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Ammonium nitrate: thermal stability and explosivity modifiers

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Abstract

Two basic approaches to diminish the explosivity of AN have been suggested: dilution of ammonium nitrate (AN) with a chemically inert material or incorporation of small amounts of material which increases the chemical reaction zone [Method of Desensitizing AN and the Product Obtained, United States Patent Office, No. 3,366,468 (1968); Fertilizer additives: can AN be defanged? C&E News (1995) 6]. While small-scale tests of these "deterred" AN formulations appeared promising, larger amounts (30 pounds under confinement) were found to be detonable, though with reduced performance [Institute of Makers of Explosives Report, 1995]. In this study thermal analysis was used to screen a large number of AN formulations in search of possible deterrents. The sodium, potassium, ammonium and calcium salts of sulfate, phosphate, or carbonate as well as certain high-nitrogen organics (urea, oxalate, formate, guanidinum salts) were chosen because they should enhance AN thermal stability and because they could be used with agricultural products. This study considers whether laboratory tests can be used as benchmarks in evaluating explosivity. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Explosivity; Ammonium nitrate; Thermal stability; Decomposition

1. Introduction

The US Census Bureau data for 1998 showed the total ammonium nitrate (AN) melt production to be about 18.2 billion pounds. About 13.8 billion pounds were produced for fertilizer, about 5.2 billion pounds in solid form and 8.6 billion pounds in various solutions formulations [1–3]. Only, ~3.3 billion pounds were converted to solid products for use in ANFO (AN/fuel oil) and related blasting products; another 1 million pounds were used in emulsion and slurry formulations for blasting purposes [4,5]. Pure AN is considered to be highly stable and relatively safe. The Department of Transportation has classified it as an oxidizing agent for transport, storage and handling purposes [6]. Combined with fuel, AN is used in many explosive applications, and it is relatively safe in comparison with other compounds of equal effect [7,8]. Over the past century there have been many large accidents as well as terrorist bombings involving AN. Table 1 summarizes some of the AN accidents [9,10]. Terrorist use of AN began in the bombing campaign of the Provisional Irish Republican Army (PIRA) (1969–1994). During that period there were 14,000 bombing incidents, most involving commercial explosives or sodium chlorate/nitrobenzene (NB). At the peak of the campaign in the early 1970s, the British government issued a ban on the sale of chlorate, NB, and pure AN in Northern Ireland. (Similar restrictions were imposed in Ireland.) Nevertheless, large fertilizer bombs were used in the City of London. Approximately 1000 pounds were used at St. Mary le Axe (April 1992) and about 3000 pounds at Bishops Gate (April 1993) [11]. In other countries, AN has been used less frequently in terrorist bombings; a notable exception was the bombing of the Murrah Federal Building in Oklahoma City, 19 April 1995.

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Table 1
History of AN accidents[a]

Where	When	Amount AN	Unit	Material	Circumstance/damage	Mechanism	Speculation	Dead	Reference
Stolberg, Germany	12 April 1920	Waggon-load		Caked AN		Blast → explode	Blasting to break caked AN		[43]
Vergiati, Italy	26 November 1920	4.4E6+1.2E5	lb	AN + TNT in magazine	Destroyed all 1600 in.; windows broke 21 million	Blast → explode	First explosion in magazine of bombs, third reported here	0	[47]
Kriewald, Germany	26 July 1921	2 car-loads		Caked AN	60 in. × 20 in. crater	Blast → explode	Blasting to break caked AN	19	[43–46]
Oppau, Germany	21 May 1921	900000	lb	AN/AS 2/1	Buildings flatten to 3000 in.; 2000 injured	Blast → explode	AN/AS detonable or hiding explosives	561	[9,43,45,46]
Tessenderloo, Belgium	29 April 1942	150–200	T	AN pile	Plant destroyed, crater 164 in. × 36 in.	Blast → explode	Blasting caked AN; or tools ignited AN and CO_3/PO_4	200	[9,43,45–47]
Oakdale, PA	15 September 1916	3000	lb	AN IN preboil tank		Fire → explode	NA from TNT plant and possibly tar		[43,46]
Emporium, PA Hercules	7 November 1925	500	lb	AN with wax in water, heel in evaporation pan		Fire → explode			[43,46]
Gibbstown, NJ DuPont	26 October 1932			AN	High pan	Fire → explode			[43,46]
Texas City, TX	16–17 April 1947	2–5.5 K	T	Waxed prill	1000 injured; US$ 60 million damage, destroyed 5 million	Fire → explode	Wax coated prills on Grand Camp and highflyer	600	[9,43,45,47]
Pinole, CA Hercules	12 February 1953	2400–3600	lb	AN, $NaNO_3$, organic—mixed to start making dynamite		Fire → explode			[43,46]
Roseburg, OR	7 August 1959	4.5 + 2	T	AN car-prill + dynamite	125 injured, US$ 9 million; stored downtown	Fire → explode	Explosives involved	13	[9,45]
Traskwood, AR	17 December 1960	23 boxcars		1 car AN bag, 1 bulk, fertilizer solution, NA		Fire → explode	Petroleum and paper in cars—involved		[9,46]
Norton, VA Atlas	27 December 1961	20 + 35	T	AN + ANFO	Five injured	Fire → explode	Welding AN/FO transfer pipeline	0	[9,43,46,47]
Mt. Vernon, MO	9 November 1966	50	T	Bagged AN fertilizer	10 in. deep carter	Fire → explode			[43]
Prvor, OK Cherokee N Plant	17 January 1973	14000	T	High density AN in PE bags	Eight injured	Fire → explode	10% detonated destroying building	0	[43,47]
Barksdale, WI	April 1920	30000	lb			Fire no explosion			[43,44,46]
Brooklyn, NY	14 April 1920	2–5E6	lb	AN	Hold of SS Hallfried	Fire no explosion	Fire started in hold with chlorate and newsprint	0	[43,44,47]
Sinnnemahoning, PA	10 September 1922	4300	lb	AN	High pan	Fire no explosion			[43]
Cleveland	1922					Fire no explosion			[46]
Muscle Shoals, AL	4 April, 3 May, 1925	2 events		Boxcars with 220 flour barrels of AN		Fire no explosion	Same batch AN as in Hercules fire below		[43,44,46]
Gibbstown, NJ DuPont	April 1940	1.5, 6.5E5	lb	AN in paper sack and steel drums		Fire no explosion			[43,44,46]
St. Stephens, Canada	1 September 1947	400	T	AN fertilizer bagged		Fire no explosion	B said like Benson, AZ; DoD said fire in warehouse		[43,44,46,47]
Presque Isle, ME	26 August 1947	80000	lb	AN + superphosphate, K, meal, etc. fertilizers		Fire no explosion			[43,44,46]
Independence, KS	14 October 1949	1.4–2.7 K	T	FGAN (4% wax)	Piled in paper bags 15 ft high	Fire no explosion	2.5 in. separation vented, fire in next warehouse ignited AN		[43,44,46,47]
Mt. Braddock, PA Olin	16 January 1958	–		AN + $NaNO_3$	Fire in mixer in dope house	Fire no explosion		0	[47]
Boron, CA	10 May 1960	20	T	Prilled AN in 80 lb bags		Fire no explosion	Fire hot enough to collapsed steel roof		[43,44]
Peytona, WV	9 November 1966			Boxcar at dock with AN grade		Fire no explosion	Steel car hot enough to turn red		[43]
Potosi, WI	24 October 1967	50	T	100 lb bags	Steel boxcar of AN, wood lined	Fire no explosion	Fire in consumed wood lining left some AN		[43,44]
Bucharest, Romania	20 December 1974	33	lb	AN + wood powder	Two slight injuries	Fire no explosion	Fire in mixer of 15 kg wood powder + trace AN	0	[47]
Tahawas, NY IRECO	1 March 1976	100	lb	AN	No injuries, minor damage	Fire no explosion	Two explosions, cause: electrical or arson	0	[47]

Rocky Mountain, NC	1978	500	T	AN fertilizer		Fire no explosion	Storage facility destroyed by fire		[44]
Moreland, ID	1979	200	T	AN fertilizer		Fire no explosion			[44]
Boxcars	1946–1949	80–100 K	lb	13 railroad cars caught fire		Runaway → fire → no explosion	AN loaded hot 93 °C		[43,44,46]
Kensington, UK	2 March 1896	18	lb	AN for N_2O production		Thermal runaway → detonation	AN decomposed purposely; pressure rupture		[43,46]
Gibbstown, NJ DuPont	14 January 1916	400	lb	Molten AN, 160 °C	High pan	Thermal runaway → detonation	NA from TNT plant		[43,46]
NewBrunswick, NJ Nixon	1 March 1924	4800 + 35−50 K	lb	AN in grain kettle and 35–50 K warm AN at 0.3% paraffin		Thermal runaway → detonation	AN being recycled from Amatol 2% TNT and wax	7	[43,46,47]
Merano, Italy	1936					Thermal runaway → detonation			[46]
Milan, TN	2 March 1944	4800	lb	Molten AN, 154 °C	High pan; 17 injured; damage past 600 in.	Thermal runaway → detonation	Oil in air lines	4	[43,46,47]
Benson, AZ Apache	2 December 1944	8500	lb	AN 149 °C	High pan	Thermal runaway → detonation			[43]
Brest, France	28 July 1947	3.3–6 K	T	Waxed prill	250 injured; SS Ocean Liberty	Thermal runaway → detonation		21	[43,45,47]
Red Sea, Israel	23 January 1953	4–8 K	T	AN fertilizer–paper bag	Destroyed SS Tirrenia	Thermal runaway → detonation	Spontaneous ignition of paper bags		[43,47]
New Castle, PA	28 December 1956	5200	lb	AN	One injured, exposion in evaporator	Thermal runaway → detonation		0	[47]
Typpi, Oy, Finland	9 January 1963	8–10	T	Molten AN, 160 °C		Thermal runaway → detonation	Dodecyl benzene sulphonate added to prevent caking		[43]
Delaware City, DE	1977			83% AN solution for N_2O production		Thermal runaway → detonation	Heated to 518 °F (270 °C), production exceeded equipped		
Morgan, NJ	1918	9E+06	lb	AN	150 in. × 30 in. crater under AN pile	Fire → blast → detonation	Amatol loading, explosive detonated		[43,46]
Amboy, IL	7 April 1966	30000	lb	AN in truck next to bunker at 2000 lb TNT and 10000 lb AN		Blast no detonation	Explosion of bunker did not set off truck of AN		[43]
Joplin, MO	1989			AN production in Stengel Reactor			High temperature rx 450–500 °F		

[a] High pan is for evaporation water from AN before AN goes to graining kettles.

