

LIABILITY TO SELF-HEATING OF PARTICULAR SAMPLES OF FERTILIZER GRADE AMMONIUM NITRATE

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Results of testing the liability of various samples of fertilizer grade ammonium nitrate (AN) to self-heating are presented. Test methods applied comprises: DTA, TG, determination of mass loss at constant temperature, pH-measurement of aqueous solutions. The assessment of liability to self-heating is based on comparison to the relevant results of a standard AN product.

Criteria for evaluation of the test results and the assessment of hazardous conditions are suggested.

The self-heating of ammonium nitrate is recognized as the main cause of accidents during the production, storage and transportation of this fertilizer. The self-heating phenomenon depends on the relation of heat generation to the conditions of heat transmission as well as heat absorption by endothermic processes. If in a certain system the heat generation (HG) exceeds the loss of heat by means of heat transmission or heat absorption—in both cases referred to the unit of mass and time—a spontaneous rise in temperature is detectable.

The heat generation in the self-heating process of AN is the consequence of its decomposition that takes place in the sequence of consecutively, partly simultaneously running reactions [1]. The HG changes within a very broad range and depends also on the interaction of other substance either catalysing or inhibiting the decomposition [1–3].

It is not possible to estimate all the factors influencing the heat equilibrium, especially the conditions of mass and heat transmission in each particular case of production, storage and transportation of ammonium nitrate. In safety regulations only general conditions can be laid down, e.g. the mass of stored fertilizer, minimal distance from residential buildings, materials used for construction of this store.

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More realistic for technical reasons and cheaper is the control of the second factor of the heat equilibrium—HG—by means of the control of the rate of decomposition and its thermal effect under special, standardized test conditions. By referring these quantities to the values characterizing pure ammonium nitrate it is possible to examine the influence of any admixture, either an incidental impurity or a deliberately introduced additive. If, due to the presence of admixtures, the rate of decomposition or HG increases, then under the same conditions of mass and heat transmission the self-heating hazard and the probability of accidents is supposed to be enlarged.

There are different methods, described in the literature, which were applied in investigations of thermal stability of AN. They consist either in direct measurement of the HG of the energy source [4] or in determining the temperature above which the decomposition under the measurement conditions becomes exothermic [1]. In the latter method DTA and TG as well as accelerating rate calorimeter (ARC) are applied [5]. The results of measurements—regardless of the method applied—are not universal, but they concern the decomposition conditions under which the measurements have been performed. The direct measurements of HG and the use of ARC are time consuming—from several tens of hours to several tens of days. Corrosive effects of AN and products of its decomposition create additional difficulties.

This investigation is aimed at evaluating the liability to the self-heating of a number of ammonium nitrate fertilizers, most of them supplied to the European fertilizer market. In these investigations an original test method has been applied [6].

Experimental

Description of the test

It has been assumed that the most significant quantities characterizing the decomposition of ammonium nitrate and connected with the spontaneous increase of its temperature, are the decomposition rate and its thermal effect. To determine the above quantities, the differential thermal analysis DTA and thermogravimetry TG as well as the measurement of the change in mass at constant temperature, were applied. Moreover, the pH of aqueous solutions containing 3.2% mass of the sample (pHWR) was determined, since this pHWR is related to the concentration of nitric acid in the analysed sample. Acid presence stimulates exothermic reactions and accelerates the decomposition.

Based on the measurements performed under the same conditions, the characteristic defining quantities have been determined. The changes in their values

referred to the properties of standard ammonium nitrate were used for estimation of self-heating ability of the samples being examined. Quantity 1—i.e. the temperature T_{peg} above which the decomposition is an exothermic process was marked on the curve DTA (Fig. 1). Further quantities 2 and 3, i.e. the temperature $T_{2\%}$ at which the relative loss of mass achieves the value of 2% referred to the initial mass of the sample, and $T_{5\%}$, at which the relative loss of mass achieves 5%, were marked on the curve TG. The next two quantities, i.e. the rate of mass loss in the steady state of the decomposition (V_{ust}) and the maximal rate of decomposition (V_{max}) were determined from the change in the mass of the sample examined as a function of its heating time at 200° (Fig. 2).

