

Fire Hazards of Ammonium Nitrate-Sulfur Systems

Charles M. Mason, David R. Forshey, and Frank J. P. Perzak

The addition of sulfur to ammonium nitrate-based fertilizers has raised questions regarding the hazard of these mixtures when exposed to fire. Several techniques were used to evaluate this hazard. Ammonium nitrate-sulfur (AN-S) mixtures, of sufficiently large diameter, detonated when initiated by an explosive shock. Diammonium phosphate, triple superphosphate, and potassium chloride added to AN-S mixtures decreased the shock sensitivity relative to AN-S. AN-S mixtures burning

at pressures greater than 1000 p.s.i. resulted in rapid combustion; deflagration to detonation transition was accomplished experimentally in some cases. Sulfur has the same effect on detonability as other fuels when added to AN or AN-S systems. The thermal stability of AN-S mixtures was about the same as AN mixed with fuel oil or polyethylene. Addition of chloride ion materially reduced the thermal stability.

The recognition of sulfur deficiency in soils in many regions of the United States is resulting in the addition of elemental sulfur to many fertilizer compositions. Since many of these compositions contain a large proportion of ammonium nitrate (AN), and since combinations of AN and oxidizable material are known to be highly reactive (Van Dolah *et al.*, 1966), the Sulphur Institute asked the U.S. Bureau of Mines to investigate the reactivity of AN-S mixtures. AN is a potential explosive, although a weak and insensitive one. The addition of any oxidizable material to AN enhances its explosive properties because of the added energy that can develop. In this sense, elemental sulfur is a fuel and AN-S mixtures are subject to the hazard of explosion. To evaluate the hazard of such mixtures, particularly under circumstances of fire exposure, the ease of initiation of detonation, thermal stability, and burning characteristics of various AN-S mixtures were investigated. The effect of other common fertilizer constituents was included in the study.

DETONABILITY

The relative ease of detonability of AN-S mixtures was a basic concern in this investigation, in terms of both sensitivity to initiation of various AN systems by high intensity shocks and the ease of transition to detonation under intense fire exposure.

In determining shock sensitivity of any material, several factors must be taken into account. The apparent sensitivity is influenced by confinement, density, and particle size; by intimacy of mixing of fuel and oxidizer; by charge diameter (the charge must be larger than a critical diameter if initiation of a propagating detonation is the determining criterion of sensitivity); and by temperature. The initial shock need not have an amplitude adequate for immediate initiation of detonation, because the burning material may cause the pressure in the shock front to increase, leading to growth to steady-state detonation (Griffiths and Grocock, 1960; Maćek, 1962).

One commonly used technique for measuring ease of initiation of detonation is the card gap test (Joint Army-

Navy-Air Force Panel on Liquid Propellant Test Methods, 1960). With it, sensitivity is related to the amplitude of the shock wave needed to effect initiation of stable detonation. The amplitude of the shock wave is varied, usually over the range of 2 to over 100 kilobars (1 kilobar equals approximately 15,000 p.s.i.) by inserting a stack of cards (cellulose acetate wafers) or polymethyl methacrylate disks between a standard explosive donor and the sample. Sensitivity is expressed in terms of a gap value—that is, the thickness of the cards in the gap between the donor and the material being tested for which there is a 50% probability that a sustained detonation will be initiated in the acceptor charge; the greater the gap the lower the shock intensity required to initiate detonation and the greater the sensitivity. The gap value is usually determined by employing an experimental design called the up-and-down method (Dixon and Massey, 1957; Statistical Research Group, 1944).

Recently, the Bureau of Mines developed a revised procedure for card gap determination that is more definitive than the original test; it was used to evaluate the detonability of AN-S mixtures. Samples, contained in 16-inch lengths of 1½- and 3-inch schedule 40 seamless steel pipe, were shocked by 160- and 360-gram tetryl boosters. The 2-inch-long boosters used had 2- and 3-inch diameters, respectively (density 1.57 grams per cc.). A probe, containing a resistance wire through which a constant current flows, was placed lengthwise in the sample (Figure 1). The continuous shorting out of the wire by the detonation front causes a change in voltage which allows one to record the propagation of the front with an oscilloscope. An expendable pressure transducer, which is under development at this center, is inserted in the top of the charge. This transducer records the peak pressure transmitted to it from the detonating explosive, further indicating whether or not a detonation has been initiated.

Three general types of records were obtained: (1) The sample detonated at constant velocity as indicated by a straight line of constant slope (Figure 2A); these results were recorded as positive. (2) Detonation failed to propagate the entire length of the sample, as indicated by a line whose slope rapidly approached zero (Figure 2B) and by incomplete destruction of the container; these results were recorded as negative. (3) Detonation propagated the

Explosives Research Center, Bureau of Mines, U.S. Department of the Interior, Pittsburgh, Pa. 15213.

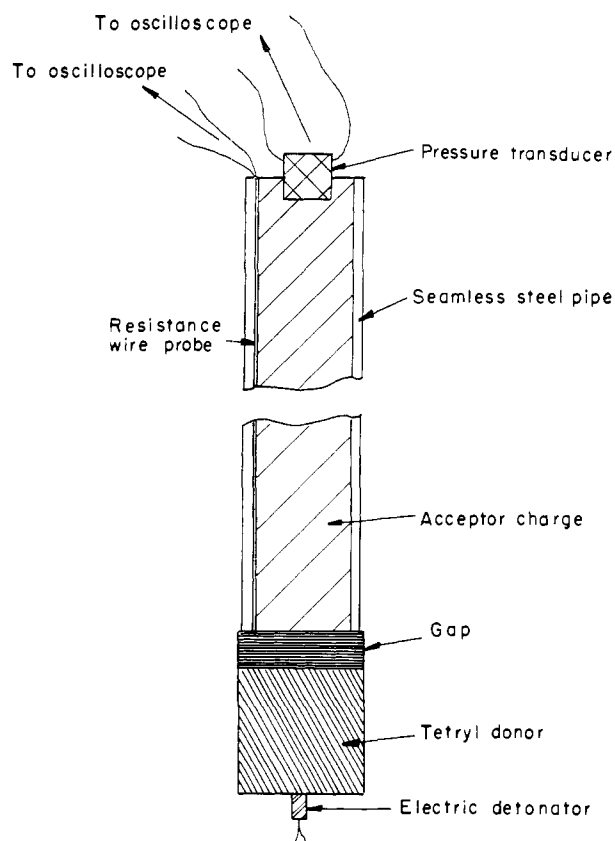


Figure 1. Shock sensitivity apparatus used in determining gap value for prilled AN-S mixtures

entire length of the sample but with a decreasing rate of detonation. This was indicated by a trace with decreasing slope, as shown in Figure 2C. These results were recorded as negative, as the reaction was decaying and did not represent a self-sustaining detonation in this diameter. The pressure traces obtained from the pressure transducer are shown as broken lines in Figure 2, indicating in each case the time of arrival of the front at the top of the charge. This third case is indicative that the sample was below its critical diameter and a propagating detonation would be possible at some larger charge diameter with a larger donor.

Prilled Ammonium Nitrate with -120-Mesh Sulfur Systems. In order to estimate the effect of the concentration of sulfur on the sensitivity of AN-S, several mixtures of prilled brand E (brand A, B, etc., is used to identify AN of different sources) AN with flowers of sulfur (-120-mesh) were studied in 1½-inch diameter containers at zero gap. The experiments were conducted at 140° F. because this was the lowest temperature at which detonation could be achieved with any mixture in the diameter used. Table I contains a summary of the data. Only the mixture containing 5% sulfur gave positive results.

Card gap values were determined for mixtures of both prilled and micropulverized AN with 5% sulfur (-120-mesh), apparently the most sensitive AN-S composition, over the temperature range from ambient to 210° F. The shock sensitivity of mixtures of prilled AN and sulfur increased from no initiation in five trials at 105° F. to a gap value of 1.40 inches as the temperature was raised to 210° F.

