	0.55
	(-14)		54	>	87	(120, 126)	129	171			
	. ,	50	< 54	=	86	(118, 126)	129	171			
		53	< 56	<	88	(120, 128)	131				
		52	< 55	=	88	(120, 128)	131	172			
4	(-8)	50	< 54	>	87	127	132	173		1.15	0.70
			54	>	85		132				
		(48-51)	52	>	84	((124))	130	170			
		49			86	105, 115	133	170			
5		(50)	≤ 55	=	87	99	134	175		1.15	0.85
			54	>	89		134	174		1.05	0.75
			56				135	173			
			55	>	87-9	6	134	173			
10			59	>	84	125	139	160	173		
		52	≥ 56	<	87	92	141	159	173	1.45	1.10

() mark weak peaks; <, > compare weak intensities.
B.H. = Bell and Howell water analyzer.
K.F. = Karl Fischer method.







Figure 2. Selected TMA curves.

possible by the reaction of copper-(II) with iodide, a second determination was made with a water analyzer of Bell and Howell. In this procedure, water vapor from the heated sample is absorbed by  $P_2O_5$  and determined by electrolysis.

## 3. Results and Discussion

The results of DTA are given in Table 2. Selected DTAand TMA-diagrams are shown in Figs. 1 and 2. In Table 2 some peak temperatures are enclosed in brackets, which mark weak peaks. The signs "<, >, =" between peak temperatures compare the intensities of two peaks.

There are 5 groups of peaks in the DTA-diagrams. The first group appears below  $0^{\circ}$ C indicating the transition V/IV. The peaks tend to disappear with the samples of higher copper content. As they are weak and flat, the temperatures cannot be precisely determined.

Peaks of a second group appear at about 50 °C. An intensive sharp peak at 54 °C–56 °C indicates the phase change IV/II. It is often accompanied by weaker peaks at lower temperatures. These must be attributed to the phase change IV/III. The third peak group between 80 °C and 90 °C proves the occurrence of phase III, as they must be attributed to the phase change III/II.

The fourth group indicates the phase transition II/I between 120 °C and 140 °C, and the last one is caused by the melting of the samples.

The water content of the samples is relatively high. Obviously, the frequent handling of the samples and the opening of the bottles have led to some absorbance of moisture from the atmosphere, as the content after the production was below 0.15%. This water content causes the appearance of phase III, which, however, never includes the whole samples.

The ratios of the phases II and III in the temperature range of about 50 °C–90 °C can be estimated comparing the intensity of the peak at 54 °C–56 °C with its preceding double peak and with the intensity of the peak at 80 °C–90 °C. In only few diagrams (e.g. the last diagram in Fig. 1 with 10% CuO) phase III prevails. The transition temperatures IV/III, however, do not drop below 50 °C. This observation distinguishes the samples from pure ammonium nitrate, whose transition temperatures IV/III drop remarkably below 50 °C at these water contents.

Therefore, it must be concluded, that the diammine copper complex is still effective. It restricts the occurrence of phase III to only a part of the samples and it keeps transition temperatures above  $50 \,^{\circ}$ C avoiding caking and preserving the free flowing of the materials.

The DTA diagrams reveal further influences of the additive resulting in higher temperatures for the transition II/I and for melting. Besides, double peaks above 120 °C are observed, which cannot be interpreted. Eventually, they are caused by inhomogeneous distribution of the additive.

The TMA-diagrams in Fig. 2 confirm the DTA results. No volume increase is observed below 50 °C. A higher content of diammine copper-(II) seems to restrict the volume jump. But in some samples of the same copper content different volume increases were observed (see Fig. 1, sample with 5% CuO). It may be concluded that different water contents lead to different ratios of phase III and volume increases, respectively.

#### 4. References

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