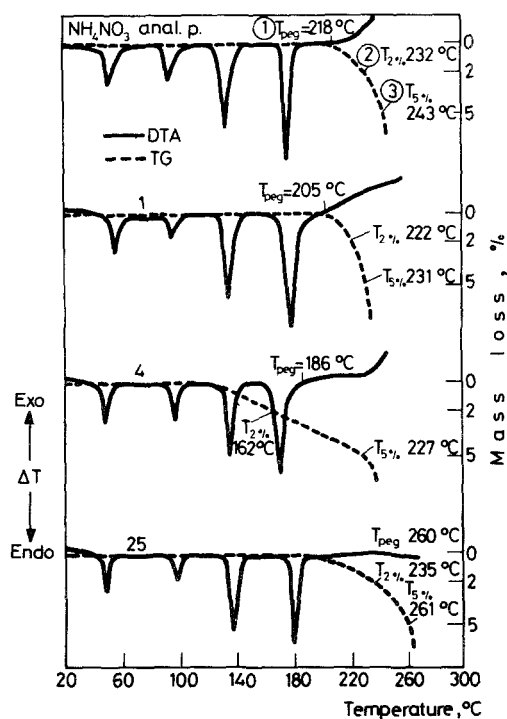


Fig. 1 Typical thermal analysis curves of ammonium nitrate fertilizers

Testing method

DTA and TG analysis were performed simultaneously in an apparatus of the author's own construction [1] equipped with a pipe furnace in an upright position. The sample subject to DTA was placed in a glass crucible which was positioned on a PtRh-thermocouple put in a special ceramic sample holder. The latter was placed

inside the pipe of the furnace and closed the bottom side of the pipe. Immediately above the sample for DTA there was the sample for TG which was suspended from the arm of an automatic balance by a thin platinum wire. The wire was lead through a small opening in a glass cap closing the upper end of the pipe furnace. Heating rate: 2.5 deg min^{-1} . Gas phase: air, free flow. Glass crucibles were characterized by the ratio of crucible sectional area to the sample mass $Y = 1 \text{ cm}^2 \cdot \text{g}^{-1}$. The values of initial masses of the samples being analysed amounting to 500 mg. Sensitivity of the temperature measurement for DTA was $\pm 0.1 \text{ deg}$, and that of mass loss for TG: $\pm 0.2 \text{ mg}$. Calcinated Al_2O_3 acted as the reference system. The mass of samples used for isothermal measurements was equal to 1000 mg.

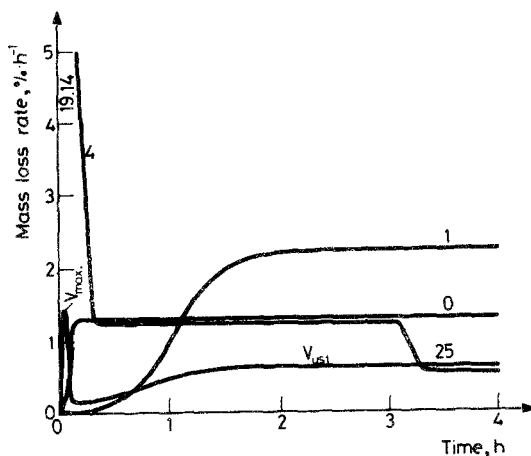


Fig. 2 Typical loss of mass rate curves of ammonium nitrate fertilizer samples (initial mass 1000 mg, temperature 200°C)