This event generated concern in the US regarding the explosive nature of AN. Because AN explosives are easily prepared and the Oklahoma City bombing was so devastating, a number of research programs aimed at desensitizing commercially available AN were developed.

AN melts at 169 °C and begins to decompose as soon as it melts, the first step being dissociation into ammonia and nitric acid Eq. (1). Studies have shown that the decomposition of AN operates by an ionic mechanism in the temperature range 200–300 °C and formation of nitronium ion is rate-determining [12,13]. Acidic species, such as ammonium ion, hydronium ion or nitric acid, increase the rate of AN decomposition dramatically, Eq. (2), while bases such as ammonia or water retard decomposition. Above 290 °C, a free-radical decomposition mechanism dominates and homolysis of nitric acid is the rate-controlling step [12,13].

$$NH_4NO_3 \Leftrightarrow NH_3 + HNO_3 \qquad (1)$$

$$HNO_3 + HA \overset{-A}{\Leftrightarrow} H_2ONO_2^+ \rightarrow NO_2^+ + H_2O,$$
$$\text{where } HA = NH_4^+, H_3O^+, HNO_3$$

$$NO_2^+ + NH_3 \overset{\text{slow}}{\rightarrow} [NH_3NO_2^+] \rightarrow N_2O + H_3O^+ \qquad (3)$$

$$NH_4NO_3 \Leftrightarrow N_2O + 2H_2O \qquad (4)$$

As a fertilizer and an explosive, AN is often mixed with a number of additives. A low temperature, ionic decomposition pathway for AN suggests acidic additives destabilize while basic additives stabilize thermal decomposition. This study sought to thermally stabilize AN using additives compatible with fertilizer use. Our hypothesis was that increased thermal stability could lead to reduced detonability. The basis for this premise is two-fold. First, a material which retards AN decomposition may increase the reaction zone of the composition to the point that a detonation cannot be propagated. Second, two AN formulations, which have been considered non-detonable, contain species that thermally stabilize AN. Experiments following the Oppau explosion strongly suggested that the 50/50 mixture of AN and ammonium sulfate was non-detonable. (The accident was explained as resulting from a pocket of concentrated AN [9].) To thwart PIRA, AN sold in Northern Ireland is sold as a mixture containing 21% dolomite (the double salt calcium/magnesium carbonate). This mixture has enhanced thermal stability. (Unfortunately, PIRA found a way to detonate this mixture, albeit with diminished performance [11].)

2. Experimental section

Relative thermal stabilities were determined by differential scanning calorimetry (DSC) with a TA Instruments DSC 2910, scanning from 50 to 500 °C, at a scan rate of 20 °C/min and using thin walled 1.47–1.50 mm o.d. glass capillary tubing [14]. Three replicates were run; the average temperature of the exotherm or endotherm maxima and the heat of reaction are given in tables. A shift from the position of the exothermic maximum of the mixture from that of neat AN (326 °C) to lower temperatures was interpreted as destabilization, while a shift to higher temperatures was considered indicative of stabilization. Considering experimental errors, only shifts of 10 °C or greater were generally considered significant. Additives were ground together with the AN; the amount added to AN was generally calculated in weight percent (wt.%) (where 5 wt.% is defined as 5 g additive in 100 g AN). Higher percentages of additives were also examined. In comparing additives, mole percent (mol%) was also used to ensure that differences in molecular weights of the additives did not influence observed trends. A translation between our definition of wt.% and mol% is shown in Table 2 along with the DSC characteristics of the neat additives.

Isothermal decompositions of AN and AN mixtures (0.5–1.0 mg) were conducted in 200 ul glass tubes (2.0–2.2 mm i.d.), which were flame sealed. After the samples were heated for given time intervals at 260 or 320 °C in molten metal baths, the glass tubes were broken and rinsed with water to quantitatively remove the contents. The contents were diluted to 10 ml for quantitative analyses of ammonium ion (NH_4^+) and nitrate ion (NO_3^-). The fraction of nitrate remaining was determined using a Hewlett-Packard (HP) 1084B liquid chromatograph (LC) equipped with a Dionex Ionpack AG4A guard column and AS4A analytical column. The mobile phase was 1.8 mM Na_2CO_3/1.7 mM $NaHCO_3$ at a flow rate of 1.5 ml/min. Detection was with a Waters 486 Tunable Absorbance Detector (214 nm). Injection volumes were 20 ul. The fraction of ammonium ion remaining was determined

Table 2
DSC peaks (maxima or minima) of neat additives and conversion of weight (wt.%) to mole (mol%)[a]

Sample	F.W.	Endotherms						Exotherms		wt.%		mol%	
		Peak 1	Endotherm	Peak 2	Endotherm	Peak 3	Endotherm	Peak 4	Exotherm				
		T_{min} (°C)	E (J/g)	T_{min} (°C)	E (J/g)	T_{min} (°C)	E (J/g)	T_{max} (°C)	E (J/g)	5	20	10	20
AN	80	128	51	168	68			326	1182				
$NaNO_3$	85	308	149							4.5	15.8	10.6	21.0
KNO_3	101	132	46	335	89					3.8	13.7	12.3	24.0
$Ca(NO_3)_2$	164									2.4	8.9	18.6	33.9
Na_2CO_3	106									3.6	13.1	12.8	24.9
$NaHCO_3$	84	200	683							4.5	16.0	10.4	20.8
K_2CO_3	138									2.8	10.4	16.1	30.1
$KHCO_3$	100	231	326	290	116					3.8	13.8	12.2	23.8
$CaCO_3$	100									3.8	13.8	12.2	23.8
$MgCO_3$	84	405	1025							4.5	16.0	10.4	20.8
$(NH_4)_2CO_3$	96	100	713							4.0	14.3	11.8	23.1
Na_2SO_4	142	257	73							2.7	10.1	16.5	30.7
$NaHSO_4$	120	180	116							3.2	11.8	14.3	27.3
K_2SO_4	174									2.2	8.4	19.5	35.2
$KHSO_4$	136	212	145							2.9	10.5	15.9	29.8
$(NH4)_2SO_4$	132	366	18							2.9	10.8	15.5	29.2
$(NH_4)HSO_4$	115	140	95							3.4	12.2	13.8	26.4
$CaSO_4$	136									2.9	10.5	15.9	29.8
Na_3PO_4	164									2.4	8.9	18.6	33.9
Na_2HPO_4	142	312	36	340	11	416	12			2.7	10.1	16.5	30.7
NaH_2PO_4	120	213	185	335	128					3.2	11.8	14.3	27.3
K_3PO_4	212									1.9	7.0	22.7	39.8
K_2HPO_4	174	314	27	369	66					2.2	8.4	19.5	35.2
KH_2PO_4	136	230	34	275	241					2.9	10.5	15.9	29.8
$CaHPO_4$	136									2.9	10.5	15.9	29.8
$(NH_4)_2HPO_4$	132	220	414							2.9	10.8	15.5	29.2
$(NH_4)H_2PO_4$	115	213	279							3.4	12.2	13.8	26.4
Urea	60	136	229	274	216	430	291			6.3	21.1	7.7	15.8
Guanidinum CO_3	181	242	911	349	76	401	73			2.2	8.1	20.1	36.1
Guanidine NO_3	122	215	192					390	805	3.2	11.6	14.5	27.6
HMTA	140							295	650	2.8	10.3	16.3	30.4
$NH_4CH_3CO_2$	77	120	167	211	119	366	194			4.9	17.2	9.7	19.4
KCH_3CO_2	98									3.9	14.0	12.0	23.4
NH_4CHO_2	63	122	238	200	136	321	707			6.0	20.3	8.0	16.4
$KCHO_2$	84	160	83							4.5	16.0	10.4	20.8
$(NH_4)_2C_2O_4$	124	130	13	247	682					3.1	11.4	14.7	27.9
$K_2C_2O_4$	184	168	117	392	103					2.1	8.0	20.4	36.5
Icing sugar		174	25					285	523				
Nitromethane	61							433	2889	6.2	20.8	7.8	16.0
Nitrobenzene	123							472	861	3.1	11.5	14.6	27.8
Sulfur		117	56										

[a] Carbon and diesel no peaks in DSC 50–500 °C.

using a ConstaMetric 3200 MS low pulsation solvent delivery system equipped with a Waters IC-Pak Cation M/D column and Waters 431 conductivity detector. A mobile phase consisting of 0.1 mM EDTA/3.0 mM HNO_3 and a flow rate of 1 ml/min was used. Injection volumes were 10 ul. If NO_3^- or NH_4^+ were present in the additive, that amount of the ion was assumed to be inert and subtracted from the fraction remaining before calculating the rate constant. Decomposition gases contained within in the reaction tubes at 260 and 320 °C were quantified by direct injection into a HP5890 gas chromatograph (GC) with thermal conductivity detection and a Heyesep DB 100/120 column (9.1 m×32 mm).

3. Results

3.1. Differential scanning calorimetry studies

Neat AN scanned at 20 °C/min from 50 to 450 °C exhibited two endotherms and one exotherm followed by a final endotherm (Fig. 1). The first endotherm (~125 °C) is the result of the II to I phase change and the second at about 169 °C is the melting point of AN [15]. The endotherm, following the exotherm, has been previously examined in our lab and found to be the vaporization of water formed during AN decomposition [13]. The observed exotherm was about 100 °C wide and had an exothermic maximum of 326 °C. The various additives had either no effect on the observed AN endotherms or depressed the AN melting point, in some cases, to where it merged with the II to I phase change endotherm. The more additive mixed with AN, the more the melting point of AN was depressed, which was in keeping with colligative properties. Of principal interest was the effect of various additives on the position of the AN exotherm.