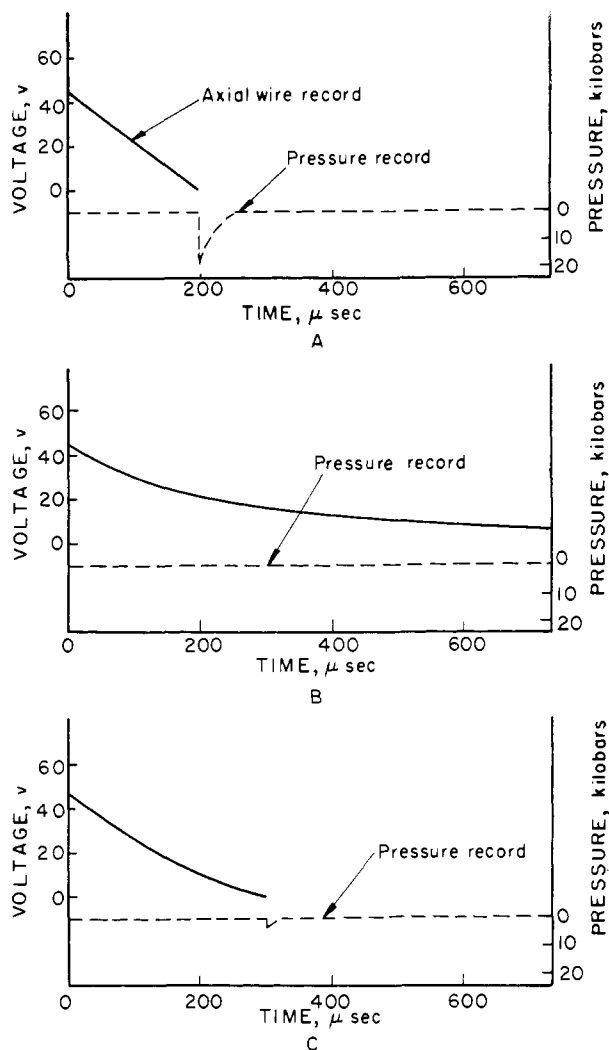


Figure 2. Typical voltage trace and pressure trace for a positive shot, A, a negative shot, B, and a decaying shot, C

Table I. Shock Sensitivity of Ammonium Nitrate-Sulfur Mixtures at 140° F.^a

Type AN, Brand E (Prilled)	
Sulfur, %	Result
0.0	0/5 ^b
1.0	0/5
5.0	3/5 ^c
10.0	0/5
15.0	0/5

^a -120-mesh sulfur.

^b No initiations in five trials.

^c Three initiations in five trials.

The shock sensitivity of the micropulverized AN-S mixtures as measured by the gap value was nearly independent of temperature and type of AN. Detonation rates were obtained for those mixtures which did detonate (Table II).

The rate of detonation of prilled AN-5% sulfur mixtures varied from 6980 to 7540 feet per second. This rate did not vary significantly with temperature or for the two brands of prills employed, but was higher for micropulverized

AN-5% sulfur mixtures (8200 to 9180 feet per second). The pressure measured by the transducer when a positive result was obtained was likewise independent of temperature or brand of prill (18 to 22 kilobars for prilled AN-5% sulfur mixtures and 7 to 11 kilobars for micropulverized AN-5% sulfur mixtures). This difference in results for prilled and micropulverized AN mixtures results from the lower density of the latter mixtures.

To provide a basis for comparison with prilled and micropulverized AN with 5% sulfur, the shock sensitivity of brand E AN and AN-FO (prilled and micropulverized) was determined.

The sensitivity of prilled AN-S mixtures, 1.18-inch gap at 175° F. and 1.4-inch gap at 210° F., was between that of prilled AN-FO, 1.65-inch gap at 70° and at 140° F., and prilled AN, less than zero gap (0/5) at 70° and at 210° F. Conversely, the shock sensitivity of micropulverized AN-S mixtures, 2.65-inch gap at 70° and at 175° F., is greater than either that of micropulverized AN, 1.85-inch gap at 175° F., or micropulverized AN-FO, 2.15-inch gap at 70° and at 175° F. The difference between micropulverized AN and AN-FO is small and may have resulted from the two systems being shot at different densities (Table III).

Prilled Ammonium Nitrate-Prilled Sulfur Systems. Gap values for insensitive explosive systems are not readily obtained in the small diameters (less than 3 inches) which are the usual limits in the facilities of the Explosives Research Center. As demonstrated by the data in Tables II and III, raising the temperature and confining the material

will effectively reduce the critical diameter (Van Dolah *et al.*, 1966) until positive results (detonation initiation and propagation) will be obtained in some of the trials. The relative sensitivity can thus be evaluated in terms of T_{50} , that temperature at which the material would be initiated to detonation in 50% of the trials. Sensitivity, on this relative scale, can be considered inversely proportional to T_{50} .

The T_{50} values may be estimated as the mean temperature between the temperatures at which three positive results and three negative results are observed out of six trials.

Relative shock sensitivity was thus determined in terms of T_{50} for various combinations of AN-S with diammonium phosphate (DAP), triple superphosphate (TSP), and KCl. With the exception of granular TSP, all the materials in these mixtures were prilled. The mixtures were contained in 16-inch lengths of 3-inch schedule 40 seamless steel tubing using 360-gram tetryl boosters (3-inch diameter by 2-inch length; density, 1.57 grams per cc.). All samples were heated for 18 hours at a predetermined temperature before being tested. The temperature of the samples was increased by 5° F. increments until three positive results were obtained in six trials or the softening temperature was reached. Figure 3 shows an assembled charge prior to firing and a blank using prilled urea; Figure 4 shows a positive and a negative result.

For some mixtures the softening point was reached before initiation to detonation could be obtained and T_{50} was thus greater than the softening temperature. Mixtures of AN plus 5% S plus 20% DAP, 10% TSP, or 10% KCl

Table II. Shock Sensitivity and Detonation Rate of Ammonium Nitrate-5% Sulfur Systems as a Function of Temperature^a

(Number of initiations per number of trials indicated by 3/5, etc., where five trials gave three initiations)

Type AN	Density, G./Cc.	Temperature, ° F.				
		70	105	140	175	210
Brand E (prilled)	0.84	...	0/5	3/5 6980 ft./sec. ^c	1.18-inch gap ^b 6890 ft./sec. ^c	1.40-inch gap 7540 ft./sec. ^c
Brand A (prilled)	0.79	...	0/10	0/5	0/5	1.25-inch gap 7380 ft./sec. ^c
Brand A (micropulverized)	0.61	2.40-inch gap 8850 ft./sec. ^c	2.85-inch gap 8200 ft./sec. ^c	2.85-inch gap 8530 ft./sec. ^c	2.75-inch gap 9180 ft./sec. ^c	...
Brand E (micropulverized)	0.61	2.65-inch gap 8330 ft./sec. ^c	2.65-inch gap 8200 ft./sec. ^c	...

^a Sulfur is -120-mesh; zero gap unless otherwise shown.

^b 50% gap value.

^c Average detonation rate for five trials.

Table III. Shock Sensitivity of Brand E Ammonium Nitrate and Brand E Ammonium Nitrate Mixtures as a Function of Temperature

(Number of initiations per number of trials indicated by 3/5, etc., where five trials gave three initiations)

Material	Density, G./Cc.	Temperature, ° F.				
		70	105	140	175	210
Prilled AN	0.81	0/5	0/5
Prilled AN-- 5% sulfur ^a	0.84	...	0/5	3/5	1.18 inch ^b	1.40 inch
Prilled AN-- 5% fuel oil	0.85	1.65 inch	...	1.65 inch
AN (micropulverized)	0.61	1.85 inch	...
AN-5% sulfur (micropulverized)	0.61	2.65 inch	2.65 inch	...
AN-5% fuel oil (micropulverized)	0.65	2.15 inch	2.15 inch	...

^a -120-mesh sulfur.

^b 50% gap value.

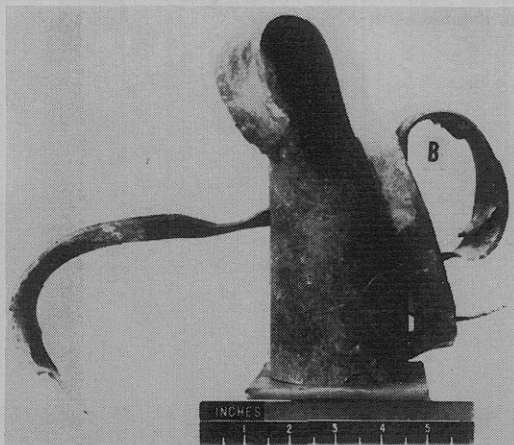
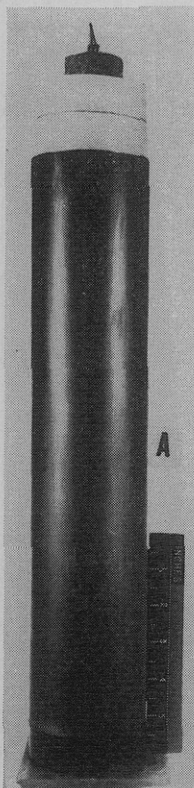


Figure 3. Charge assembly

- A. Charge prior to firing
- B. Result of a blank test using prilled urea

could not be initiated up to 205° F. Two commercially available granulated fertilizers of composition NPK (the designation 10-20-30 is used to show the per cent nitrogen, phosphorus as P_2O_5 , and potassium as K_2O , in the order named) 10-20-30 plus 3% commercial S and 12-24-24 plus 3% S could not be initiated up to 205° F. The T_{50} values for the mixtures are shown in Table IV. In contrast to previous results using flowers of sulfur with prilled AN when the maximum sensitivity was observed with 5% sulfur (Tables I to III), the maximum sensitivity using prilled sulfur with AN prills was at 15% sulfur. This difference probably results from the difference in contact between the AN and the sulfur. Five per cent of the flowers of sulfur coated the prills well; 5% of prilled sulfur gave only limited contact with the AN.

