

Selected magnesium compounds as possible inhibitors of ammonium nitrate decomposition

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Ammonium nitrate (AN) is considered to be a very hazardous and difficult to handle component of mineral fertilizers. Differential thermal analysis coupled with thermogravimetry and mass spectrometry was used to determine the possible inhibiting effect of selected magnesium compounds on thermal decomposition of AN. Each additive was mixed with AN to create samples with AN:magnesium compound mass ratios of 4:1, 9:1 and 49:1. Most of analyzed compounds enhanced thermal stability of ammonium nitrate, increasing the temperature of the beginning of exothermic decomposition and decreasing the amount of generated heat. Magnesium chloride hexahydrate was determined to accelerate the decomposition of AN while magnesium sulphate, sulphate heptahydrate, nitrate hexahydrate together with magnesite and dolomite minerals were defined as inhibiting agents.

Keywords: ammonium nitrate, thermal analysis, magnesium compounds, exothermic decomposition, phase transition.

INTRODUCTION

 Ammonium nitrate (AN) is a chemical compound that has many practical applications. It is mainly used in production of fertilizers and explosives**¹** . It is one of the most commonly used fertilizers due to its high nitrogen content, good solubility in water and a relatively low price**²** . During the production process of nitrogen fertilizers, there are various additives used in order to change temperature ranges of unwanted phase transitions that might worsen properties of a fertilizer. The decomposition of ammonium nitrate is accompanied by the formation of large quantities of gaseous products. Because of that, ammonium nitrate is considered to be a compelling substitute for conventional rocket propellants³⁻¹⁰. There are many defined factors known to accelerate the decomposition of ammonium nitrate. The rate and direction of the ammonium nitrate decomposition depends on temperature, conditions of heat and mass transfer with the environment, pH and the presence of other substances in the system, such as chloride, chromium, nickel, copper, cobalt, zinc ions or organic compounds**11–18**. Carbonates, urea, phosphates, sulphates and some other compounds were found to slow down the exothermic decomposition process**19–23**. The decomposition of ammonium nitrate can pose a serious threat to people working on the production, transportation or storage of fertilizers. Despite all the knowledge about the decomposition of this chemical compound, it is still dangerous, as evidenced by events happening in various locations around the world²⁴. There is a variety of proposed mechanisms that can approximately describe the process of the exothermic decomposition of ammonium nitrate, however many kinetic models and mechanisms of the decomposition are still a topic of discussion up to this date**25–28**.

The aim of this study was to analyze the influence of selected magnesium compounds on phase transitions and the decomposition process of AN. Magnesium is considered to be an important element that is necessary for plants to correctly grow and develop. Since it is present in many fertilizers based on ammonium nitrate, it is important to analyze the thermal stability of systems containing ammonium nitrate mixed with magnesium compounds. This work provides fundamental knowledge for further investigation on the safety of AN in systems with various sources of magnesium.

MATERIALS AND METHODS

Materials

Fertilizer-grade ammonium nitrate was used in the study and was obtained from one of the domestic producers of nitrogen fertilizers. Magnesium compounds, i.e. magnesium chloride hexahydrate (POCH, purity ≥ 99.0 wt%), magnesium nitrate hexahydrate (POCH, purity ≥ 99.5 wt%), magnesium sulphate (CHEMPUR, purity $\geq 99.5 \text{ wt\%}$, magnesium sulphate heptahydrate (POCH, purity $\geq 99.5 \text{ wt\%}$), dolomite and magnesite (minerals containing magnesium carbonate, both obtained from domestic producer of nitrogen fertilizers) were used without any further purification. Contents of dolomite and magnesite are given in Table 1. Synthetic air (Air Liquide Polska) was used as a purge gas during all measurements.