Most of the anions were available as the Na^+, K^+, NH_4^+, or Ca^{2+} salts. Among the halide salts, the positions of the DSC exothermic maxima were nearly the same for all four Cl^- salts, varying by only about 6 °C (Table 3). We chose the K^+ salt for most of our studies since potassium is often used for agricultural products. With the exception of fluoride, the halides had a destabilizing effect on the thermal stability of AN. Chloride lowered the exothermic maximum the most (about 70 °C). Added nitrate had no significant effect on the temperatures of the exothermic maxima, compared to neat AN; nor was there any appreciable difference observed when the cation was varied from Na^+ to K^+ to Ca^{2+} (Table 4). Table 5 summarizes DSC exotherms for other oxide salts mixed with AN. Most of the inorganic additives (sulfates, carbonates or

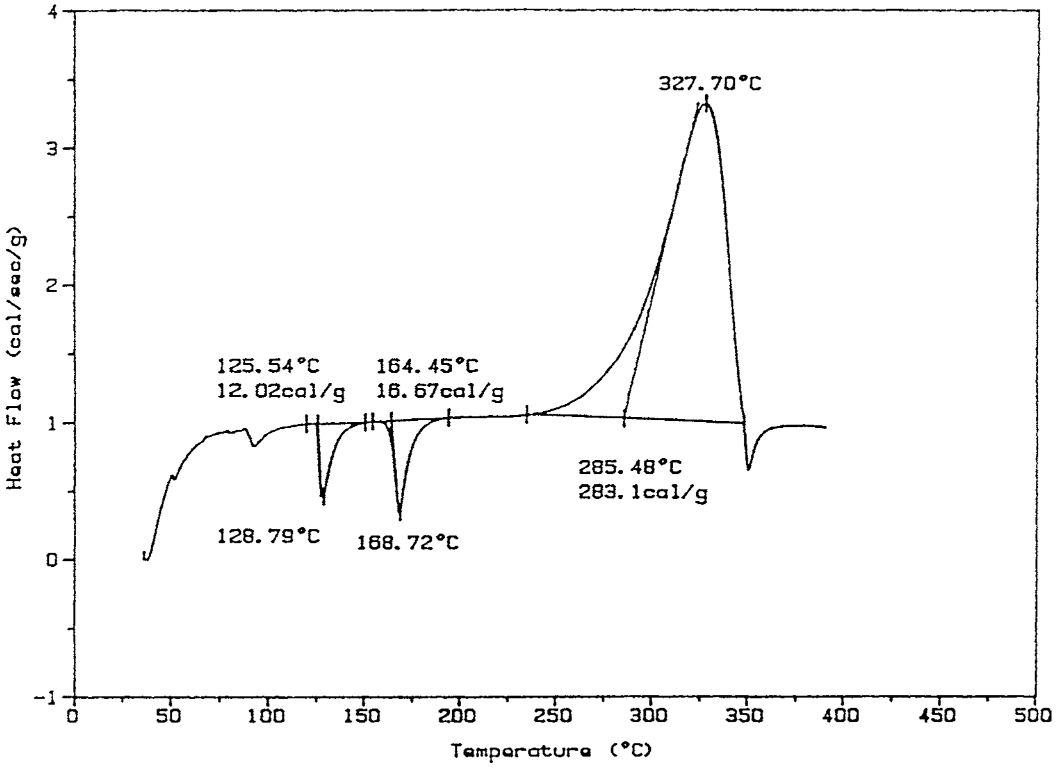

Fig. 1. DSC thermogram of neat AN.

Table 3
Effect of halide salts on AN, DSC exotherm maximum (20°/min)[a]

wt.%	NaCl	KCl	NH_4Cl	$CaCl_2$	KF	KCl	KBr	KI
5	262	256	257	261	348	256	319	319
10	263	254	256	262				
20	264	256	256	266	381			

[a] Neat AN exothermic maximum: 326 °C.

Table 4
Effect of nitrate salts on AN, DSC exotherm maximum (20°/min)

	5 wt.%	20 wt.%
AN		326
$NaNO_3$	328	328
KNO_3	326	323
$CaNO_3$	330	328

phosphates) raised the decomposition exotherm of AN. The exception was bisulfate. All the organic compounds examined raised the temperature of the AN exotherm. In addition, they lowered the melting point of AN so that the sharp AN phase transition at 129 °C and its melt at 169 °C became a single, broad, poorly defined endotherm. For guanidinum carbonate, the endotherm began as low as 83 °C (Table 6).

3.1.1. Isothermal kinetics studies

Because DSC is a temperature scan technique, it is difficult to ascribe the observed relative thermal stability to a specific temperature range. For this reason, the rate constants of AN with a number of select additives were determined from the slope of first-order plots of isothermal thermolyses at 320 and 260 °C. For the additives that contained additional nitrate or ammonium ions, the contribution of the additive was subtracted so that the relative loss of that ion did not appear disproportionately slow. The plots exhibited varying degrees of linearity, depending on the additive. Only the initial linear section of the curve was used to determine the slope. Tables 7 and 8 show the linearity of fit (R^2), the number of data points (out of eight data points) and percent of decomposition for the portion of the plot used to calculate the indicated rate constant. Only neat AN and AN with $CaSO_4$ demonstrated linear first-order plots to greater than 50% decomposition at both temperatures examined.

3.1.2. In situ AN

While it is clear that some of the additives chosen for this study impart thermal stability to AN, it is not clear that they will make it less detonable. A more radical approach to reducing AN detonability might be to use a formulation consisting of two compounds, one containing the ammonium cation and the other the nitrate anion (e.g. $AX + EN$ or $A_2Y + GN_2$). These examples would be equivalent to a 50/50 mixture AN with EX or a 2/1 mixture of AN with GY, respectively. For fertilizer purposes it should make no difference, but we speculate that detonability would be greatly decreased by the less intimate contact between oxidizer and fuel. The first step to confirming this hypothesis was to determine thermal stabilities. Eight formulations were examined and compared to the equivalent AN formulation (Table 9). Addition of about 33 mol% $CaCO_3$ substantially stabilized AN (increase in exothermic maximum is greater than 100 °C). Using the in situ approach of generating this formulation (A: ammonium carbonate/calcium nitrate) appeared to provide no further stability (i.e. the exotherm of AN/$CaCO_3$ was 433 °C while that of the in situ mixture A was 440 °C). Likewise, the addition of 50% sodium or potassium hydrogen carbonate or potassium acetate or formate so stabilized AN that additional stability was not evidenced in the in situ formulations (D–G). The addition of 33 mol% potassium oxalate so greatly enhanced AN thermal stability that no peak was observed at the limit of the DSC scan (500 °C) in the mixture or in the in situ formulation (H). The cases where the in situ approach appeared to be successful were with additives that did not dramatically improve AN thermal stability. Addition of $CaSO_4$ to AN had almost no stabilizing effect, while, the in situ formulation, ammonium sulfate and calcium nitrate (B) provided a significant stabilizing effect. Similarly, when diammonium phosphate and calcium nitrate (C: exothermic maxima 373 °C) were mixed, there was a greater stabilizing effect than when 33 mol% calcium phosphate was added directly to AN (exothermic maxima 341 °C). To simulate the effect of rain, three of the formulations (A, B, C) were dissolved in water, mixed, and thoroughly dried. For formulation A, when the mixture had been wetted then dried, most of the enhanced stability was lost, presumably through decomposition of the ammonium carbonate. However, the exothermic maxima of formulations B and C were essentially unchanged by moisture.

Table 5
Effect of oxide salts on the DSC exotherm (20°/min) of AN (neat = 326 °C)

	E_2CO_3				$EHCO_3$				E_2SO_4				$EHSO_4$				E_3PO_4				E_2HPO_4				EH_2PO_4			
	5 wt.%	mol%	20wt.%	mol%	5wt.%	mol%	20wt.%	mol%	5wt.%	mol%	20wt.%	mol%	5wt.%	mol%	20wt.%	mol%	5wt.%	mol%	20wt.%	mol%	5wt.%	mol%	20wt.%	mol%	5wt.%	mol%	20wt.%	mol%
Na	354	3.6	381	13	348	4.5	378	16	333	2.7	349	10	331	3.2	329	12	329	2.4	345	9	338	2.7	366	10	328	3.2	339	12
K	351	2.8	374	10	345	3.8	372	14	332	2.2	343	8	332	2.9	328	11	339	1.9	362	7	339	2.2	364	8	337	2.9	348	11
NH_4	349	4.0	374	14					337	2.9	348	11	331	3.4	322	12					340	2.9	364	11	336	3.4	347	12
Ca	360	3.8	389						333	2.9	334	11									336	2.9	337	11				
Mg			378	10																								
pH	7.4–8.5				7.3–7.4				4.8–5.6				1.7–1.8				8.2–8.3				6.4–7.4				4.2–4.3			

Table 6
AN exotherm in the presence of selected organic species

Sample name	Exotherm T_{max} (°C)	Heat released		
		E (cal/g)	E (J/g)	pH
Neat AN	326	283	1182	4.9
AN + 5% urea	370	350	1465	
AN + 10% urea	384	368	1539	
AN + 20% urea	394	395	1653	5.0
AN + 30% urea	402	415	1738	
AN + 20% NH_4 acetate	372	368	1541	6.3
AN + 10 mol% hexamethylenetetramine	377	675	2824	6.5
AN + 10 mol% K acetate	357	243	1016	6.3
AN + 20 wt.% NH_4 formate	384	332	1389	5.9
AN + 10 mol% K formate	368	245	1026	5.9
AN + 20 wt.% NH_4 oxalate	385	362	1513	5.9
AN + 10 mol% K oxalate	383	308	1287	6.4
AN + 10 mol% guanidine NO_3	341	355	1486	4.8
AN + 10 mol% guanidine CO_3	408	358	1496	8.2

3.1.3. Decomposition gases

Table 10 shows the gaseous decomposition products of AN and its various formulations. For neat AN and most of its mixtures about 1.0 mol of gas were produced/mol of AN, and the principal decomposition gas was N_2O

$$NH_4NO_3 \rightarrow N_2O + 2H_2O \tag{5}$$

Table 7
Rate constant (s^{-1}) of AN formulation at 320 °C

Additive	10^3 k/s[a] (NO_3^-)	R^2	Data	Up to % dec.	10^3 k/s (NH_4^+)	R^2	Data	Up to % dec.	Amount	Exothermic T (°C)
AN	10.9	1	6	67	13.2	1	7	80	Pure	327
AN + $NaNO_3$	9.42	0.99	4	34	11.2	1	4	39	10 mol%	328
AN + KNO_3	9.28	0.99	4	42					10 mol%	323
AN + $Ca(NO_3)_2$	8.88	1	4	55	11.8	0.99	4	65	20 wt.%	328
AN + Na_2CO_3	4.23	1	5	29	5.29	0.95	5	35	10 mol%	381
AN + $CaCO_3$	2.10	1	6	40	2.10	0.97	6	53	20 wt.%	389
AN + $KHCO_3$	9.41	1	4	43	9.30	0.99	5	53	10 mol%	372
AN + K_2CO_3	6.68	0.99	4	33					10 mol%	374
AN + Na_2SO_4	19.6	1	3	44	21.3	1	3	47	20 wt.%	349
AN + $(NH_4)_2SO_4$	30.1	1	5	74	23.6	0.99	4	51	20 wt.%	348
AN + $CaSO_4$	19.3	1	4	58	22.4	1	4	64	20 wt.%	334
AN + NaH_2PO_4	22.9	0.99	3	37	21.4	0.94	4	49	10 mol%	339
AN + KH_2PO_4	21.9	1	3	35					10 mol%	348
AN + Na_2HPO_4	14.4	0.99	4	47	14.4	1	4	47	10 mol%	366
AN + K_2HPO_4	11.4	0.98	4	40					10 mol%	364
AN + $(NH_4)_2HPO_4$	27.4	1	4	55	21.6	0.99	4	48	10 mol%	364
AN + $CaHPO_4$	28.6	1	5	57	34.1	1	6	74	10 mol%	337
AN + K_3PO_4	13.8	0.99	4	34	13.5	0.97	4	34	10 mol%	362
AN + urea	8.53	1	7	92	4.08	0.99	7	70	20 wt.%	394
AN + guanidinum CO_3	11.2	1	4	48					10 mol%	408
AN + NH_4CHO_2	7.03	1	8	63					20 wt.%	384
AN + $(NH_4)_2C_2O_4$	6.74	0.99	8	60					20 wt.%	385
AN + HMTA	22.3	0.99	13	72					10 mol%	377

[a] k/s is rate constant k in units of 1/seconds.