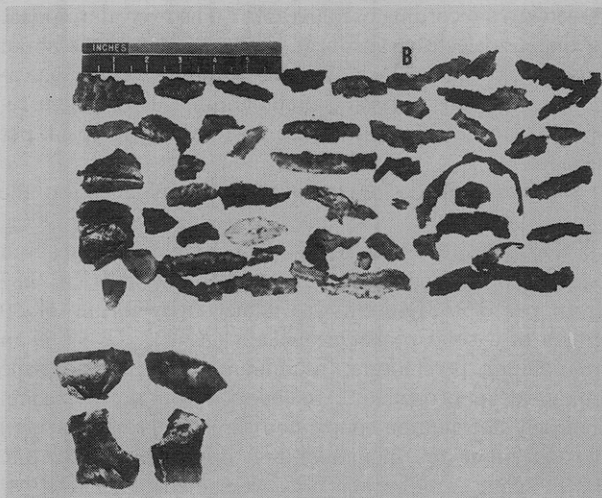
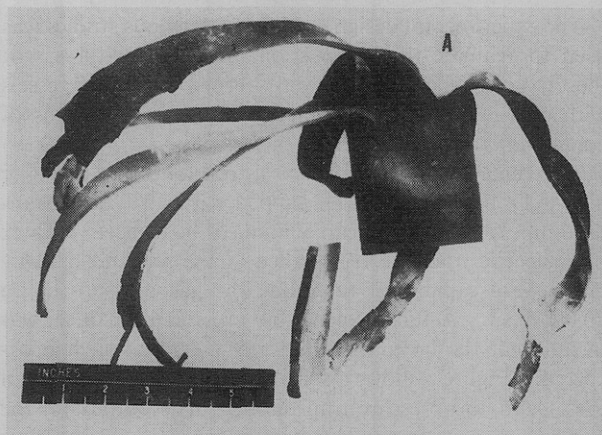


Figure 4. Results obtained with AN-S mixture

- A. Negative
- B. Positive

Table IV. Shock Sensitivity of Prilled Ammonium Nitrate-Prilled Sulfur Mixtures

Material	T_{50} , ° F.
AN + 5% S	145
AN + 10% S	135
AN + 15% S	100
AN + 5% S + 10% DAP	190
AN + 5% S + 20% DAP	>205 ^a
AN + 5% S + 10% TSP	>205 ^a
AN + 5% S + 10% KCl	>205 ^a
AN + 15% S + 10% DAP	175
AN + 15% S + 10% TSP	195
Fertilizer 10-20-30-3	>205 ^a
Fertilizer 12-24-24-3	>205 ^a

^a Maximum temperature used owing to softening of mixtures above 205° F.

COMBUSTION IN POROUS BEDS

Since AN-S mixtures are detonable, the possibility that detonation may develop in AN-S mixtures under conditions of fire exposure must be examined. Inasmuch as AN-S mixtures are not different in behavior from other AN-fuel mixtures, the problem is essentially the same as that studied extensively in this laboratory for AN fuel mixtures and reported elsewhere (Van Dolah *et al.*, 1966).

The experimental design used in the previous studies was used to evaluate the combustion of AN-S mixtures. In these studies, the mixtures were burned in vented vessels with orifices of varying diameters serving as a means of controlling the pressure inside the vessels.

The vented vessel used was a 4-foot-long steel pipe 4.5-inch O.D. by 3.15-inch I.D. capped with 3000-p.s.i. standard pipe caps; the top cap contained the orifice. Quartz piezoelectric transducers installed at the top and halfway down were capable of recording the gas pressure up to 70,000 p.s.i. A third expendable pressure transducer was installed at the bottom to indicate if detonation had occurred. Figure 5 shows a schematic diagram of the vented vessel and the pressure transducers. The outputs of the quartz piezoelectric transducers were fed through amplifiers directly to a recording oscillograph. The over-all response of the piezoelectric transducer system was limited to about 8 kc. per second, which was the response of the galvanometers in the recording oscillograph. This system responds to rates of pressure rise up to about 10^6 p.s.i. per second.

Samples at the desired temperature were loaded into the pipe. The weight of the sample varied from about 3.8 kg. for the pulverized mixtures ($\rho = 0.66$ gram per cc.) to about 5 kg. for the prilled and granulated AN mixtures ($\rho = 0.87$ gram per cc.). Ignition was achieved by means of 30 grams of a solid rocket propellant (ANP). (ANP is an ammonium perchlorate, aluminum, and polyurethane binder rocket propellant. In chopped form it provided an intensely hot ignition source and some prepressurization.) To determine the maximum pressure developed by the ANP igniter, calibration runs were made with ANP at various orifice sizes using cast iron shot as an inert filling medium. The pressures developed by the ANP igniter alone are designated as "ANP pressure."

Results of the AN-S burning runs can be classified qualitatively on a positive or negative basis. A result is determined to be positive when the heavy steel container is fragmented into small pieces (Figure 6) and a high pressure, about 10 kilobars, is measured on the expendable pressure gage indicative of a transition from deflagration to detonation. A negative result typically burns about 500 grams of sample and gives a rapid pressure rise which gradually levels out and then decreases slowly; this type of burning would represent no hazard in a fire. Occasionally, the sample decomposes completely in a few seconds but only enlarges the vent hole. Figure 7 shows a pressure-time trace for 15% sulfur (-120 mesh) by weight with brand E AN which converted to a detonation and one which did not. The AN-S mixture which detonated decomposed steadily at about 1200 p.s.i. for about 50 milliseconds, after which the pressure increased suddenly to about 4000 p.s.i. in the next 20 milliseconds. At about 4000 p.s.i. the pressure time trace became discontinuous, since the rate of pressure rise exceeded 10^6 p.s.i. per second, too fast to be recorded.

In AN-S mixtures, burning that led to detonation was observed only when the pressure developed by the burning mixture was greater than about 1000 p.s.i. although in a number of cases only fast burning was observed at greater pressures (up to 1750 p.s.i.) without transition. Taking the orifice size as an indication of relative hazard, hot

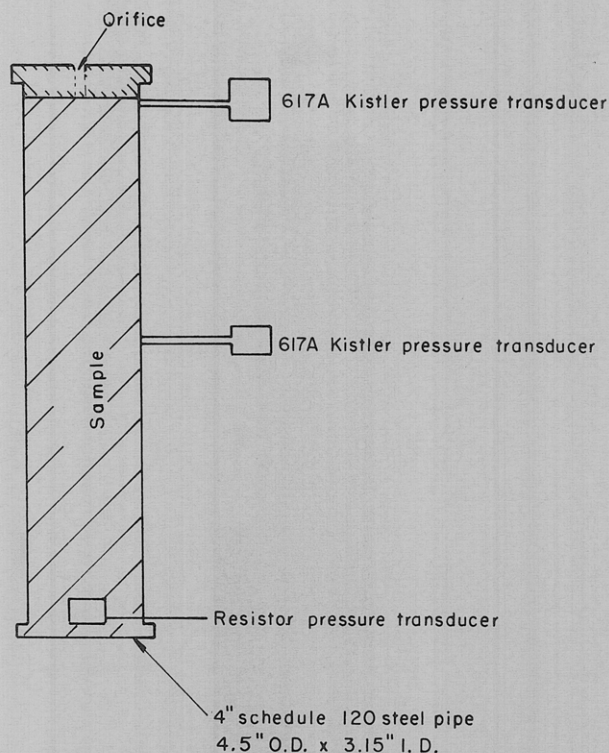


Figure 5. Container used to study pressure required for transition to detonation of AN-S mixtures

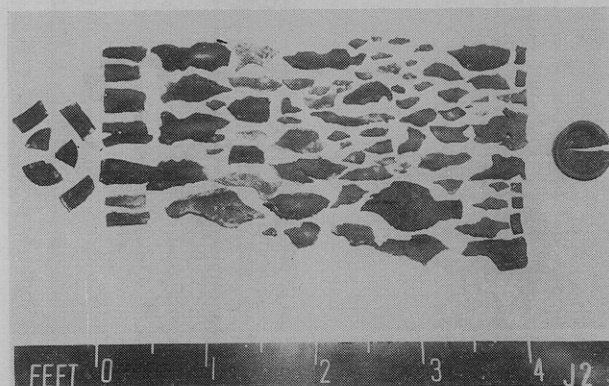


Figure 6. Schedule 120 seamless steel, vented ($1/8$ -inch) container fragmented by burning 15% sulfur plus brand E AN prills

pulverized mixtures of AN with 15% sulfur are more hazardous than hot prilled AN with 15% sulfur. Hot micropulverized AN containing 5% polyethylene (PE) was examined for comparison purposes and appears to represent a fuel contaminant of about the same hazard as 15% sulfur.