The pHWR was measured at temperature of the solution in the range of $18\text{--}22^\circ$. The pHWR of original samples and those heated at temperature of $200^\circ \pm 1^\circ$ were measured after the steady state of the decomposition had been reached. Under test conditions the decomposition of analytically pure ammonium nitrate achieved the steady state after 1–2 hours. The value of pHWR amounted then to about 3.8. It has been assumed that the decomposition of samples of ammonium nitrate pure and with additives, achieves the steady state when their pHWR has a value below 3.9 and at the same time, the rate of mass loss does not change more than 0.05% by mass during one hour. If during 4 hours of heating several values of the rate of mass loss are determined, then the last value is taken as V_{us1} , but the maximal value V_{max} should be also given in the list of test results. If, after the measurement of V_{us1} , pHWR of the sample has a value greater than 3.9 then the test should be repeated by heating

the sample until pHWR reaches the value lower than 3.9. In general the value of HNO_3 -concentration in the sample corresponding to a pHWR of 3.9, signalled by the bend of the curve indicating the loss in mass, is reached before the mass loss amounts to 25–35%. Repeating the determination of V_{ust} with increased heating time is not necessary if the other defined quantities (T_{peg} , $T_{2\%}$, $T_{5\%}$, V_{max}) decisively influencing the evaluation of fertilizers' quality, indicate a greater liability to self-heating of the sample being tested than pure AN.

Description of samples and testing results

Twenty five samples of ammonium nitrate fertilizers containing more than 33.5% N were tested. They were manufactured in a period ranging from 1970 to 1985, most of them within a period from 1977 to 1985.

Table 1 gives the survey of results of measurements. In addition, examples of a typical behaviour of specific samples are presented in diagrams (Figs 1 and 2).

Values for the following quantities T_{peg} , $T_{2\%}$, $T_{5\%}$, V_{ust} , V_{max} were estimated on the basis of at least two measurements taken as a sufficiently reliable values—the arithmetical mean. Figs 1 and 2 were constructed from the average value on the basis of original DTA and TG curves, as well as of the diagrams presenting the loss of mass of the sample heated at a constant temperature.

The results obtained from the particular samples in the test have been related to corresponding defining quantities of the standard AN*. The particular results are listed in Table 1 as a difference to the corresponding value of the standard sample (ΔT_{peg} , $\Delta T_{2\%}$, ... etc.). The standard sample of ammonium nitrate—pure for analysis—contained less than: 0.005% by mass of substances insoluble in water; 0.0001% by mass NO_2^- ; 0.001% by mass CNS^- ; 0.004% by mass SO_4^{2-} ; 0.0005% by mass Cl^- ; 0.0001% by mass Fe; 0.005% by mass Ca^{2+} ; 0.001% by mass Mg^{2+} ; 0.00005% by mass As; 0.0002% by mass of heavy metals and 0.5% by mass H_2O . The value of quantities characterizing the standard are: $T_{\text{peg}} = 218^\circ$, $T_{2\%} = 232^\circ$, $T_{5\%} = 243^\circ$, $V_{\text{ust}} = 1.26\% \cdot \text{h}^{-1}$, $V_{\text{max}} = 1.26\% \cdot \text{h}^{-1}$, pHWR (before heating) = 5.004, pHWR (after heating) = 3.82.

The presence of additives and admixtures influences the value of pHWR of the sample before and after heating. In many cases the value of pHWR of the sample after decomposition (pHWR_{aft}) differs from the value characterizing the standard and is defined as a parameter of the steady state of decomposition: pHWR < 3.9. In the Table 1 the results of V_{ust} measurements during which pHWR did not reach a value below 3.9 even not after 8 hours heating are marked by means of an asterisk.

* in Fig. 2 sample 0.

Table 1 Results of testing ammonium nitrate fertilizer samples, related to corresponding defining quantities of standard ammonium nitrate ($T_{peg} = 218$ °C, $T_{2\%} = 232$ °C, $T_{5\%} = 243$ °C, $V_{ust} = 1.26\% \cdot h^{-1}$, $V_{max} = 1.26\% \cdot h^{-1}$, $pHWR_{bef} = 5.04$, $pHWR_{aft} = 3.82$)