Table 1. Contents of selected mineral additives

Mineral filler	$MgCO3$ content $[wt\%]$	$CaCO3$ content [wt%]		
Dolomite	41.4	55.3		
Magnesite	89.9	0.0		

Every tested sample was prepared with the use of agate mortar and pestle. Appropriate amounts of each compound, necessary to acquire a desired mass ratio in a sample (AN:magnesium compound equal to 4:1, 9:1 and 49:1), were ground together in order to obtain a homogenic mixture. Next, a sample containing approximately 20.0 mg of AN was weighted and placed in a 0.3 mL alumina crucible and closed with a pierced lid.

Methodology

Measurements were performed with the use of differential thermal analysis coupled with thermogravimetry and mass spectrometry (DTA–TG–MS). A thermal analyzer STA 449 F3 with a thermobalance and a mass spectrometer QMS 403 C, Netzsch, were used. The equipment was previously calibrated.

It is important to focus on exothermic decomposition of AN, as it is the main cause of disasters experienced in the past, in order to correctly define thermal stability of samples containing AN mixed with magnesium compounds. When the mass of a sample is low or the surface-to-volume ratio is high, the dissociation process dominates the observed decomposition and an endothermic peak is obtained during a thermal analysis of AN- -containing sample. As stated in previous work studying thermal stability of AN in systems with potassium salts**²⁹**, the use of a 0.3 mL alumina DTA crucible, pierced lid and the mass of approximately 20.0 mg of AN allows observing the exothermic peak during the ammonium nitrate decomposition process.

Each sample was heated up to 450° C at the rate of 5° C/min in synthetic air with a 30 mL/min total flow of the purge gas. Every measurement was preceded by heating an empty crucible to 600°C in order to remove any impurities and a correction to 500° C for a compensation of thermal effects associated with characteristics of the crucible. Before each measurement, the furnace

chamber was evacuated three times and filled with synthetic air. Each mixture was analyzed three times in order to ensure that obtained thermograms are correct and mean values with corrected standard deviation for each sample were presented in Table 2. In the same way, for comparison purposes, a 20.0 mg sample of ammonium nitrate without the addition of any filler was also examined with the use of an empty crucible as a reference material. Obtained results were analyzed with the use of a professional software supplied by the manufacturer of the measuring equipment. The selected ion monitoring for mass-to-charge ratios (m/z) consisted of following signals: 12 (CO, CO₂), 15 (NH₃), 17 (NH₃, H₂O), 18 (H₂O), 29 (CO), 30 (NO, NO₂), 36 (HCl), 44 (N_2O, CO_2) , 46 (NO_2) and 64 (SO_2) .

RESULTS AND DISCUSSION

Ammonium nitrate

Parameters that define an enhanced thermal stability of ammonium nitrate are: higher temperature of phase transitions from the IV to III or II crystalline phases or the lack of them, increased temperature of the beginning of the AN decomposition and the slower rate of the decomposition process. These parameters are valuable mainly because they allow defining a safe temperature