Carbonaceous fuels, as well as sulfur (1% carbonaceous material was assumed to be equivalent stoichiometrically to about 3% sulfur), contribute to the rate of burning (Van Dolah *et al.*, 1966). Pulverized AN mixtures fueled with 10% sulfur or 7% sulfur plus 1% PRP [PRP consists of a 1:3:1 weight ratio of petrolatum-rosin-paraffin blended into hot chemically pure AN to form a granulated product (gran.), -12, plus 60 mesh, which when micropulverized gives a product 44% through 200 mesh] were burned in the vented vessel; results were not very different

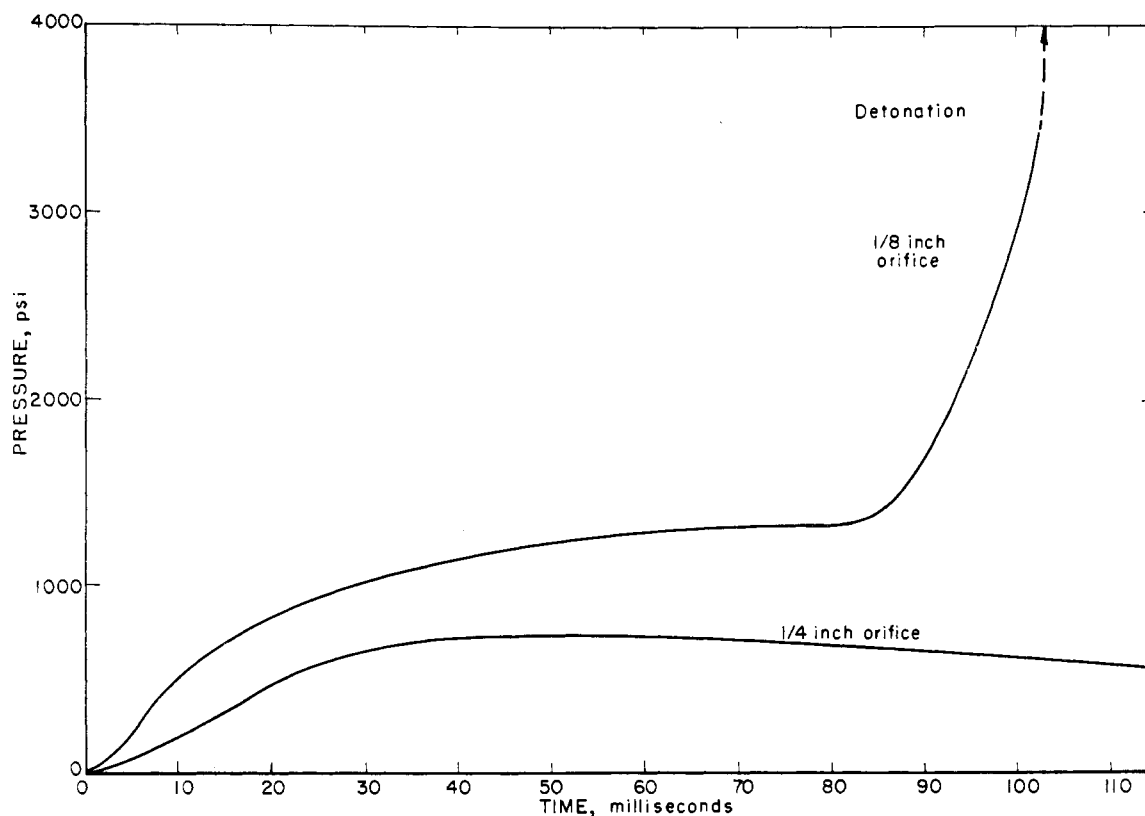


Figure 7. Pressure-time traces for 15% sulfur (–120-mesh) plus brand E AN prills (212° F.) burning in a vented vessel 3.15-inch I.D. by 4 feet long

Positive result giving a detonation obtained with a 1/8-inch orifice and negative result with a 1/4-inch orifice

from those with 15% sulfur. There did not appear to be a synergistic effect when the two types of fuels were used together. Thus, the presence of both PRP fuel and sulfur in stoichiometric AN mixtures gave no significantly different result than either of the fuels alone. Pulverized AN mixtures fueled with 15% dark (unrefined raw sulfur contaminated with a small amount of organic material) sulfur converted to a detonation more readily—that is, with a larger orifice than mixtures fueled with bright sulfur. For comparison, results for prilled AN, micropulverized AN, and prilled AN with 5% fuel oil are included in Tables V

and VI. A smaller orifice size was always required to give a deflagration to detonation transition when prilled instead of pulverized AN was used with the same amount of sulfur. These results appear in Tables V and VI in order of decreasing hazard.

Because of the catalytic effect of KCl on the decomposition of AN, and AN-containing fertilizer, discussed in detail below, a vented vessel evaluation was made of the effect of KCl on the deflagration to detonation transition. AN-S and AN-FO mixtures containing 1% KCl were investigated. Taking the orifice size as a hazard criterion,

Table V. Burning Behavior of Brand E Ammonium Nitrate–Sulfur Systems in 4-Foot Vented Vessels^{a, b}

Conditions	Positive Result ^c		Negative Result	
	Orifice, inch	Pressure, p.s.i.g.	Orifice, inch	Pressure, p.s.i.g.
AN + 15% S, pulverized, ignition at 212° F.,	0.438	1000	0.500	500
AN + 15% S, (dark), pulverized	0.375	500	0.438	880
AN + 10% S, pulverized	0.375	1200	0.438	<100
AN + 15% S, pulverized	0.313	^d	0.375	950
AN + 15% S, prills, ignition at 212° F.	0.188	1160	0.250	700
AN + 15% S, prills	0.125	1900	0.188	1940
AN + 10% S, prills	0.125	2200
AN + 5% S, prills	0.125	1100

^a All mixtures contained bright sulfur unless otherwise noted.

^b Ambient temperature 85° F. unless otherwise noted.

^c A positive result indicates that, at pressure given, the sample decomposed for about 100 to 150 milliseconds with little increase in pressure prior to a sudden increase in pressure, resulting in disintegration of the vessel. A negative result indicates that the pressure is the maximum pressure measured during the experiment.

^d In contrast to the other runs, the pressure rose continuously at a rate too fast to be recorded after ignition until disintegration of the vessel.

Table VI. Burning Behavior of Brand E Ammonium Nitrate-Fuel Systems in 4-Foot Vented Vessels^{a, b}

Conditions	Positive Result ^c		Negative Result	
	Orifice, inch	Pressure, p.s.i.g.	Orifice, inch	Pressure, p.s.i.g.
AN + 5% PE, pulverized ignition at 212° F.	0.438	1200	0.500	700
AN + 7% S + 1% PRP, pulverized	0.313	1100	0.375	700
AN + 5% fuel oil, prills	0.125	1700	0.188	1120
AN + 5% fuel oil + 1% KCl, prills	0.125	2250	0.188	1430
AN + 10% S + 1% KCl, prills	0.125	1975
AN + 7% S + 1% PRP, granular	0.125	2350
AN + 5% S + 1% KCl, prills	0.125	2450
AN, pulverized	0.125	6400

^a See footnote ^a, Table V.

^b See footnote ^b, Table V.

^c See footnote ^c, Table V.

no significant difference was noted between the samples with and without KCl. These results also appear in Table VI.

THERMAL STABILITY

Generally, the lower the temperature at which a reaction between chemical substances begins and the more energy that is released, the greater the hazard from fire exposure. Thermal stability is one means of estimating this hazard; differential thermal analysis (DTA) techniques may be employed to estimate thermal stability. The substance under investigation is heated at a predetermined rate and its temperature history, in comparison with that of a reference material, is carefully followed during the heating period. When chemical reaction or physical change takes place in the sample, heat liberated or absorbed causes the temperature in the sample to differ from the temperature in the comparison material; this difference in temperature (ΔT) is measured. The temperature at which chemical reaction or physical change begins is taken as the temperature where ΔT first becomes measurable (Garn, 1965).