No. of sample	Results of DTA and TG, °C			Mass loss rate, % · h ⁻¹		Δ pHWR	
	ΔT_{peg}	$\Delta T_{2\%}$	$\Delta T_{5\%}$	ΔV_{ust}	ΔV_{max}	before	after
1	2	3	4	5	6	7	8
1	-13	-10	-12	1.01	1.01	0.62	-0.15
2	-5	-7	-8	1.55*	1.55	1.05	1.52
3	-41	-16	-5	-0.46*	4.14**	1.13	0.34
4	-32	-70	-16	-0.37*	19.14	2.49	1.28
5	-31	-16	-9	-0.46*	6.27**	0.50	0.83
6	-9	-4	-2	-0.40*	0.9	0.16	0.33
7	-15	-13	-9	-0.13	-0.13	-0.10	-0.32
8	-11	-5	-5	-0.01	-0.01	0.71	-0.48
9	-6	-3	-2	-0.15	-0.15	-0.8	-0.71
10	-4	-7	-6	-0.21	-0.01	0.33	-0.86
11	-13	-3	2	-0.52	0.21	-0.23	0.03
12	-5	-1	1	-0.36*	-0.36	0.31	0.36
13	-9	1	5	-0.41*	-0.41	-0.41	0.59
14	-5	1	2	-0.46	-0.46	0.50	0.01
15	-1	2	1	-0.27*	-0.27	1.41	0.38
16	0	-8	-13	-0.36	1.08**	1.10	0.04
17	0	-6	-2	0.04*	0.04	0.63	0.33
18	2	-2	-1	-0.08	-0.08	0.27	0.04
19	16	-20	-5	0.18*	2.74	2.40	1.22
20	21	-21	-20	0.94*	0.94	2.41	0.87
21	32	-23	-14	1.11*	2.38	2.46	0.58
22	22	-10	2	-0.30*	1.39**	2.47	0.49
23	26	-24	-5	-0.36*	2.26	2.40	1.28
24	38	-30	4	-0.49*	0.92**	1.54	1.63
25	42	3	18	-0.64*	0.22**	1.68	2.60

* pHWR value differs from that of the steady state.

** Short term increasing of the loss mass rate, did not last longer than 15 minutes.

In several examples (e.g. Fig. 2 sample 25), in the initial decomposition stage, a transitory maximum rate in the loss of mass is observed. They are marked in the Table 1 (section V_{max}) by means of two asterisks.

Discussion

The fertilizers under test revealed a great differentiation in properties. Their defining quantities varies in a great interval:

ΔT_{peg}	from -41	to +42;	T_{peg}	from 177	to 260°
$\Delta T_{2\%}$	-70	+ 3	$T_{2\%}$	162	235°
$\Delta T_{5\%}$	-20	+18;	$T_{5\%}$	223	261°
ΔV_{ust}	- 0.52	+ 1.01;	V_{ust}	0.74	2.27% by mass · h ⁻¹
ΔV_{max}	- 0.46	+ 19.41;	V_{max}	0.8	20.4% by mass · h ⁻¹

So, certain samples undergo exothermic decomposition under the testing conditions starting from 177°, whereas others do this above 260°. A definite degree of decomposition for some samples is obtained at the temperature 162 and 223°, for other samples at higher temperature 235 and 261°, respectively. Differences in the values of V_{ust} and V_{max} mean, that decomposition of samples may be accelerated or inhibited, compared with the standard AN.

Change in the value of defining quantities takes place in different variants. The simultaneous decrease of the values of T_{peg} , $T_{2\%}$, $T_{5\%}$ and the increase of V_{ust} and V_{max} for one and the same sample should be considered as the most unfavourable case pointing to increased liability of the fertilizer to self-heating. Such change of defining quantities indicates an increased participation of exothermic reactions in the process of AN decomposition and a gain in HG. An example for this variation are the data concerning samples 1 and 2 (Table 1, Figs 1 and 2).

Similar unfavourable properties are revealed by samples 3 to 6. The decomposition rate of these samples in the steady state is, indeed, smaller in comparison with the standard, but in the initial stage of decomposition the rate of mass loss reaches the maximum (Table 1, Figs 1 and 2, sample 4). V_{max} is even 16 times greater than the decomposition rate of the standard, and, simultaneously, by an increased participation of exothermic reactions at a lower temperature there is a marked decrease of T_{peg} by 32°.