Table 8
Rate constant (s^{-1}) of AN formulation at 260 °C

Additive	10^4 k/s (NO_3^-)	R^2	Data	Up to % dec.	10^4 k/s (NH_4^+)	R^2	Data	Up to % dec.	Amount	Exothermic T (°C)
AN	1.95	0.997	8	56	2.20	0.984	8	59	Pure	327
AN + $NaNO_3$	1.79	0.99	3	20	1.89	0.99	4	29	10 mol%	328
AN + KNO_3	1.72	1	6	66					10 mol%	323
AN + $Ca(NO_3)_2$	2.75	0.99	4	39	2.57	0.99	4	36	20 wt.%	328
AN + Na_2CO_3	1.26	1	3	34	1.70	1	3	46	10 mol%	381
AN + $CaCO_3$	0.067	0.93	4	9	0.09	0.800	6	18	20 wt.%	389
AN + $KHCO_3$	2.00	0.98	4	51	2.01	0.960	4	52	10 mol%	372
AN + K_2CO_3	1.18	0.99	5	49					10 mol%	374
AN + Na_2SO_4	1.17	0.98	4	35	1.42	0.993	4	40	20 wt.%	349
AN + $(NH_4)_2SO_4$	1.97	0.99	5	38	1.79	0.967	4	28	20 wt.%	348
AN + $CaSO_4$	2.27	0.996	8	62	2.33	0.989	8	64	20 wt.%	334
AN + NaH_2PO_4	2.02	1	4	31	2.24	0.994	4	34	10 mol%	339
AN + KH_2PO_4	1.57	0.95	6	40					10 mol%	348
AN + Na_2HPO_4	1.05	0.95	4	18	1.01	0.9	4	18	10 mol%	366
AN + K_2HPO_4	0.56	0.98	5	34					10 mol%	364
AN + $(NH_4)_2HPO_4$	1.29	0.98	4	38	1.14	1	4	34	10 mol%	364
AN + $CaHPO_4$	2.80	0.97	4	40	3.06	0.97	5	50	10 mol%	337
AN + K_3PO_4	1.17	0.99	3	25	1.16	1	3	25	10 mol%	362
AN + urea	0.34	0.97	3	12	0.16	1	3	6	10 mol%	394
AN + guanidinum CO_3	1.57	0.98	5	53					10 mol%	408
AN + NH_4CHO_2	0.38	1	3	13					20 wt.%	384
AN + $(NH_4)_2C_2O_4$	0.12	0.96	6	21					20 wt.%	385
AN + HMTA	0.31	0.97	7	43					10 mol%	377

Table 9
Exothermic maxima of mixtures of AN and in situ formulations

	In situ mixture AN → additive	Nitrogen (wt.%)
A	$\underset{440\,^{\circ}\mathrm{C}\,(979\,\mathrm{J/g}),\,364\,^{\circ}\mathrm{C}\,(929\,\mathrm{J/g})}{(NH_4)_2CO_3 + Ca(NO_3)_2} \rightarrow \underset{433\,^{\circ}\mathrm{C}\,(397\,\mathrm{J/g})}{2NH_4NO_3 + CaCO_3}$[a]	21.7
B	$\underset{355\,^{\circ}\mathrm{C}\,(561\,\mathrm{J/g}),\,356\,^{\circ}\mathrm{C}\,(494\,\mathrm{J/g})}{(NH_4)_2SO_4 + Ca(NO_3)_2} \rightarrow \underset{333\,^{\circ}\mathrm{C}\,(669\,\mathrm{J/g})}{2NH_4NO_3 + CaSO_4}$[a]	19.0
C	$\underset{373\,^{\circ}\mathrm{C}\,(665\,\mathrm{J/g}),\,361\,^{\circ}\mathrm{C}\,(573\,\mathrm{J/g})}{(NH_4)_2HPO_4 + Ca(NO_3)_2} \rightarrow \underset{341\,^{\circ}\mathrm{C}\,(682\,\mathrm{J/g})}{2NH_4NO_3 + CaHPO_4}$[a]	19.0
D	$\underset{>500\,^{\circ}\mathrm{C}}{(NH_4)HCO_3 + NaNO_3} \rightarrow \underset{>500\,^{\circ}\mathrm{C}}{NH_4NO_3 + NaHCO_3}$	17.1
E	$\underset{>500\,^{\circ}\mathrm{C}}{(NH_4)HCO_3 + KNO_3} \rightarrow \underset{>500\,^{\circ}\mathrm{C}}{NH_4NO_3 + KHCO_3}$	15.6
F	$\underset{409,\,465\,^{\circ}\mathrm{C}\,(1400\,\mathrm{J/g})}{(NH_4)CH_3CO_2 + KNO_3} \rightarrow \underset{416,\,471\,^{\circ}\mathrm{C}\,(1600\,\mathrm{J/g})}{NH_4NO_3 + KCH_3CO_2}$	15.7
G	$\underset{326\,^{\circ}\mathrm{C}\,(79\,\mathrm{J/g})}{(NH_4)CHO_2 + KNO_3} \rightarrow \underset{337,\,409\,^{\circ}\mathrm{C}\,(310\,\mathrm{J/g})}{NH_4NO_3 + KCHO_2}$	17.1
H	$\underset{\text{No exotherm}}{(NH_4)_2C_2O_4 + KNO_3} \rightarrow \underset{>500\,^{\circ}\mathrm{C}}{2NH_4NO_3 + K_2C_2O_4}$	17.3

[a] Sample was evaporated from aqueous solution.

Table 10
Decomposition gas of neat AN and AN with additives

AN with 10 mol% additive indicates 20 wt.%[a]	Time (h) at 320 °C	Gas product mol/mol AN					Gas ratio (N_2O/N_2)	Time (h) at 260 °C	Gas product mol/mol AN					Gas ratio (N_2O/N_2)
		N_2	CO_2	CO	N_2O	Total			N_2	CO_2	CO	N_2O	Total	
AN	1	0.19			0.78	0.97	4.1	93	0.26			0.60	0.86	2.3
AN + $NaNO_3$	5	0.14			0.87	1.01	6.1	93	0.22			0.60	0.82	2.8
AN + KNO_3	18	0.21			0.71	0.91	3.4	93	0.25			0.59	0.84	2.4
AN + $Ca(NO_3)_2$[a]	24	0.17			0.85	1.02	4.9	93	0.29			0.66	0.95	2.3
AN + Na_2CO_3	18.7	0.32	0.10		0.62	1.03	1.9	72	0.36	0.00		0.48	0.84	1.3
AN + $CaCO_3$[a]	24	0.50	0.10		0.40	1.01	0.8	417	0.60	0.12		0.35	1.07	0.59
AN + $MgCO_3$	20	0.33	0.07		0.63	1.04	1.9	0						
AN + $KHCO_3$	24	0.22	0.02		0.70	0.93	3.3	72	0.24	0.01		0.58	0.83	2.4
AN + K_2CO_3	43	0.26	0.05		0.62	0.93	2.4	72	0.26	0.01		0.62	0.89	2.3
AN + Na_2SO_4	1	0.22			0.74	0.96	3.4	72	0.38			0.56	0.94	1.5
AN + $(NH_4)_2SO_4$	24	0.26			0.79	1.05	3.1	68	0.37			0.55	0.91	1.5
AN + $CaSO_4$	1	0.23			0.77	0.99	3.4	93	0.41			0.54	0.95	1.3
AN + NaH_2PO_4	16	0.18			0.81	0.99	4.5	93	0.29			0.51	0.81	1.8
AN + KH_2PO_4	43	0.27			0.67	0.94	2.5	72	0.30			0.51	0.81	1.7
AN + Na_2HPO_4	4	0.28			0.66	0.93	2.4	89	0.43			0.45	0.88	1.1
AN + K_2HPO_4	18	0.27			0.71	0.98	2.7	235	0.43			0.43	0.86	1.0
AN + $(NH_4)_2HPO_4$	16	0.23			0.84	1.07	3.7	68	0.45			0.51	0.96	1.1
AN + $CaHPO_4$	16	0.16			0.83	0.99	5.2	93	0.28			0.57	0.85	2.0
AN + K_3PO_4	2	0.28			0.64	0.93	2.3	68	0.37			0.44	0.81	1.2
AN + urea[a]	24	0.93	0.20		0.25	1.38	0.3	235	0.63	0.06		0.39	1.08	0.61
AN + guanidinum CO_3	24	0.53	0.17		0.78	1.48	1.5	72	0.62	0.17		0.59	1.37	0.95
AN + HMTA	24	0.81	0.28	0.14	0.25	1.48	0.3	93	0.72	0.18	0.09	0.07	1.05	0.10
AN + $K_2C_2O_4$	20	0.60	0.30	0.01	0.41	1.32	0.7	0						
AN + NH_4CHO_2[a]	24	0.54	0.16	0.03	0.52	1.24	1.0	235	0.50	0.26		0.30	1.06	0.60
AN + $(NH_4)_2C_2O_4$[a]	24	0.59	0.21	0.03	0.61	1.43	1.0	72	0.52	0.24		0.34	1.10	0.66

[a] Most additives present at 10 mol%, but at 320 °C. Additives are at 20 wt.% and at 260 °C formate and oxalate are 20 wt.%.