The DTA apparatus used in this investigation consisted of an insulated cylindrical brass block, 3 inches O.D. by 7 inches long, wound with a heating element. Three holes, 1/2-inch diameter by 5 inches long, were bored in the block to receive glass test tubes used to contain the reference material, in this case potassium chloride, and two samples. Glass-encased thermocouples of 30 B & S gage Chromel-Alumel wire were inserted in the reference material and in each of the two samples. The differential thermocouple and reference thermocouple were connected to the X and Y axes of a two-pen XY recorder. The temperature of the reference material was obtained from the X axis readings of the recorder after suitable calibration. The temperature differential between the brass block and the reference material was less than 2° F. at the heating rates employed. The heating rate, 4° to 5° F. per minute, was controlled so that the temperature of the brass cylinder increased linearly with time. Figure 8 shows the effect of heating rate on the DTA traces. The drift from the base line is more pronounced at the faster heating rate (Figure 8A compared with Figure 8C) and obscures the start of mild endothermic and exothermic reactions at 212° and 430° F., respectively, which are seen in Figure 8. A heating rate of 4° to 5° F. per minute was chosen, since the discernment of phase change or reactions was adequate.

Sulfur-Ammonium Nitrate-Potassium Chloride Mixtures. The effect of sulfur on the decomposition of AN and of AN containing a small amount of potassium chloride was studied.

The DTA traces for these mixtures are shown in Figure 9. Figure 9A is a typical trace obtained for chemically pure ammonium nitrate (CP-AN), showing the phase changes below the melting point, the melting point at 338° F., the exothermic decomposition above 430° F., and the exothermic fume-off at 600° F. Comparing trace 9B with 9A shows that the addition of 5% sulfur (by weight) to AN caused no appreciable change in behavior. The addition of chloride ion as KCl to AN accelerates the decomposition with a pronounced exothermic reaction starting at 415° F. (Figure 9C). The introduction of KCl into AN-S caused the development of an exothermic reaction starting at about 240° F. near the melting point of sulfur. The evidence of an exothermic reaction at about 240° F. was always present to some extent in AN-KCl-S mixtures. Whenever a pronounced peak at about 240° F. was obtained with AN-KCl-S mixtures, nitrogen dioxide fumes were observed in the test tube above the sample.

Thermal Stability of Fertilizer Mixtures Containing Sulfur. The DTA technique was used to study the thermal stability of the 17 dry-blended fertilizer compositions listed in Table VII. These were prepared from c.p. and commercial fertilizer chemicals. Two commercial fertilizers containing sulfur were also examined. Analysis of these fertilizers and the components used are listed in Table VIII. The mixtures had a phosphorus to sulfur weight ratio of 1.3 to 1 and nitrogen to sulfur ratios which varied between 1 and 6. The synthetic fertilizers were compositions prepared from chemically pure AN (CP-AN), sulfur, monoammonium phosphate (MAP), diammonium phosphate (DAP), potassium chloride (KCl), and a laboratory preparation of triple superphosphate (TSP). Since commercial blends are made from fertilizer-grade chemicals, duplicates of several of the mixtures were prepared using fertilizer-grade AN, sulfur (dark and bright), diammonium phosphate (DAP), muriate of potash (KCl), and commercial TSP. Six of the mixtures which showed strong exothermic reactions were also prepared without sulfur to determine what effect sulfur had on their decomposition. Table IX summarizes the results and shows the temperature for the start of exothermic reactions with slow heating (4° to 5° F. per minute).

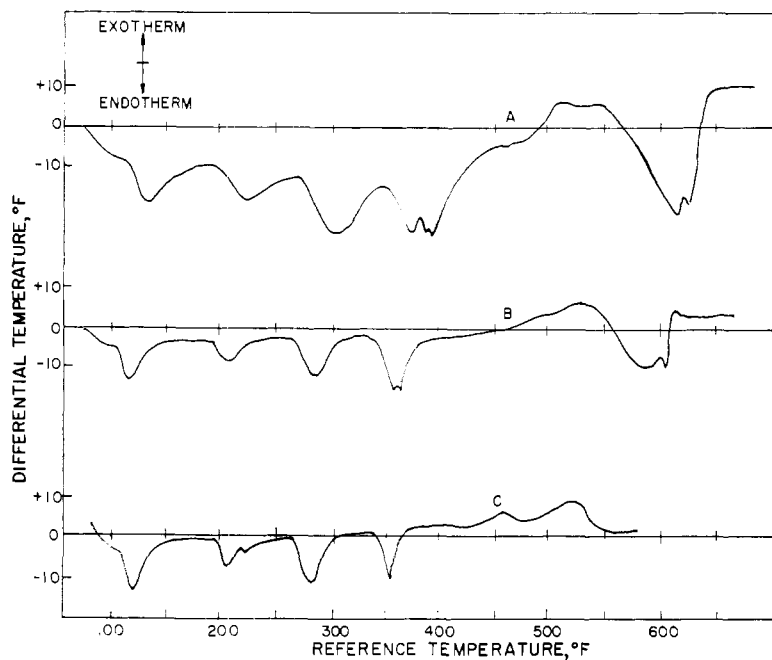


Figure 8. Differential thermal analysis of chemically pure AN at different heating rates

A. 12° F. per minute B. 4.7° F. per minute C. 2.5° F. per minute

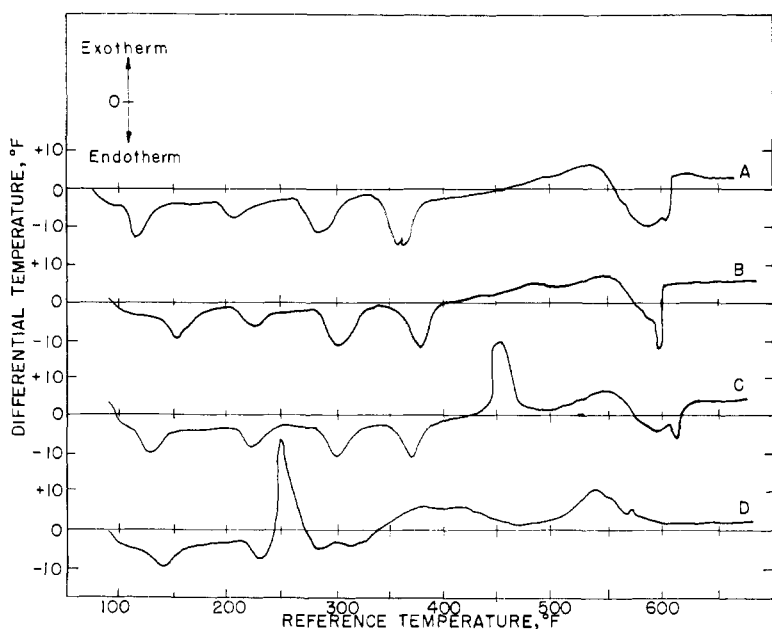


Figure 9. Typical DTA traces obtained with AN-S-KCl mixtures

A. AN, 100% B. AN/S, 95/5 C. AN/KCl, 99.5/0.5 D. AN/S, 95/5 plus 0.5% KCl

The DTA traces obtained for the 20-10-10 and the 28-14-0 mixtures are typical of the two different kinds of decompositions observed for these 17 various compositions. The 20-10-10 material prepared from c.p. compounds, using either MAP or TSP as the phosphate source, showed strong exothermic reactions beginning at about 350° F. whether sulfur was present or not. The DTA traces for these 20-10-10 mixtures are shown in Figure 10. The 28-14-0 material decomposed endothermically until 520° F., where a mild exothermic reaction occurred. The overall reaction was endothermic and this mixture gave identical results whether sulfur was present or not. The DTA traces for the 28-14-0 mixtures with and without sulfur are shown in Figure 11.

The start of exothermic reactions in the self-heating regions of AN for these fertilizers was due to chloride, since similar reactions occurred for the other AN-KCl systems (Figure 9, C and D) but were absent from the 10 chloride-free blends. Chloride catalyzes the decomposition of AN (Keenan and Dimitriadis, 1962). Two sets of each of the 28-14-0-5, 24-20-0-7, 24-12-0-4, and 20-16-0-5 mixtures were prepared, one from c.p. constituents and one from fertilizer-grade constituents. Mixtures made from fertilizer-grade constituents showed mild exothermic reactions beginning 50° to 150° F. earlier than the ones made from chloride-free c.p. constituents. The addition of 1% KCl to the c.p. blends gave results comparable with those obtained from the fertilizer-grade mixtures. This lower

Table VII. Formulation of Synthetic Fertilizer Materials Used

(Based on P/S = 1.3)

Formulation, N-P ₂ O ₅ -K ₂ O	Material, Grams					
	NH ₄ NO ₃	Elemental sulfur	TSP	MAP	DAP	KCl
28-14-0	1398	92	584	...
26-13-0	1384	86	...	542
24-24-0	964	160	1000	...
24-20-0	1161	132	...	834
24-20-0	1061	132	834	...
24-12-0	1439	80	534
23-23-0	940	152	959	...
22-22-0	1024	148	...	917
20-30-0	627	200	1250	...
20-16-0	1213	106	712
20-16-8	992	106	...	667	...	267
20-10-10	1200	66	445	334
20-10-10	1093	66	...	417	...	334
17-17-17	686	112	709	567
16-16-16	749	106	...	667	...	534
14-14-14	852	92	623	467
12-24-6	719	160	1067	200

Table VIII. Composition of Commercial Fertilizer Materials^a

Material	N Available				
	Total	NO ₃	P ₂ O ₅	K ₂ O	S
12-24-24-3S	10.9	1.0	20.1	24.8	3.7
10-20-30-3S	10.1	1.3	18.5	31.0	2.6
Triple superphosphate	44.5	...	1.9
Muriate of potash (KCl)	59.0	...
Diammonium phosphate	18.5	Nil	46.2

^a The authors are indebted to the Division of Chemical Development, Tennessee Valley Authority, for analysis of these materials.