Table 2. Effects of selected magnesium compounds on thermal stability of AN

	AN:Salt ratio	Temperature of phase transitions [°C]			3%	Exotherm	End of	Heat evolved	
Salt		$IV \rightarrow II$	$III \rightarrow II$	$ \rightarrow $	Melting	mass loss [°C]	maximum [°C]	decomposition [°C]	during decomposition [J]
Ammonium nitrate	Pure	$51.0 \pm$ 0.2	$84.4 \pm$ 0.1	124.1 ± 0.1	$166.6 \pm$ 0.1	235.2 ± 3.8	283.3 ± 2.4	297.0 ± 1.4	26.23 ± 1.57
Magnesium chloride hexahydrate	4:1	$51.1 \pm$ 0.2	$66.3 \pm$ 0.2		\sim	112.9 ± 1.3	286.2 ± 1.8	303.9 ± 2.0	40.41 ± 3.21
	9:1	$\frac{1}{50.7 \pm 1}$ 0.2	$61.6 \pm$ 0.1	124.5 ± 0.4		121.6 ± 1.0	268.8 ± 2.3	309.4 ± 1.3	45.98 ± 2.74
	49:1	$50.7 \pm$ 0.2	$88.6 \pm$ 0.2	124.2 ± 0.3	$158.1 \pm$ 1.0	222.3 ± 2.1	286.6 ± 1.1	309.0 ± 1.1	43.78 ± 2.88
Magnesium nitrate hexahydrate	4.1	$47.6 \pm$ 0.3	$86.4 \pm$ 0.2	124.7 ± 0.2	\blacksquare	114.8 ± 2.2	304.2 ± 3.2	311.7 ± 1.4	20.91 ± 1.23
	9:1	$48.0 \pm$ 0.3	$87.9 +$ 0.3	124.9 ± 0.1	\blacksquare	120.8 ± 1.8	292.7 ± 2.1	311.5 ± 1.3	23.79 ± 1.89
	49:1	$51.0 \pm$ 0.1	$88.1 \pm$ 0.2	124.3 ± 0.4	$162.2 \pm$ 1.5	234.7 ±1.8	285.6 ± 2.2	311.7 ± 2.0	24.38 ± 1.78
Magnesium sulphate	4:1	$\frac{1}{50.9 \pm \frac{1}{10}}$ 0.1	$88.0 \pm$ 0.3	124.3 ± 0.4	$166.5 \pm$ 1.3	231.8 ± 1.9	287.4 ± 2.1	348.7 ± 1.8	19.31 ± 1.13
	9:1	$49.7 \pm$ 0.2	$89.4 \pm$ 0.3	124.3 ± 0.2	$166.4 \pm$ 0.8	229.6 ±2.2	282.9 ± 2.7	344.1 ± 1.8	19.45 ± 1.34
	49:1	$50.5 \pm$ 0.1		123.7 \pm 0.2	$165.2 \pm$ 0.9	234.2 ± 1.4	283.9 ± 1.9	315.5 ± 1.2	16.87 ± 1.52
Magnesium sulphate heptahydrate	4:1	$46.7 \pm$ 0.2	$86.6 \pm$ 0.2	124.2 ± 0.3	$160.3 +$ 15	$90.2 \pm$ 2.8	283.2 ± 3.1	345.7 ± 2.1	27.01 ± 2.12
	9:1	$46.2 \pm$ 0.2	$85.0 \pm$ 0.1	123.7 \pm 0.2 $\,$	$163.1 \pm$ 1.1	$94.1 \pm$ 2.1	288.3 ± 26	340.0 ± 1.6	17.28 ± 1.38
	49:1	$44.3 +$ 0.2	$83.9 +$ 0.2	123.8 \pm 0.3	$165.2 \pm$ 1.2	231.8 ±1.8	288.2 ± 1.7	312.2 ± 1.7	13.422 ± 1.02
Dolomite	4:1	$\frac{1}{51.2 \pm \frac{1}{2}}$ 0.2		124.2 ± 0.2	$165.9 +$ 0.9	242.3 ± 2.7	312.9 ± 2.9	322.7 ± 19	20.33 ± 2.31
	9:1	$51.2 \pm$ 0.1		124.4 ± 0.4	$166.6 \pm$ 0.7	242.3 ± 1.8	311.0 ± 26	322.4 ± 2.1	22.01 ± 1.78
	49:1	$51.1 \pm$ 0.1	$86.0 \pm$ 0.3	124.3 ± 0.1	$167.0 \pm$ 1.1	242.4 ± 2.6	291.0 ± 2.1	317.1 ± 2.0	19.47 ± 1.87
Magnesite	4:1	$50.9 +$ 0.2		124.2 ± 0.3	$165.7 \pm$ 1.4	249.9 ± 2.1	286.9 ± 3.1	313.2 ± 1.6	25.91 ± 2.00
	9:1	$50.9 +$ 0.2		124.3 ± 0.2	$166.6 \pm$ 1.1	240.9 ±1.6	281.2 ± 1.9	311.8 ± 2.3	28.42 ± 2.47
	49:1	$50.6 \pm$ 0.2	$85.4 \pm$ 0.3	124.0 ± 0.5	166.5 \pm 1.1	231.6 ± 1.7	289.6 ± 2.3	312.1 ± 1.7	24.35 ± 1.32

during the manufacturing process and hazards connected with production and storage of products containing AN.