At 320 °C, 0.97 mol gas were produced/mol neat AN; at 260 °C, neat AN produced slightly less gas (0.86 mol/mol). When inorganic species were added the total gas did not vary by more than 10% from the amount produced by neat AN. The nitrogen-containing organic species significantly contributed to the amount of gas produced. The moles of gas/mol AN increased as much as 50% with some of these additives present. Except when calcium carbonate or one of the high-nitrogen organics was added to AN, the primary decomposition gas was nitrous oxide (N_2O) with some nitrogen (N_2), the ratio being sensitive to the temperature of decomposition. At 320 °C, the final ratio N_2O/N_2 was 4.1 for neat AN, while at 260 °C it was 2.3. This trend was followed in most of the AN mixtures. At 320 °C the N_2O/N_2 ratio ranged from 2 to 6, while at 260 °C the range was 1–3 (Table 10). The exceptions were the formulations where AN was mixed with 20 wt.% calcium carbonate or some of the high-nitrogen organics; these produced more nitrogen gas than AN. At 320 °C, gases were sampled at various stages during the decomposition. The data indicate that nitrous oxide is the first and main gas produced by AN, and nitrogen is primarily formed later in the decomposition. This was particularly true of the high-nitrogen compounds, urea, guanidinum carbonate and hexamethylenetetramine (HMTA). At roughly 30% decomposition, the N_2O/N_2 ratio is three to four times higher than it is at complete reaction, presumably because at long reaction times these nitrogen-containing additives begin to decompose and contribute nitrogen gas.

3.1.4. Effect of fuels on AN

Although AN can act as its own oxidizer and fuel, for practical explosive use it is mixed with added fuel. Historically, a variety have been used. Carbon black was the first fuel to be used with AN; later liquid hydrocarbons were employed [4]. To examine the effect of various fuels on AN thermal stability, AN and potassium nitrate (KNO_3) were mixed with various fuels and screened by DSC (Table 11). In addition, DSC traces were obtained for AN with varying amounts of fuel: diesel, mineral oil (MO), and sugar (powdered or icing sugar) were examined (Table 12). As the diesel fuel was increased from 2 to 10 wt.% (10 to 36 mol% CH_2) and the sugar was increased from 5 to 20 wt.% (12 to 35 mol% OCH_2), the total energy released increased from 1184 J/g (neat AN) to more than 3138 J/g. With mineral oil a similar increase in heat released was observed up to the addition of 15 wt.% (46 mol% CH_2) mineral oil. However, at 30 wt.% (63 mol% based on CH_2) mineral oil, a substantially fuel-rich formulation, the heat released begins to decrease. As previously observed, addition of liquid hydrocarbon split the DSC

Table 11
DSC exotherms for ammonium and potassium nitrates with fuels[a]

5 wt.% additive	First exotherm			Second exotherm			Total (cal/g)	Total (J/g)
	°C	cal/g	J/g	°C	cal/g	J/g		
Pure AN	326						283	1184
Pure AN + carbon	211	303	1268	334	131	548	434	1816
Pure AN + mineral oil	268	221	925	358	364	1523	585	2448
Pure AN + diesel	284			344			483	2021
Pure AN + sugar	185	112	469	343	253	1059	365	1527
Pure AN + sulfur	248			301			528	2209
Pure AN + nitrobenzene	334	285	1192				285	1192
Pure AN + nitromethane	331	228	954				228	954
Pure AN + aluminum	332	184	770				184	770
Pure KN+								
Carbon				460	75	314		
Mineral oil	221	6	25					
Sulfur	331	47	197					
KN + 15% C + 10% S	315	205	858	407	168	703	528	2209

[a] No exotherms were observed for diesel nor aluminum alone.

Table 12
DSC peaks for AN with various amounts of fuels[a]

Sample name	Endotherms																		
	Peak 1		Endotherm		Peak 2		Endotherm		Peak 3		Exotherm		Peak 4		Exotherm		No.	Total (J/g)	% first exotherms
	T_{min} (°C)	Standard	E (J/g)	Standard	T_{min} (°C)	Standard	E (J/g)	Standard	T_{max} (°C)	Standard	E (J/g)	Standard	T_{max} (°C)	Standard	E (J/g)	Standard			
Neat AN	128	0	51	0	168	1	68	0	326	1	1182	149					3	1182	
AN + 2% diesel	129	1	53	0	169	0	73	4	331	1	1187	59					3	1187	
AN + 4% diesel	129	0	54	0	169	1	73	0	330	1	1541	64					3	1541	
AN + 5% diesel	129	0	49	0	170	0	62	4	284	10	900	25	344	2	1121	84	3	2020	45
AN + 6% diesel	128	0	52	0	169	1	68	0	294	0	996	0	341	0	1188	0	3	2191	45
AN + 8% diesel	128	0	50	4	168	0	66	4	296	1	1464	209	348	4	1284	75	3	2750	53
AN + 10% diesel	129	0	51	0	169	0	70	4	291	0	1699	121	358	1	1510	33	2	3210	53
Sugar	174	6	112	17					285	0	525	27					2	525	
AN + 5% sugar	128	0	35	0	157	0	30	0	185	0	468	29	343	1	1057	27	3	1525	31
AN + 7% sugar	130	0	36	0	155	0	20	0	183	1	711	16	345	0	1135	72	3	1846	39
AN + 8% sugar	129	0	32	0	153	0	20	0	183	0	802	27	348	1	1257	72	3	2059	39
AN + 15% sugar	130	0	66	8					186	1	1340	50	364	0	1486	19	3	2827	47
AN + 20% sugar	129	1	51	4					185	1	1660	46	364	1	1486	38	3	3146	53
AN + 5% MO	129	0	48	4	169	0	61	4	268	1	924	83	358	1	1521	63	3	2445	38
AN + 15% MO	129	0	46	0	169	0	57	4	292	7	898	92	363	2	1877	99	3	2774	32
AN + 30% MO	129	0	38	0	169	1	55	4	308	12	955	50	375	3	1509	94	3	2464	39

[a] Mineral oil and diesel showed no peaks in DSC between 50 and 500 °C.

exotherm into at least two peaks, one reaching maximum at higher and one at lower temperatures than neat AN [13].

4. Discussion

4.1. Thermal stability

With the exception of fluoride, the halides had a destabilizing effect on the thermal stability of AN. Chloride lowered the exothermic maximum the most (about 70 °C). The destabilizing effect of chloride is well known [16–31]. Nevertheless, chloride is sometimes added to fertilizer formulations and to permissible AN explosives. Many researchers have noted the synergism between HNO_3 and Cl^- [18,19,23–25], and several claimed acid is essential for chloride catalysis, but the acid may come from the decomposition of AN, itself [26,27]. The catalytic activity of chloride is generally acknowledged to require an induction period, which acidity obviates or alkalinity lengthens indefinitely (presumably by suppressing AN decomposition) [23,24]. The presence of chloride is thought to generate acidity, and many have observed the increase in nitrogen rather than nitrous oxide decomposition gas formation [16,17,20,21,27]. There appears to be no general agreement on the exact mechanism by which chloride causes destabilization. Keenan and coworkers suggested the key step to the destabilization is

$$NO_2^+ + Cl^- \rightarrow NO_2 + Cl^+ \qquad (6)$$

They noted that there must be an initial excess of acid to allow formation of nitronium ion [22]. We have observed that the relative destabilizing effect of the halide, X^-, is in line with the acidity of HX. The pK_a values of HCl, HBr and HI are −7.0, −9.5, and −10.0, respectively [28]. The fluoride ion is a much stronger base than the other halides (pK_a of HF is 3.2) [28] which probably explains its stabilizing influence on AN.

Most of the oxo-anions, with the exception of bisulfate, raised the temperature of the AN exotherm (Table 5). These observations are in line with AN thermal stability being affected by the acidity of the additive [18,19,29–31]. The anions SO_4^{2-}, PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^-$, CO_3^{2-}, and HCO_3^- are conjugate bases of weak acids and, as such, they are somewhat basic. A mode of action for these anions is as follows:

$$NH_4^+ + A^- \rightarrow NH_3 + HA\ (A = \text{any anion}) \qquad (7)$$

The carbonate anion is especially basic and in the presence of acid forms carbonic acid, which is unstable and decomposes to water and carbon dioxide gas. In contrast, HSO_4^- which is formed from the dissociation of a strong acid (sulfuric acid) is a weak base. Rubtsov et al. [18,19] also observed that salts that possessed anions more basic than nitrate caused a marked reduction in the decomposition rate. Included in Table 5 are pH values of solutions consisting of 5 ml of water and 0.100 g of specified AN formulations (i.e. 20 wt.% additive). Solutions containing the most basic anions (CO_3^{2-}, HCO_3^- and HPO_4^-) yielded pH values in the range 7.4–8.3. These species, when added to AN at the 20 wt.% level, produced exothermic maxima 40–60 °C higher than neat AN. Those additives producing pH values in the range 4–5 (SO_4^{2-} and $H_2PO_4^-$) only raised the maximum by 10–20 °C when included with AN at the 20 wt.% level (Table 5). The bisulfates (HSO_4^{2-}) produced strongly acidic aqueous solutions. Although they did not lower the temperature of the AN exotherm when added at the 5 wt.% level, at the 20 wt.% level they did. The trivalent phosphate anion, PO_4^{3-}, though basic is not stable; and gas evolution was observed when its sodium salt was mixed with AN and an odor was detected when high concentrations of the potassium salt were added to AN.

Most of the anion additives were examined in the presence of several different counter ions. Varying the cation (Na^+, K^+, NH_4^+, and Ca^{2+}) did not greatly affect the position of the exotherm nor the rate constant. However, it has been noted previously that ammonium ion is not entirely innocuous, being the salt of a weak base [13], and some anomalies were observed with the calcium salts. With most of the additives, if the AN exotherm was shifted by 5 wt.% additive, the effect was magnified when 20 wt.% additive was used. However, this was not the case with $CaSO_4$ and $CaHPO_4$. At 5 wt.% these calcium salts increased the AN exotherm to about the same degree as the other sulfates or hydrogen phosphates; but addition of 20 wt.% showed no further increase (Table 13). We interpreted this result to mean these salts do not have a stabilizing effect on AN. The

Table 13
Effect of calcium salts on the DSC exothermic maximum of AN

Additives to AN	$CaNO_3$	$CaCO_3$	$CaSO_4$	$CaHPO_4$	AN neat
DSC 5 wt.% additive (°C)	330	360	333	336	326
DSC 20 wt.% additive (°C)	328	389	334	337	
Rate constants (260 °C) 10^6 k/s	294	2.8	227	220	195
Rate constants (320 °C) 10^3 k/s	11.5	1.59	15.0	22.5	10.9

isothermal rate constants at 260 °C confirm this (Table 13). It may be that the slight stabilizing effect of the oxo-anion is overcome by a destabilizing effect from the cation. Calcium being a small cation with high charge density may possess a measure of acidity, such as we have previously described for metals with high charge-to-radius ratios [32]. Such acidity would be deleterious to the thermal stability of AN.

$$Ca^{2+} + 2H_2O \rightarrow Ca(OH)_2 + 2H^+ \quad (8)$$

However, with this interpretation the high thermal stability imparted to AN by calcium carbonate is difficult to explain. It is possible that the acidic nature of the calcium cation is counteracted by the extremely basic nature of the carbonate anion.