Table IX. Temperatures for the Start of Exothermic Reactions in Different Fertilizer Blends

Fertilizer Composition N-P ₂ O ₅ -K ₂ O-S	Start of Exothermic Reactions, ° F.	Fertilizer Composition, N-P-K-S	Start of Exothermic Reactions, ° F.
28-14-0-0	500 W ^a	20-16-8-0	350 S
28-14-0-5 ^{*b}	450 W	20-16-8-5	350 S
28-14-0-5 ^{**c}	450 W	20-16-8-5 [*]	350 S
26-13-0-4	515 W	20-10-10-0 (TSP)	330 S
24-24-0-8	530 W	20-10-10-3 (TSP)	330 S
24-20-0-7	525 W	20-10-10-0 (MAP)	350 S
24-20-0-7 [*]	535 W	20-10-10-3 (MAP)	350 S
24-20-0-7 ^{**}	525 W	20-10-10-3 [*]	350 S
24-12-0-4	480 W	17-17-17-0	460 M
24-12-0-4 [*]	300 W	17-17-17-6	460 M
24-12-0-4 ^{**}	300 W	16-16-16-0	425 S
24-12-1-4	347 M	16-16-16-5	425 S
23-23-0-8	540 W	14-14-14-0	300 M
22-22-0-7	535 W	14-14-14-5	300 M
20-30-0-10	525 W	14-14-14-5 [*]	300 M
20-16-0-5	435 W	12-24-6-8	330 S
20-16-0-5 [*]	345 W	12-24-6-8 [*]	330 S
20-16-1-5	266 W		

^a 500 W means a weak exotherm ($\Delta T = 0^\circ$ to 10° F) observed starting at 500° F. M means a medium exotherm ($\Delta T = 10^\circ$ to 20° F.). S means a strong exotherm (ΔT over 20° F.).

^b Compositions marked with * prepared from commercial fertilizer components; all others from c.p. chemicals.

^c Compositions marked with ** used dark sulfur; all others used bright sulfur.

stability is attributed to the presence of chloride impurity. The 28-14-0-5 (DAP containing mixture), however, using either fertilizer-grade materials or c.p. constituents with the addition of 1% KCl, did not show any chloride effect. This is explained by the basic character of the DAP in the AN melt which would probably stabilize the AN decomposition. There was no measurable difference observed in the stability of mixtures prepared from commercial grade dark sulfur or bright sulfur.

The application of the DTA technique to commercial fertilizers to determine the temperature for the start of reaction and the approximate heats of reaction was demonstrated by using two different commercial fertilizers. The two grades, 10-20-30-3S and 12-24-24-3S, were ground to pass -100-mesh and their DTA traces compared with the granular mixtures as received. The granulated materials contain about 3% water by weight, which was lost on grinding in air. The DTA traces for these runs are shown in Figure 12 for both grades, powdered and granular. The pronounced endotherm near the boiling point of water in the traces for the granular material is noticeably absent from the traces for the powdered materials. After the melting region, beginning at 300° F., the traces for the powdered and granular samples are about the same. The ΔT is shifted somewhat because of heat capacity differences between the reference and the samples for the 12-24-24-3 material. The exothermic area (between the ΔT curve and the base line) at about 500° F. is not, however, directly related to the total heat evolved, since bubbling occurred and there is poor thermal contact between the sample and the thermocouple.

The thermal stability of four European nitrophosphate fertilizers, 13-10-13 with and without 3% sulfur and 22-16-0 with and without 3% sulfur, was examined. These fertilizers differ from domestic fertilizers in the method of manufacture.

The 13-10-13 material was made by the P.E.C. carbonitric process. Phosphate rock is acidulated with nitric acid, producing a slurry of phosphoric acid and calcium nitrate. The slurry is treated with ammonia and carbon dioxide.

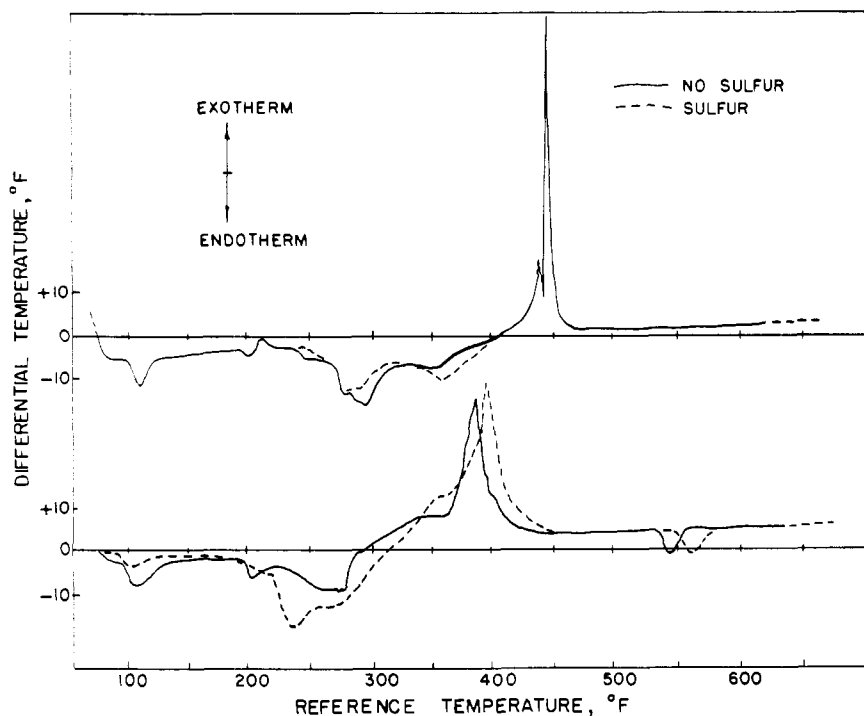


Figure 10. Differential thermal analysis of 20-10-10 fertilizer showing effect of 3% elemental sulfur (top, MAP; bottom, TSP) base

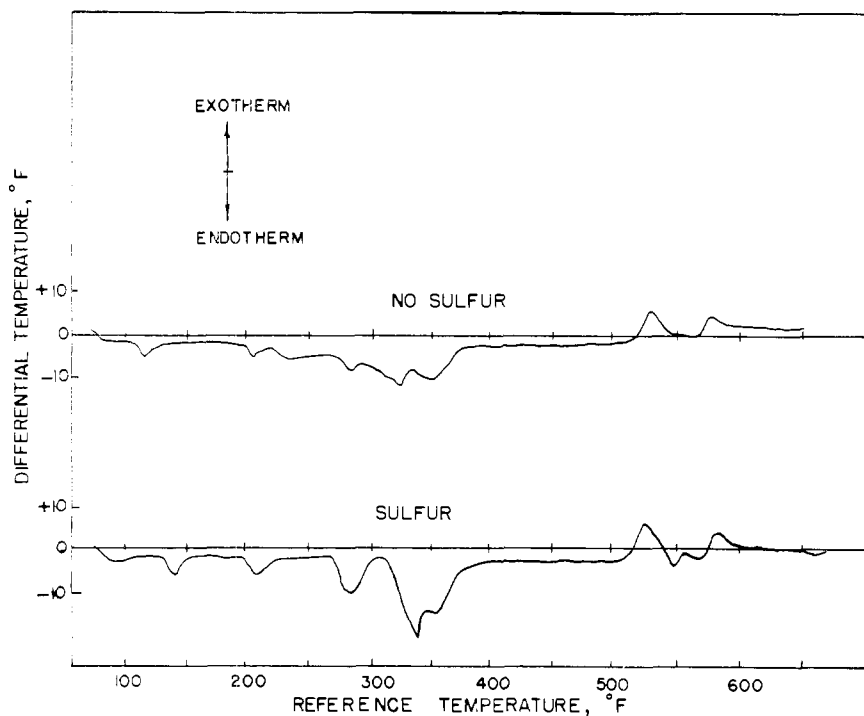


Figure 11. Differential thermal analysis of 28-14-0 fertilizer showing effect of 3% elemental sulfur

The end product contains dicalcium phosphate, ammonium nitrate, calcium carbonate, and potash, which is added as potassium chloride. It also contains a small amount of magnesium sulfate which functions as a stabilizer.