Results of the thermal analysis of the 20.0 mg pure ammonium nitrate sample are shown in Figure 1. A partial transition IV \rightarrow II was observed at around 51.0°C as a first endothermic signal. Ammonium nitrate undergoes a transition from IV to II crystalline phase when there is almost no water in the system. III→II transition occurred at 84.5°C and a II→I crystallographic transformation at 124.0 $^{\circ}$ C. The sample melted approximately at 166.5 $^{\circ}$ C. The decomposition took place in the temperature range from 220 to 298°C. Thermal decomposition resulted in a complete mass loss. Mass spectrometry results confirmed that evacuated gaseous products consisted of H_2O , NH₃, NO, NO₂ and N₂O. MS signals obtained for the sample of pure AN were presented in Figure 2. The baseline was a linear function beginning at the temperature of first MS signals generation of said products up to the point of the DTA signal stabilization.

Figure 1. DTA-TG results for the pure AN sample

Figure 2. MS signals for gaseous products created during thermal analysis of the pure AN sample

Magnesium chloride hexahydrate

The phase transition from IV to II crystalline phase was visible for all AN samples containing magnesium chloride hexahydrate at temperatures close to 51°C, other endothermic signals differed significantly from signals characteristic for pure ammonium nitrate. $3 wt\%$ losses were recorded at 112.2, 121.2 and 223.1°C for samples 4:1, 9:1 and 49:1, respectively. Low temperatures of the beginning of a gradual decrease in mass are caused by the release of water contained in the used additive,

which is confirmed by a slight increase in the signal for H2O registered by mass spectrometry. The 4:1 sample was characterised by the maximum of the exothermic signal obtained at 285.1°C and the end of decomposition at almost 303°C. Characteristically for the addition of chloride salts to AN, presence of $MgCl_2 \cdot 6H_2O$ in analyzed systems caused a significant increase in the value of heat generated during the decomposition process of tested mixtures. As described in the study of potassium chloride**²⁹**, the addition of 10 and 2 wt% of magnesium chloride hexahydrate allowed observing two different stages of the decomposition reaction. During the first, more violent stage, hydrogen chloride was formed along with nitrogen oxides, ammonia and water. After the hydrogen chloride left the analyzed system, there was a change in the mechanism of the observed decomposition process and the transition to stage 2, characteristic for the pure AN sample. Obtained DTA and TG results for all 3 examined samples are shown in Figure 3. MS signals obtained for 4:1 and 9:1 samples of AN:MCH were presented in Figure 4.

Figure 3. DTA and TG results for AN:magnesium chloride hexahydrate samples

Magnesium nitrate hexahydrate

Magnesium nitrate hexahydrate is used in the fertilizer industry as a nitrogen fertilizer which is also a source of magnesium with a composition of 10.5-0-0-15Mg. Decreases in mass of tested samples at low temperatures was caused by the release of water of crystallization, which was confirmed by obtained increases in MS signals for water. 20 wt% addition of the described salt to AN caused a decrease in the transition temperature between phase IV and II by 3.5° C in comparison to AN, an increase

Figure 4. MS signals for gaseous products created during thermal analysis of the 4:1 AN:magnesium chloride hexahydrate sample

in temperature of III \rightarrow II transformation by almost 2^oC and a disappearance of the endothermic melting signal. The exotherm maximum of the decomposition of the 4:1 mixture was obtained at 302.9°C, and the end of the process was observed at 312.9°C. The thermal analysis of the 9:1 sample resulted in obtaining very similar endothermic signals to the 4:1 sample. The maximum of the exotherm was obtained at 291.5° C. The melting process of the 49:1 sample was visible on the DTA curve at 161.3°C. Despite the small amount of magnesium nitrate hexahydrate in the system, a significant increase in temperature was obtained for the end of the exothermic decomposition and no increase in total heat released during the process was registered. It allows concluding that magnesium nitrate hexahydrate can be qualified as an inhibitor of exothermic decomposition of ammonium nitrate. Figure 5 shows DTA and TG results of abovedescribed samples. MS data obtained for the 4:1 sample is presented in Figure 6.