The oxalate, formate, and acetate salts, added to AN at the 10 mol% level, substantially raised the pH (5.9–6.3 pH units) and the temperature of the DSC exotherm. Unfortunately, both the ammonium and potassium acetate and ammonium formate increase the hygroscopicity of what was already a hygroscopic material. Oxlate salts significantly increase the stability of AN, but there is some concern about its toxicity [33]. HMTA and guanidinum carbonate also stabilize AN, but the stabilizing effect of HMTD appears to disappear at 320 °C.

Trends suggested by DSC were confirmed by isothermal studies (Tables 7 and 8). Table 14 compares the relative stabilities of the various AN mixtures to AN as determined by the positions of the DSC exothermic maxima and by the isothermal rate constants at 260 and 320 °C. For DSC the results were assigned as “ND” (decomposition not much different from neat AN) if the exothermic maximum was within 20 °C of that of AN; “S” (decomposition slower than neat AN) if the exotherm was more than 20 °C above that of AN. Isothermal rate constants are given a similar subjective rating, with the rating “ND” (not different from AN) if the rate were not more than two times or less than half that of neat AN. We observed that if the DSC exothermic maximum of the AN/additive mixture was at least 20 °C higher than neat AN, then that mixture would exhibit a reduced rate constant at 260 °C, but the relative stability ordering among the various admixtures did not hold constant between DSC and the 260 °C rate constants.

Examining the assignments in Table 14, it is obvious that the isothermal data at 260 °C are more comparable to the DSC data than those obtained at 320 °C. This is surprising since the DSC exotherms of AN and all the mixtures occurred above 320 °C, but it is in line with our previous observation that the composition of gaseous products produced by the decomposition of AN during a DSC scan were closer to the composition of AN decomposed at 270 °C than at 320 °C [13]. Furthermore, the additives which stabilize AN at 260 °C have much less of an effect at 320 °C (Table 14). This is reasonable since the decomposition of AN is more susceptible to acids and bases at low temperatures where an ionic decomposition mechanism is dominant than at high temperature (above 290 °C) where a free-radical decomposition pathway becomes important. Thus, species which retarded AN decomposition at 260 °C were not as effective at 320 °C (e.g. HMTD).

The additives which best stabilize AN are the carbonates and the organic bases. Comparing the 260 °C isothermal rate constants of the carbonate salts, calcium carbonate clearly stabilizes AN better than the sodium and potassium salts. This is especially surprising in light of the destabilization apparent with other calcium salts. In an attempt to understand the effect of the calcium carbonate, we examined the effect of added magnesium carbonate using DSC and 260 °C thermolysis. The DSC exotherm of AN mixed with magnesium carbonate was similar to the other carbonates (Table 14). Its 260 °C isothermal rate constant indicates more stabilization than the alkali

Table 14
Ammonium nitrate mixtures: relative decomposition rates as predicted by the DSC exotherm or by the isothermal rate constants (additives about 10 mol%)[a]

	DSC		260 °C 10^4 k/s		320 °C 10^2 k/s		pH	N_2O/N_2	CO_2
Ammonium nitrate		326		2.0		1.0	4.9	4.1	0
Ammonium nitrate + $NaNO_3$	ND	328	ND	1.4	ND	0.78	4.7	6.1	0
Ammonium nitrate + KNO_3	ND	323	ND	2.2	ND	0.74	4.8	3.4	0
Ammonium nitrate + $Ca(NO_3)_2$	ND	328	ND	2.9	ND	0.68	4.9	4.9	0
Ammonium nitrate + Na_2SO_4	ND	349	S	1.0	ND	0.9	5.1	3.4	0
Ammonium nitrate + $(NH_4)_2SO_4$	ND	348	ND	1.6	F	2.0	4.8	3.1	0
Ammonium nitrate + $CaSO_4$	ND	334	ND	2.3	ND	1.5	5.6	3.4	0
Ammonium nitrate + NaH_2PO_4	ND	339	ND	1.4	ND	1.6	4.3	4.5	0
Ammonium nitrate + KH_2PO_4	ND	348	ND	1.4	ND	1.3	4.2	2.5	0
Ammonium nitrate + Na_2HPO_4	S	366	S	0.5	ND	0.9	7.3	2.4	0
Ammonium nitrate + K_2HPO_4	S	364	S	0.5	ND	0.8	7.4	2.7	0
Ammonium nitrate + $(NH_4)_2HPO_4$	S	364	S	0.9	F	2.1	7.4	3.7	0
Ammonium nitrate + $CaHPO_4$	ND	337	ND	2.2	F	1.9	6.4	5.2	0
Ammonium nitrate + K_3PO_4	S	362	S	0.7	ND	1.0	8.2	2.3	0
Ammonium nitrate + Na_2CO_3	S	381	S	1.0	S	0.4	8.5	1.9	0.10
Ammonium nitrate + K_2CO_3	S	374	S	1.0	S	0.5	8.5	2.4	0.05
Ammonium nitrate + $CaCO_3$	S	389	S	0.03	S	0.2	7.4	0.8	0.10
Ammonium nitrate + $MgCO_3$	S	378	S	0.17	Not run		7.9	1.9	0.07
Ammonium nitrate + $KHCO_3$	S	372	ND	1.4	S	0.7	7.3	3.3	0.02
Ammonium nitrate + guanidinum CO_3	S	408	ND	1.3	S	0.8	8.2	1.5	0.17
Ammonium nitrate + NH_4CHO_2	S	384	S	0.11	S	0.7	5.9	1.0	0.16
Ammonium nitrate + $(NH_4)_2C_2O_4$	S	385	S	0.01	S	0.7	5.9	1.0	0.21
Ammonium nitrate + $K_2C_2O_4$	S	383	S	0.01	Not run			0.70	0.30
Urea	S	394	S	0.09	S	0.7	5	0.30	0.20
HMTA	S	377	S	0.28	F	2.2	6.5	0.30	0.28

[a] ND: no great difference; S: slower; F: faster.

metal salts, but somewhat less than that of the calcium salt. Possibly it is less stabilizing than the calcium salt because as a smaller cation it is more acidic, but this does not explain the reason either calcium or magnesium carbonate should be more stable than the carbonates of sodium or potassium. (One reviewer has suggested their lower solubility in the AN melt may explain their enhanced thermal stability compared to the alkali carbonate.)

4.2. Gaseous decomposition products

Table 14 compiles the data on the various AN mixtures—the temperature of the DSC exotherm, the rate constants, pH, and gaseous decomposition products at 260 °C. We have previously noted that at lower temperatures, AN produces more nitrogen than it does at higher temperatures [12]

$$5NH_3 + 3HNO_3 \rightarrow 4N_2 + 9H_2O \qquad (9)$$

The decomposition gases are also shifted from N_2O toward N_2 in the presence of hydrocarbons [13]. Table 14 suggests there is a general trend that the more stabilizing the additive, the lower the N_2O/N_2 ratio and the higher the production of CO_2. This appears to be a better predictor of an additives stabilizing ability than pH (note urea). The additives that fall in this category are the carbonates and the organic additives. Given the composition of these, it was expected that they would produce carbon dioxide; and in producing carbon dioxide they consumed the oxygen normally used to produce nitrous oxide. While the organic species are oxidizing by nitric acid to produce carbon dioxide and nitrous acid, the carbonates react with the acid proton of nitric acid (or of ammonium, Eq. (2) to form carbonic acid and subsequently carbon dioxide and water. Either event results in the retarding of AN decomposition. Although we could not detect ammonia by our chromatographic method, urea [34] and possibly guanidinum ion [35] and HMTD produce ammonia during their decomposition; this gas would not have been detected. The formation of ammonia from the decomposition of urea would explain the fact that AN/urea decomposition at 260 °C slowed dramatically after about 12% decomposition. Calcium carbonate was the most stabilizing of the carbonates, and its N_2O/N_2 ratio is the lowest among the carbonates. The shift in decomposition gases is rather large considering the additive only comprised 10 mol% of the AN formulation. If this unique stabilizing effect of calcium carbonate is contrasted with the unique destabilizing effect exhibited by the other calcium salts Eq. (9), the apparent difference is that the decomposition of calcium carbonate forms the basic oxide CaO.

4.3. Effect of fuels on AN

Table 11 summarizes the DSC results for AN/fuel mixtures, most of which have been used as explosives. Some of the fuels reacted with AN in the temperature range of the DSC scan (carbon, mineral oil, diesel, sugar, and sulfur) and some did not (NB, nitromethane (NM) and aluminum). The thermal reaction of AN with the organic fuel is based on the interaction of nitric acid, formed by reaction (1), with the fuel

$$HNO_3 + \text{``CH''} \rightarrow CO_2 + H_2O + \tfrac{1}{2}N_2 \qquad (10)$$

The presence of carbon black in the early reaction category and of NB and NM in the later reaction category prevents speculation that liquid additives facilitate early decomposition. The DSC results appear to depend on the relative decomposition temperatures of the oxidizer and the fuel. Of the fuels examined with AN (Table 11), sugar decomposed at the lowest temperature. Clearly, with AN/fuel mixtures, the relative position of the exothermic maximum is not an indication of explosivity. AN and sugar can be made detonable, and AN with NM (Kinepak$^{®}$) is a commercial high explosive more powerful than