Simultaneous increase of T_{peg} , $T_{2\%}$ and $T_{5\%}$ with the decrease of V_{ust} and V_{max} may be considered the most advantageous change of defining quantities. The increase of the value for T_{peg} and the decrease of decomposition rate points to a diminished participation of exothermic reactions as well as diminished rate of the exothermic reactions. In this case HG is lower. Following such considerations, the sample 25 exhibits the lowest degree of self-heating liability among all the other samples under test, even including the standard AN.

Beside the two extreme examples the majority of the samples is characterized by small or medium differences in the values of the defining quantities. It appears to be indispensable to designate a certain permissible deviation for these particular values. Assuming that the liability to self-heating of ammonium nitrate fertilizers should not be greater than that of standard ammonium nitrate, the permissible deviations of the value of defining quantities can be caused only in a range of analysis errors. Taking into account the extreme values of differences in the below mentioned defining quantities while testing ammonium nitrate pure for analysis [1], it was assumed if in a sample:

$\Delta T_{\text{peg}} < -6^\circ$	criterion I
$\Delta T_{2\%} < -6^\circ$	criterion II
$\Delta T_{5\%} < -10^\circ$	criterion III
$\Delta V_{\text{ust}} > 0.2\% \text{ by mass} \cdot \text{h}^{-1}$	criterion IV
$\Delta V_{\text{max}} > 0.2\% \text{ by mass} \cdot \text{h}^{-1}$	criterion V

then AN fertilizer under investigation reveals greater liability to self-heating than standard AN.

Estimating the ability to self-heating of the remaining fertilizer samples, not mentioned so far, requires a separate approach to each of them, and elucidation of the circumstances that cause surpassing of the permissible values of the criteria. The compliance with the criteria II and III ($T_{2\%}$, $T_{5\%}$) by correct values of T_{peg} , V_{ust} , V_{max} may be based e.g. on the presence of ammonium sulphate or limestone powder in the fertilizer. Decomposition of ammonium sulphate or the reaction between calcium carbonate and ammonium nitrate in the first stage of heating the sample containing these additives, may cause additional loss of mass, and influence the decrease of $T_{2\%}$ value or even $T_{5\%}$. However, the participation of exothermic reactions in decomposition has not changed as well as HG. As a result of these two reactions, ammonia is evolved which may, additionally, cause a delay in spontaneous exothermic decomposition of ammonium nitrate and results in a higher value of T_{peg} .

Conclusions

The test of various samples of ammonium nitrate fertilizer grade, supplied to the European fertilizer market, on liability to self-heating have revealed considerable differentiation of their properties. There are fertilizers which do not differ in their properties from the ones of pure ammonium nitrate. However, there are also

produced ammonium nitrate fertilizers of increased liability of self-heating, which favours accidental risks. Certain samples contain additives that decrease their ability to self-heating.

On the basis of the investigation performed it is possible to propose criteria for the evaluation of test results, which can help to find samples of ammonium nitrate fertilizers having a greater liability to self-heating than others.

References

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Zusammenfassung — Es werden einige Ergebnisse der Überprüfung der Neigung verschiedener Proben von Ammoniumnitrat (AN) Düngemittel zur Eigenerwärmung dargestellt. Die Angewendeten Testmethoden umfassen: DTA, TG, Masseverlustmessung bei konstanter Temperatur, pH-Messungen der wäßrigen Lösungen. Die Einschätzung der Neigung zur Eigenerwärmung basiert auf einem Vergleich mit relevanten Ergebnissen eines AN-Standardproduktes. Es wurden Kriterien für die Beurteilung der Testergebnisse und für die Einschätzung gefährlicher Bedingungen gegeben.

Резюме — Представлены результаты испытаний склонности к самонагреву образцов удобрения нитрата аммония. В качестве испытательных методов были использованы ДТА, ТГ, определения потери веса при постоянной температуре и pH-измерения водных растворов. Оценка способности к самонагреву проводилась путем сопоставления с соответствующими результатами для стандартного образца нитрата аммония. Предложены критерии оценки результатов испытаний и оценка условий опасности.