Magnesium sulphate

DTA and TG curves obtained for mixtures containing AN and magnesium sulphate are presented in Figure 7. Thermal analyzes showed slight mass losses starting at low temperatures for all samples. These effects were associated with vague MS signals for water. The presence of water in the system may have been caused by the significant hygroscopicity of anhydrous magnesium sulphate and the binding of water during sample preparation in a mortar. Endothermic signals for IV→II and

Figure 5. DTA and TG results for AN:magnesium nitrate hexahydrate samples

Figure 6. MS signals for gaseous products created during thermal analysis of the 4:1 AN:magnesium nitrate hexahydrate samples

II→I transformations and melting were obtained at very similar temperatures as signals for pure ammonium nitrate. The 4:1 sample had a clearly split exothermic decomposition signal, suggesting at least two separate mechanisms of the process. The first exotherm maximum was obtained at 286.3°C, while the end of decomposition was recorded at 348.2°C. The TG curve and obtained MS signals for gaseous products confirmed the multi-stage nature of the observed exothermic decomposition process, indicating three separate stages of decomposition. At all stages, presence of water, ammonia and nitrogen oxides was detected, while the presence of sulphates in the stream of gaseous products was recorded as a small

Figure 7. DTA and TG results for AN:magnesium sulphate samples

signal during the last stage of the decomposition of the mixture. Obtained MS data for the 4:1 sample is presented in Figure 8. The thermogram obtained for the 9:1 sample was very similar to the sample containing 20 wt% of magnesium sulphate, with the difference between the intensity of exothermic signals obtained on the DTA curve and proportions of mass decreases during each individual stage of the decomposition. The thermal analysis of the 49:1 sample showed that even the addition of 2 wt% of magnesium sulphate can stabilize the decomposition of ammonium nitrate by reducing the intensity of exothermic decomposition and increasing its end temperature to over 315°C.

Figure 8. MS signals for gaseous products created during thermal analysis of the 4:1 AN:magnesium sulphate sample

Magnesium sulphate heptahydrate

Previously described analyzes showed that anhydrous magnesium sulphate can be considered as an inhibitor of the ammonium nitrate decomposition, so the cheaper form of this additive that is used in fertilization had to be examined. Figure 9 contains all results acquired after thermal analyzes of 3 samples containing AN and magnesium sulphate heptahydrate. Tested samples generated signals for all transitions between crystallographic forms in the analyzed temperature range and lost parts of their initial mass as the temperature increased due to the evaporation of water from the system. The thermal analysis of the 4:1 sample generated an endothermic melting signal at 159.4°C. The fragment of the TG curve corresponding to the process of exothermic decomposition of the tested sample resembled the result of thermogravimetric analysis for the 9:1 sample of ammonium nitrate with anhydrous magnesium sulphate. The similarity might indicate that, after evaporation of the water of crystallization, magnesium sulphate remaining in the system affects the thermal stability of ammonium nitrate in a similar way to the anhydrous equivalent of this additive. The shape of the obtained exotherm differed from results obtained for samples containing magnesium sulphate, because the first part of the exothermic signal was more intense than the signal generated in other two stages of the decomposition. The exothermic decomposition of ammonium nitrate was significantly prolonged to the higher temperature of 344.1°C. Figure 10 shows MS signals obtained for the 4:1 sample. Samples containing 10 and 2% wt of magnesium sulphate heptahydrate generated lesser amounts of heat during the exothermic

Figure 9. DTA and TG results for AN:magnesium sulphate heptahydrate samples

Figure 10. MS signals for gaseous products created during thermal analysis of the 4:1 AN:magnesium sulphate heptahydrate sample

decomposition process and the process itself ended at higher temperatures than the decomposition of pure AN.