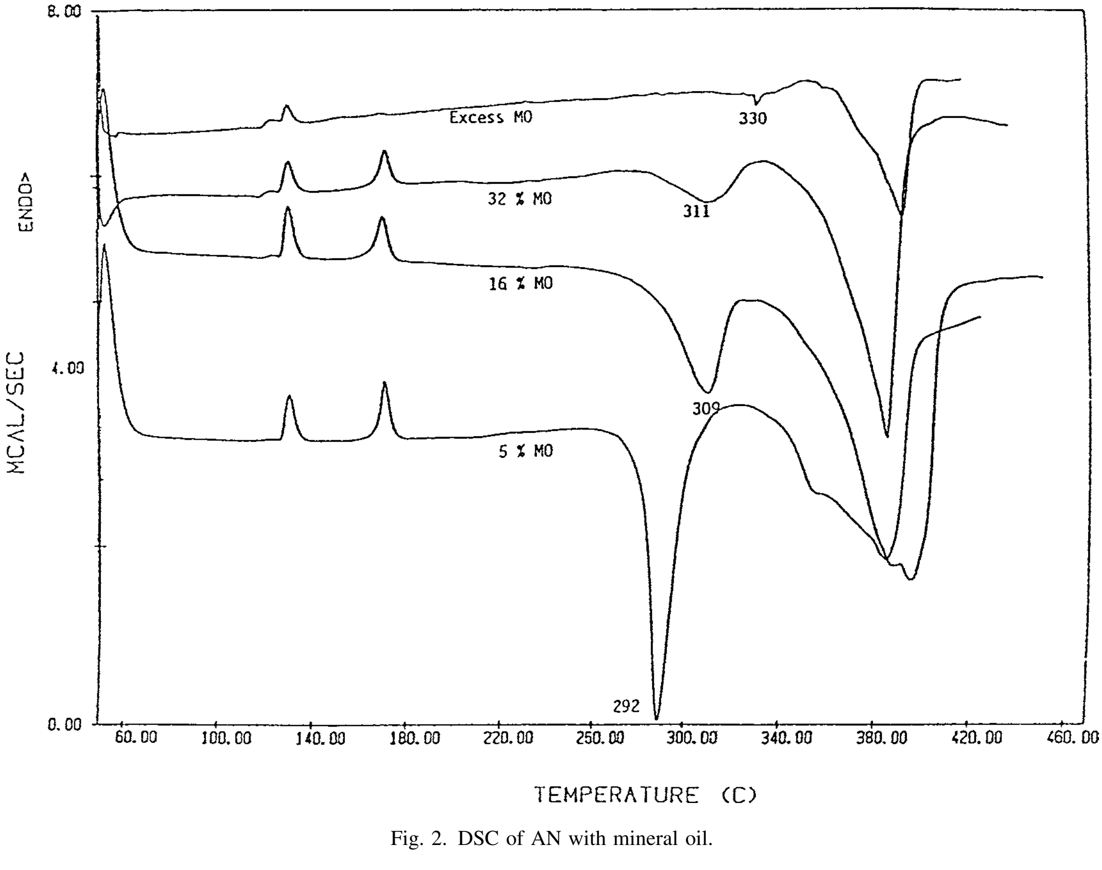

Fig. 2. DSC of AN with mineral oil.

ANFO. Typically, ANFO and AN/sugar have detonation velocities around 3.5–4.0 km/s, but mixed with an energetic liquid such as NM or hydrazine (Astrolite® G) detonation velocity of up to 8.6 km/s are reported [36].

The fuels which reacted with AN generally exhibited at least two exothermic regions. Addition of the fuel increased the overall heat release of the reaction, but the majority of heat was released in the higher temperature exotherm. In a detailed study of the effect of mineral oil on AN, we determined that the first exothermic region was associated with dissociation of AN Eq. (1) and nitric acid attack of the fuel Eq. (10). The second exothermic region we interpreted as reaction of ammonia and complete oxidation of the fuel [13]. As the amount of mineral oil was increased, the first exotherm decreased, while the second one increased (Fig. 2). When diesel was the fuel, the relative ratio of the low and high temperature exotherms remained constant as the amount of fuel increased (Fig. 3). AN mixed with sugar gave a thermogram with two distinct exotherms (185 and 343 °C) (Fig. 4). The latter moved to higher temperature (364 °C) as the level of sugar was increased to 20 wt.%, but the former remains at 185 °C and becomes a larger percentage of the total heat released. Both exothermic regions increased markedly as the amount of sugar was increased. Sugar, like NM and NB, released heat upon decomposition (exothermic maximum, 285 °C and heat, 523 J/g); but it was not nearly as energetic as NM and other species added to AN (Table 12). (Surprisingly, addition of 5 wt.% NB did not increase the amount of heat released (1192 J/g) nor substantially change the exotherm of AN. Apparently, it was too stable to react in the DSC temperature range.) Sugar, in the

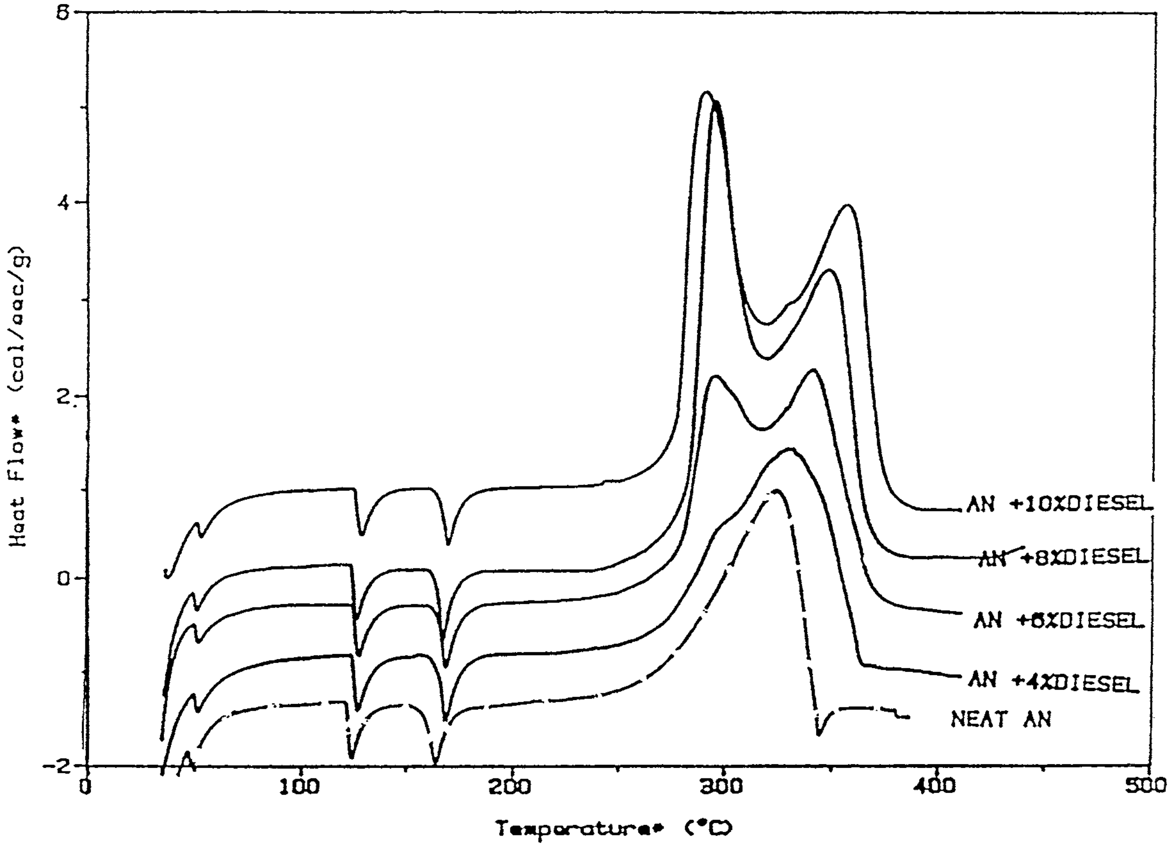

Fig. 3. DSC thermogram of AN with increasing amounts of diesel fuel.

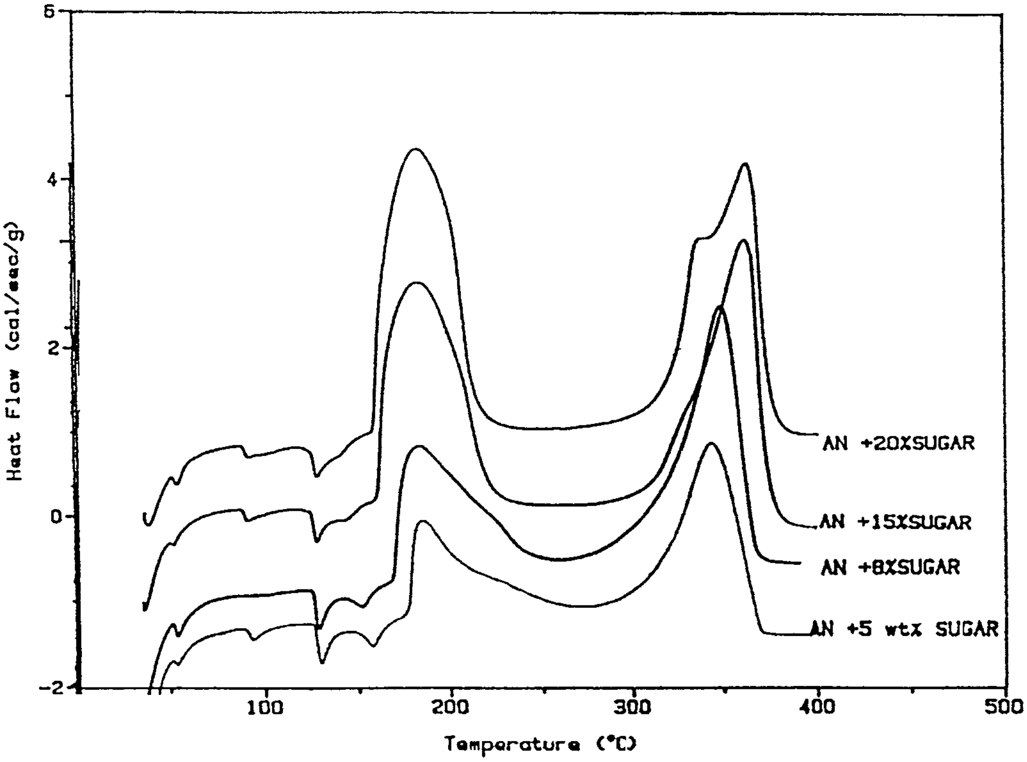

Fig. 4. DSC thermogram of AN with increasing amounts of sugar.

presence of AN, released heat at lower temperatures than either species did neat. Raising the percentage of sugar in the AN mixture from 5 to 20 wt.% increased the heat released in the first exotherm from 31 to 53% of the total. The first exotherm for the AN/sugar mixture immediately followed their endothermic melt (AN, 169 °C; sugar, 174 °C). These observations suggest a low temperature AN/sugar reaction.