The 22-16-0 material was made by the ODDA process. In this process, rock is also acidulated with nitric acid, but the undesirable calcium nitrate is removed by physical means (crystallization), instead of chemical conversion (as in P.E.C.). The remaining slurry is ammoniated, and the end product contains dicalcium phosphate, monocalcium phosphate, and ammonium nitrate.

The thermal stability of the nitrophosphate fertilizers was similar to that of domestic fertilizers having the same approximate composition (Figure 13). The addition of sulfur did not materially affect the thermal stability.

Thermal Stability of Ammonium Nitrate-Fuel Systems.

The effect of other fuels on AN thermal stability was studied to obtain data comparative with those for AN-S systems. AN with 6% fuel oil gave results similar to pure AN and AN-S (Figures 14A and 9, A and B). AN with 6% polyethylene powder (50 mesh) (AN-PE) showed an exothermic reaction starting at 410° F. which became

Figure 12. Differential thermal analysis of two commercial fertilizers showing a change when powdered due to water loss

A. Powdered 10-20-30-3S B. Granular 10-20-30-3S C. Powdered 12-24-24-3S D. Granular 12-24-24-3S

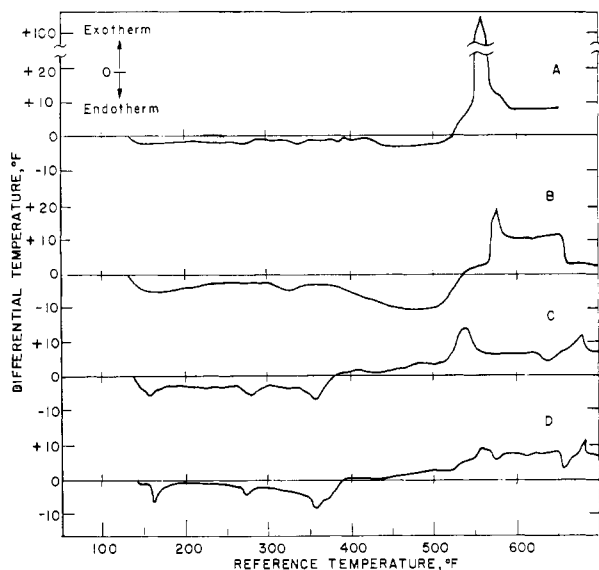
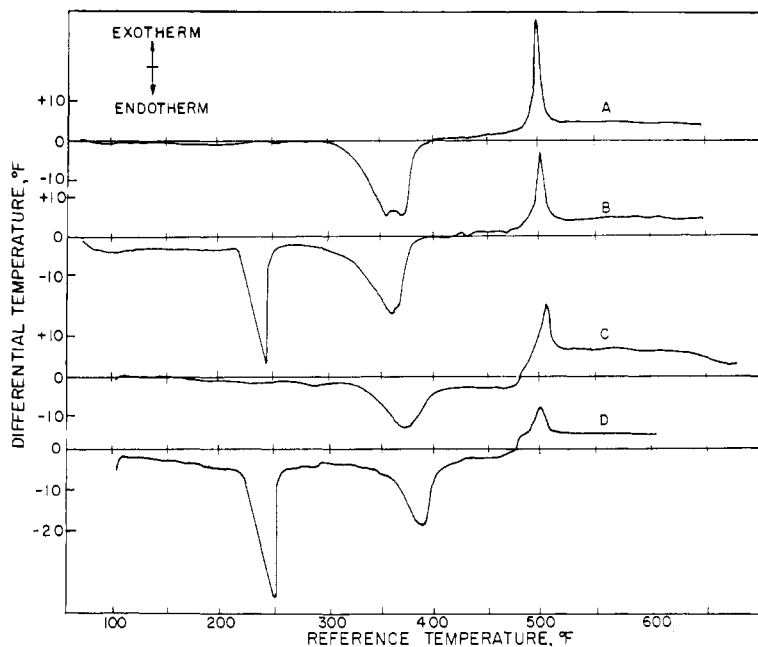


Figure 13. Differential thermal analysis of nitrophosphate fertilizers showing effect of 3% elemental sulfur

A. 13-10-13-3 B. 13-10-13-0 C. 22-16-0-3 D. 22-16-0-0

pronounced at 510° F. (Figure 14B), in contrast to the absence of any pronounced exothermic reaction with AN fueled with sulfur (Figure 9B) or fuel oil (Figure 14A). When 0.5% of KCl was added to AN-FO, an exothermic reaction was observed at 410° F. (Figure 14C). The addition of 0.5% KCl to the AN-PE system resulted in a pronounced exothermic reaction starting at 410° F. (Figure 14D). In two trials this material spontaneously ignited at 525° F.

The addition of urea, diammonium phosphate (DAP), or monoammonium phosphate (MAP) to AN, although potential fuels, has little effect and even appears to have stabilized the decomposition (Figure 15). This is probably due in part to the inhibition of the acid-catalyzed exothermic

mic reactions by basic salts in the melt. Urea, for example, is known to stabilize the decomposition of AN (Rozman and Brodtkins, 1959). Significant fuel-oxidizer reactions of AN (decomposition products) with urea, DAP, and MAP apparently do not take place until higher temperatures (greater than 550° F.).

A brief investigation of the effect of zinc contamination on AN decomposition was made by obtaining DTA traces on mixtures of zinc dust, zinc sulfate, and zinc oxide with chemically pure AN. The zinc concentration was maintained at 1% by weight for the zinc dust mixture and at 7% for the zinc sulfate and oxide mixtures.

In agreement with reports in the literature, zinc dust mixtures exhibited an exothermic reaction beginning at 370° F. just after the melting point of AN, followed by a strong exothermic reaction at the AN fume-off temperature (Charmandarian, 1952; Rogers, 1962; Varma and Sen, 1965). Zinc oxide stabilized the AN decomposition to about the AN fume-off temperature (550° F.) where a strong exothermic reaction occurred. Comparison of the DTA trace between zinc oxide (Figure 16) and urea, MAP, and DAP additives in AN (Figure 15) shows a similar stabilizing effect on the AN decomposition up to 550° F.

CONCLUSIONS

The possible sensitizing effect of sulfur on AN under conditions of exposure to fire or shock is of concern in the transportation and storage of large quantities of nitrogenous fertilizer materials. The detonability and thermal stability of AN-S mixtures were examined. The results may be compared with those obtained for other fuels and reported in a recent comprehensive study on AN in this laboratory (Van Dolah *et al.*, 1966).

AN-S systems were detonable, as is to be expected. However, relative to other detonable materials, such as commercial explosives, AN-S systems are very insensitive—that is, difficult to initiate—and have large critical di-

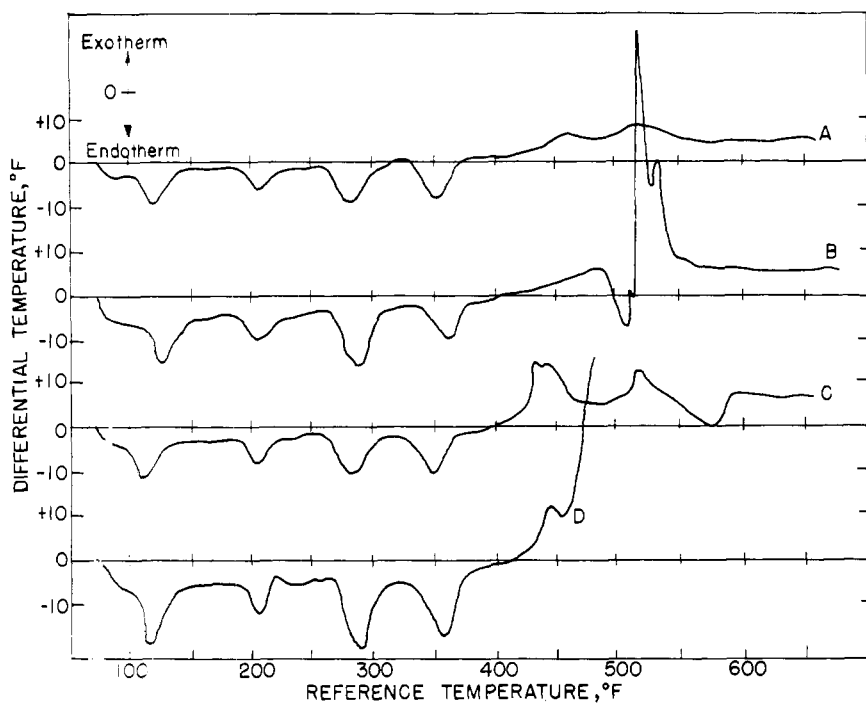


Figure 14. Typical DTA traces obtained with AN-fuel mixtures

- A. AN-FO, 94/6
- B. AN-PE, 94/6
- C. AN-FO, 94/6 plus 0.5% KCl
- D. AN-PE, 94/6 plus 0.5% KCl