Dolomite

DTA and TG results for samples of AN mixed with dolomite are shown in Figure 11 and MS data for the sample containing 20 wt% of dolomite is shown in Figure 12. Ground dolomite is a commonly used filler in the production of ammonium nitrate fertilizers. The addition of ground dolomite did not cause changes in temperatures of endothermic phase transitions recorded on the DTA curve. The 4:1 sample lost 3% of its mass at 240.7°C, reached the maximum exothermic signal at 311.4°C and finished decomposing after reaching 322.7°C. The shape of the obtained exothermic effect

Figure 11. DTA and TG results for AN:dolomite samples

Figure 12. MS signals for gaseous products created during thermal analysis of the 4:1 AN:dolomite sample

was significantly different from the pure AN sample, and reactions that occured during the decomposition process took place in a much wider temperature range. Recorded MS signals showed the appearance of carbon dioxide, water and ammonia in the gas stream leaving the furnace chamber at a temperature of about 215° C, while nitrogen oxides began to appear at a temperature close to 278°C. The 9:1 sample had similar thermal characteristics as the 4:1 sample. MS signals obtained for gaseous products of the exothermic decomposition were in similar temperature ranges. Addition of 2 wt% of dolomite caused a slight delay in reaching the maximum of the exotherm and an increase in the temperature of the end of the exothermic decomposition to 318.2°C. The amount of generated heat during the decomposition process of all analyzed samples decreased in comparison to the pure AN sample. The reactivity of the used filler was adequate and no reactions were observed at lower temperatures It effectively inhibited the exothermic AN decomposition in tested samples.

Magnesite

Ground magnesite did not cause changes in temperatures of observed endothermic transformations of ammonium nitrate. The thermal analysis of the 4:1 sample showed a relatively high temperature of the 3% mass loss at 248.6°C. The temperature of the exotherm maximum was not significantly distant from the temperature obtained for the pure ammonium nitrate sample, while the temperature of the end of the decomposition was about 15°C higher. The shape of recorded TG and DTA curves indicated a multistage process of the sample decomposition, which resulted in a rapid weight loss starting at the temperature of 256.0°C together with the generation of water, ammonia, carbon dioxide and small amounts of nitrogen oxides. As the decomposition process progressed, more intense signals for nitrogen oxides and a change in the shape of the TG slope were obtained. After the sample reached a temperature of 298.5° C, a slight increase on the DTA curve was obtained and a clear signal indicating the presence of chlorides and nitrogen dioxide in the gas stream was recorded. The 9:1 sample showed very similar thermal characteristics to the sample containing 20 wt% of magnesite. Sample 49:1 had a recorded 3% mass loss at a visibly lower temperature

than previous two mixtures $(232.8^{\circ}C)$. The end of the decomposition, as in the case of ground dolomite, was observed at elevated temperature in comparison to the pure AN sample. Figure 13 contains all DTA and TG curves for analyzed samples of AN with magnesite. MS signals for the 4:1 sample are shown in Figure 14.

Figure 13. DTA and TG results for AN:magnesite samples

Figure 14. MS signals for gaseous products created during thermal analysis of the 4:1 AN:magnesite sample

CONCLUSIONS

All tested magnesium-containing additives visibly affected the thermal stability of ammonium nitrate. Magnesium chloride hexahydrate showed undesirable properties of accelerating and intensifying the exothermic decomposition of ammonium nitrate. Magnesium sulphate, magnesium sulphate heptahydrate and magnesium nitrate hexahydrate significantly inhibited the AN decomposition process, increasing the temperature of the exotherm maximum and end of the decomposition in a similar way to additives used by producers of ammonium nitrate fertilizers. However, it is necessary to examine the effect of these stabilizing additives on the granulation process and hygroscopicity of manufactured products. Dolomite and magnesite, obtained from a domestic producer of nitrogen fertilizers, did not show excessive reactivity and can be used to stabilize ammonium nitrate.

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