To further shed light on the role of fuel, KNO_3 was examined. KNO_3, not possessing the source of hydrogen provided by AN, did not decompose nor react with fuels as readily as AN. It was so stable that it did not exhibit an exotherm in the range of the DSC (up to 500 °C); and only with a few fuels (carbon, sulfur, and their mixture in black powder) was an exotherm observed below 500 °C. In some cases, the amount of heat released was so small that they may be baseline deviations rather than exotherms. As with AN/fuel mixtures, we must conclude the position of the exotherm is not indicative of explosivity.

4.4. Explosivity testing

It is desirable to conduct explosive testing on a large-scale (100–1000 lb), especially for such a poor explosive as AN. However, laboratory-scale testing is convenient and large-scale may not be possible due to lack of funds or materials. Correlation of small- and large-scale test results is a frequently sought and seldom achieved goal. We have experimented using the small-scale explosivity device (SSED) [37–41] to obtain a relative ranking of the explosivity of energetic materials and have been successful in comparing SSED results (2 g scale) with pipe bomb fragmentation data (800 g scale). The SSED attempts to detonate 2 g samples of energetic materials confined in a 0.303 (British) brass cartridge case. The entire set-up was contained in a heavy-walled, bolted-closure, stainless steel vessel. Violence of an event was judged by the weight of the main body of the casing remaining attached to the base after detonation. Obviously, setting off a detonator (no. 8), even in an empty cartridge,

Table 15
Explosivity measure on a small-scale explosivity device (% case shattered)[a]

Test no.	No. average	Tested material	% shattered	AN in mixture	DSC exothermic T_{max} (°C)	DSC heat released (J/g)
1	3	NaCl	40			
2	3	HMX	80			
3	2	AN	56	100	328	1255
4	3	AN + 5% mineral oil	58	95	268, 358	2448
5	3	AN + 6% fuel oil	56	95	268, 358	2448
6	3	90% AN + 10% sugar	65	90	296, 348	2749
7	3	79% AN + 21% Ca/$MgCO_3$	53	79	393	1439
8	3	96.5% (79% AN + 21% Ca/$MgCO_3$) + 3.5% mineral oil	64	76		
9	3	87.7% (79% AN + 21% Ca/$MgCO_3$) + 12.3% sugar	61	69		
10	3	9 AN + 1 $NaNO_3$	43	90	328	971
11	1	AN + 10 mol% $K_2C_2O_4$	47	90	383	1289
12	3	2 AN + 1 $CaCO_3$	36	67	433	397
13	4	2 AN + 1 $CaHPO_4$	39	67	341	682
14	1	2 AN + 1 $CaSO_4$	37	67	333	669
15	3	1 AN + 1 $NaNO_3$	39	50		
16	3	1 AN + 1 Al_2O_3	34	50		
17	3	1 AN + 1 ASO_4	41	50	364	640
18	3	30 AN + 10 ASO_4 + 30 $CaCO_3$ + 30 urea (mol%)	32	30		
19	3	30% AN + 10% ASO_4 + 30% $CaCO_3$ + 30% urea	30	30	357, 388, 463	
20	3	1 AN + 9 $NaNO_3$	42	10		
21	3	10% AN + 30% urea + 30% $CaCO_3$ + 30% ASO_4	36	10	303	360
22	3	10% AN + 30% urea + 30% A_2HPO_4 + 30% $CaCO_3$	32	10	No exotherm	
		In situ formulations				
A	3	2 AN + 1 $CaCO_3$		67	440	979
C	4	2 AN + 1 $CaHPO_4$		67	373	665
B	3	2 AN + 1 $CaSO_4$		67	355	561

[a] A: ammonium; AN: ammonium nitrate; all formulations 2.00 g and cartridges 11.0 g.

will result in recovery of less than 100% of the cartridge. In tests where the cartridge was filled with 2 g of inert NaCl ~60% of the cartridge remained attached to the base, whereas with HMX, only 20% of the original case weight was recovered. Since only 60% of the casing remained attached to the base when the test material was an inert substance, the differentiation between a good explosive and a weak one is difficult. One solution might be to use smaller detonators. Reducing the amount of explosive in the detonator would reduce the damage to the cartridge/inert system, expanding the low-reactivity end of the test. However, decreasing the power of the detonator would increase the likelihood that insensitive explosives like AN-based materials would not propagate the detonation wave. For this reason no. 8 detonators were used.

The differentiation in SSED destruction among AN formulations with fuel and those without was clear. Those with fuel (mixtures 4–9, Table 15) left only 35–47% of the cartridge attached to base, while those without fuel retained greater than 50% of the cartridge. Among the non-fuel containing formulations, results suggest that the degree of destruction directly correlated with the amount of AN in the formulation. However, this may reflect a dilution effect. Low thermal stability appears to be related to high explosivity, but high thermal stability is no guarantee of low explosivity. Insufficient tests have been run to make firm correlations, and no tests have been run to correlate these SSED results to large-scale explosive testing. Neither of the mixtures discussed earlier as relatively non-detonable—AN with 21% dolomite nor a 50/50 mixture of AN and ammonium sulfate—were markedly less violent; this is backed by field experience showing them to be detonable. However, the test does indicate both formulations are less explosive than AN. Thus, at 1/3 dilution there are additives which significantly stabilize AN. Whether nitrogen content of 17–22% is sufficiently high to make these viable fertilizer mixtures is not known. In Switzerland and Ireland the only AN sold has been diluted to 27% nitrogen [42].

5. Conclusions

Both DSC and isothermal results have shown a general and strong correlation between the basicity of an additive and its ability to stabilize AN to thermal decomposition. Interestingly, DSC scans of AN more closely reflect isothermal studies at 260 °C than those at 320 °C. In fact, additives had more effect on the low temperature decomposition of AN than they did on its high temperature decomposition. This is in line with the accepted low temperature route of AN decomposition which involves formation of nitronium ion from acidic media Eq. (2). A number of additives were identified which dramatically raised the temperature of the AN DSC exotherm. In general, an increase in the DSC exothermic peak maximum signaled a decrease in the rate of AN decomposition, but the increase in the exotherm had to be greater than 20 °C to have notable effect on the decomposition rate. Ordering of thermal stability by the position of the DSC exotherm was similar but not exactly the same as an ordering in terms of 260 °C first-order rate constants. Materials that dramatically raised the temperature of the AN exotherm, thus, enhancing AN stability, were basic in nature: HMTA, and salts of carbonate, formate, oxalate, and mono-phosphate. However, basicity is not the only factor associated with stabilizing AN. Urea had a large stabilizing effect but did not raise the pH of an AN solution dramatically; rather on decomposition urea forms ammonia, thus generating a basic media. For the most part organic species

Table 16
Survey of best additives

	Formula	Additive (mol%)	DSC exotherm T_{max} (°C)	Rate constant 260 °C, 10^6 k/s	wt.% N	pH	Cartridge shattered	Dec. gas 320 °C	
								N_2O/N_2	CO_2
Ammonium nitrate	NH_4NO_3	100	326	200	35	4.9		4.1	0
AN + single additive									
$CaSO_4$	$CaSO_4$	11	334	230	29	5.0	37	3.4	0
In situ		33	355		19		35		
$CaHPO_4$	$CaHPO_4$	11	337	220	29	7.4	39	5.2	0
In situ		33	373		19		38		
K_2HPO_4	K_2HPO_4	8	364	49	29	7.4		2.7	0
K_2CO_3	K_2CO_3	10	351	100	29	8.5		2.4	0.05
$MgCO_3$	$MgCO_3$	10	378	17	35	7.9		1.9	0.07
$CaCO_3$	$CaCO_3$	14	389	2.8	29	7.4	36	0.8	0.10
In situ		33	440		22				
Guanidinum CO_3	$C_3O_3N_6H_{12}$	10	408	130	37	8.2		1.5	0.17
Urea	CON_2H_4	10	368	9.2	36	5.0		0.3	0.20
HMTA	$C_6N_4H_{12}$	10	377	29	36	6.5		0.3	0.28
NH_4 formate	CO_2NH_5	20	384	11	33	5.9		1.0	0.16
K oxalate	$C_2O_4K_2$	10	383	9.9	28	6.4	47	0.7	0.30
NH_4 oxalate	$C_2O_4N_2H_8$	8	385	9.9	34	5.9		1.0	0.21
AN + multiple additives (wt.%)									
30% AN/30% urea/30% $CaCO_3$/10% $(NH_4)_2SO_4$			357		27		32		
48% AN/20% urea/16% A_2HPO_4/16% A_2SO_4			394		33				
68% AN/36% urea/16% A_2HPO_4			404		37				

enhanced AN stability more than the inorganics. This cannot be a matter of pH alone since the pH of AN solutions were similar for both the inorganic and organic additives. Given that the only outstanding stabilizers contain carbon, calcium carbonate being dramatically better than most other inorganic salts, we speculate that the formation of carbon dioxide may be a factor in the ability of a compound to stabilize AN. Table 16 shows characteristics observed for the more thermally stable AN mixtures. There appears to be a correlation between a low 260 °C rate constant and a low N_2O/N_2 ratio or high carbon dioxide content.

Calcium carbonate in admixture with AN showed the largest retardation of the 260 °C first-order rate constant. This AN mixture is used successfully as a fertilizer. The organic bases were effective in stabilizing AN, and species could be chosen that contain nitrogen; however, use of them in fertilizers may be difficult. For the most part, they are more expensive than the inorganic additives; several (urea and the salts of formate and acetate) dramatically increase the hygroscopicity of AN; the oxalates are toxic to animals; and HMTA is the chemical precursor of RDX. Of the group considered urea is currently used. It is inexpensive, but the hygroscopicity of the urea/AN mixture requires it to be sold in solution. Three other bases targeted in this study require testing on a large-scale; these are oxalate, HMTA, and guanidinum carbonate. In situ, formation of AN by providing the ions that make up AN from two different additives (i.e. $NH_4X + ENO_3$ instead of $NH_4NO_3 + EX$) in some cases resulted in enhanced thermal stability. This appears to be the case when the decomposition point of AN plus the additive is below the melting points of the in situ ingredients. This approach deserves further study.

While this study has successfully identified several additives which stabilize AN and might be acceptable in fertilizer formulations, these formulations have not been shown to be non-detonatable. The SSED clearly differentiated between fueled and unfueled AN formulations in terms of explosivity, and the device detected the decrease in detonability accompanying dilution of AN from 100 to 90, 67, 50, 30, and 10%. However, within a given dilution of AN there was little range to distinguish whether a stabilizing additive can also reduce detonability. At this point, large-scale testing of some of the best formulations is necessary to determine failure diameter.

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