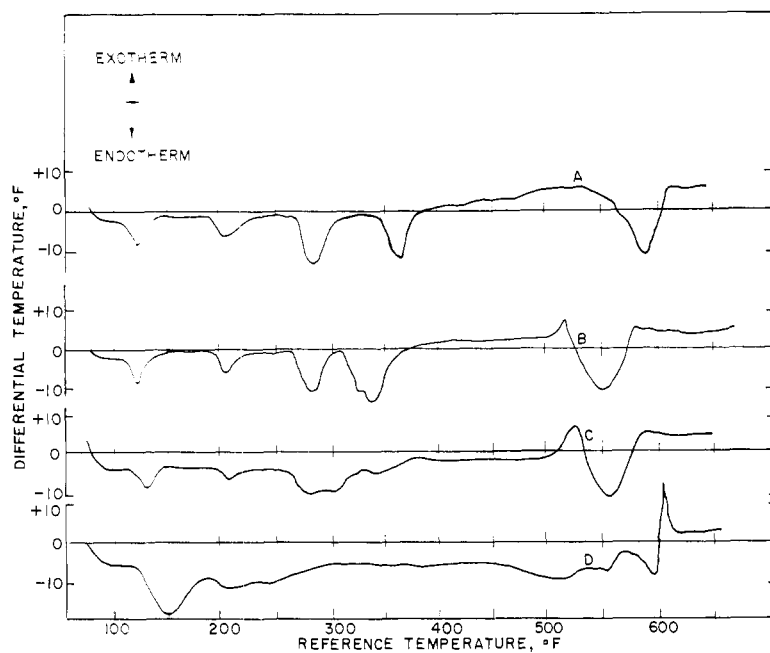


Figure 15. Differential thermal analysis of C.P. AN showing effect of added monoammonium phosphate (MAP), diammonium phosphate (DAP), and urea

- A. 100% C.P. AN
- B. 20% MAP, 80% C.P. AN
- C. 20% DAP, 80% C.P. AN
- D. 20% urea, 80% C.P. AN

ameters at ordinary temperatures. To detonate prilled AN-S mixtures in 1½-inch-diameter charges, for example, it was necessary to heat the material above 140° F. A shock stimulus of about 100 kilobars was required to initiate 3-inch-diameter charges at 100° F.

The combination of AN-S mixtures with other fertilizer constituents, such as potassium chloride and triple superphosphate to the extent of 20% or more, gave mixtures which did not detonate in the charge sizes used, indicating a desensitizing action or an increase in critical diameter. It seems unlikely, considering the magnitude of shock pressures used as initiation sources, that detonation would

be achieved with fertilizer mixtures of this type under conditions of fire exposure.

The possible transition to detonation as a consequence of fire exposure was also considered. Initial pressures in excess of 1000 p.s.i. were necessary to initiate a burning reaction with AN-S mixtures capable of accelerating to detonation. Such pressures might be achieved in many ways, such as a collapsing pile of burning AN-S, a heavy roof falling onto the burning mixture, or the explosive rupture of a heated, closed vessel or pipe in contact with the burning AN-S. These stimuli could start combustion rapid enough to lead to a detonation, particularly when started at the

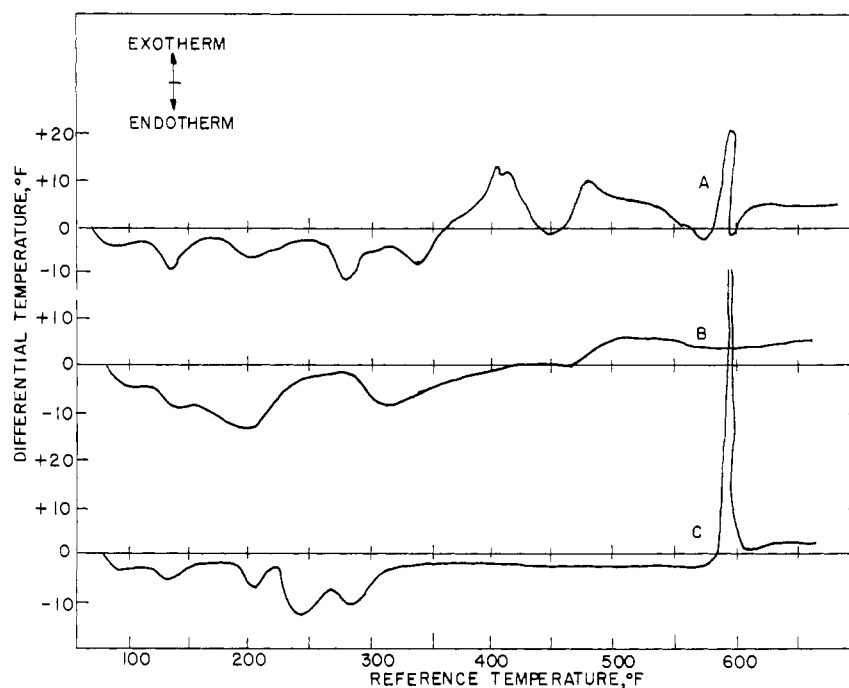


Figure 16. Differential thermal analysis of C.P. AN showing effect of zinc dust, zinc sulfate, and zinc oxide

A. 1% Zn dust B. 31% $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ C. 9% ZnO

center of a large pile, since the inertia of the AN-S may prevent sufficiently rapid release of the pressure. Even so, a deflagration to detonation transition (DDT) would appear improbable under most storage conditions. The admixture of other fertilizer materials desensitizes the AN-S mixtures to explosive shock and further reduces the probability of a transition from burning to detonation.

Examination of the thermal stability data shows that the thermal decomposition of AN does not appear to be significantly affected by the presence of sulfur. The addition of sulfur to AN-containing fertilizers also had no effect on the thermal decomposition of the fertilizer mixtures (in the absence of KCl). Evidence of a synergistic effect between KCl and sulfur appears in Figure 9, where there is the development of a strong exotherm after the melting point of sulfur (about 240° F.). One can postulate a reaction between molten sulfur and the nitrogen dioxide which is known to be produced in the chloride-catalyzed decomposition of AN (Keenan and Dimitriades, 1962). All sulfur-containing fertilizer mixtures with KCl were less stable than similar ones without KCl.

The three methods of evaluation all show that sulfur added to AN increases the hazard; in fire exposure, however, it was impossible to predict the specific effect to be observed in any one method from the results of another method.

LITERATURE CITED

- Charmandarian, M. O., *Bull. Soc. Chim. France* **1952**, pp. 975-6.
 Dixon, W. J., Massey, F. J., Jr., "Introduction to Statistical Analysis," 2nd ed., pp. 318-27, McGraw-Hill, New York, 1957.
 Garn, P. D., "Thermoanalytical Methods of Investigation," 1st ed., Academic Press, New York, 1965.
 Griffiths, N., Grocock, J. M., *J. Chem. Soc.* **1960**, pp. 4154-62.
 Joint Army-Navy-Air Force Panel on Liquid Propellant Test Methods, "Test No. 1, Card Gap Test for Shock Sensitivity of Liquid Monopropellants," Liquid Propellant Information Agency, Applied Physics Laboratory, Johns Hopkins University, Silver Spring, Md., 1960.
 Keenan, A. G., Dimitriades, B., *J. Chem. Phys.* **37**, 1583-6, (1962).
 Maček, A., *Chem. Rev.* **62**, 41-63 (1962).
 Rogers, R. N., *Ind. Eng. Chem., Prod. Res. Develop.* **1**, 169-72 (1962).
 Rozman, B. Y., Brodskins, L. I., *J. Appl. Chem. U.S.S.R. (Zh. Prikl. Khim.)* No. **32**, 291-4 (January-June 1959).
 Statistical Research Group, Princeton University, "Statistical Analysis of a New Procedure in Sensitivity Experiments," Report to Applied Mathematics Panel, National Defense Research Committee No. 101.1R, July 1944, available on microfilm from Office of Technical Services, U.S. Dept. of Commerce, Washington, D.C.
 Van Dolah, R. W., Mason, C. M., Perzak, F. J. P., Hay, J. E., Forshey, D. R., *Bur. Mines Rept. Invest.* **6773** (1966).
 Varma, S., Sen, D. K., *Technol., Sindri, India* **2** (1), 43-5 (1965).

Received for review May 2, 1967. Accepted June 19, 1967.
 Report based, in part, on work done under a cooperative agreement with the Sulphur Institute, Washington, D.C.