EXPLOSION HAZARDS OF AMMONIUM NITRATE UNDER FIRE EXPOSURE

By R. W. Van Dolah, C. M. Mason, F. J. P. Perzak,
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ABSTRACT

An attempt has been made in this investigation to define the conditions under which ammonium nitrate (AN) might detonate as a result of involvement in fire. The initiation of detonation by shocks derived from explosives or from projectile impact was investigated as a function of temperature and charge diameter. A new technique was devised to investigate the burning of raw and contaminated AN under pressure. No transition to detonation in AN was obtained in the burning experiments. The critical diameter for detonation of fertilizer-grade AN was found to be quite small when the AN was at temperatures just below melting point; this indicates that initiation of detonation may be less difficult at elevated temperatures but such initiation by gas-phase detonation was shown to be unlikely. Transition from burning to detonation was obtained with AN intimately mixed with fuels that included polyethylene, paper, and fuel oil when these were contained in vessels with restricted vents. However, the experimental results supported by an analytical study indicate that the initiation of detonation in AN from fire exposure in normal storage and from transportation incidents is quite improbable. The detonation of AN in recent incidents more likely may have resulted from the effects of adjacent explosions.

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INTRODUCTION

The conditions under which AN may explode when subjected to intense fire exposure have never been satisfactorily defined. Debate still continues on the exact causes of the four ship explosions that involved AN from 1947 to 1948, but since the AN involved in the ship explosions was an organic coated material whose burning characteristics are substantially different from presently manufactured fertilizer-grade AN, the chance of the latter detonating as the result of fire has been considered to be small or even nonexistent. The record[6] of present-day AN in fires during storage and transportation is very reassuring, with one exception. On December 17, 1960, near Traskwood, Ark., a 23-freight car derailment occurred following a journal box failure on one of the cars in the train.[7] Included were one car of AN bagged and one car of bulk AN as well as a wide variety of other materials including nitrogen-fertilizer solution, fuming nitric acid, petroleum products and paper. An intense fire occurred and subsequently through unknown circumstances the car of bagged AN detonated.

The Bureau of Mines was asked in 1961, by the Manufacturing Chemists' Association, to undertake an investigation of the potential explosion hazards of fertilizer-grade AN under the conditions of fire exposure that could occur in storage and transportation incidents. Attention was to be paid to effects of possible contamination of AN during fires, and particularly an attempt was to be made to define the potential causes of the explosion at Traskwood.

The program of investigation extended 3 years; this report comprises a summary of the new information on the potential detonability of AN that was developed during that period. The program was largely experimental with emphasis placed on the possibilities of initiation of AN by a shock derived through projectile impact, or by the detonation of adjacent explosive systems, or by accelerated burning of AN or AN-fuel systems. Transition from burning to detonation is commonly encountered in the case of sensitive and energetic explosives, but the susceptibility of AN systems to this transition had not previously been subjected to detailed study. The program included some field trials in which AN systems were exposed to fire in quantities up to about 2.5 tons. Furthermore, the problem of hazards of AN was explored analytically, particularly with attention to the effects of scale on the possibility of AN undergoing detonation if involved in fire.

Before the detonability of actual AN systems is discussed, a brief introduction to the processes involved in initiation of detonation is appropriate. The initiation processes in liquids and solids that result from impact of intense shocks are different, according to best interpretations available.[8] In the case of solids, which in reality are packed beds with varying ratios

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[6] Babcock, C. I. Ammonium Nitrate--Behavior in Fires. Nat. Fire Protect. Assoc. Quart., v. 53, No. 3, January 1960, pp. 217-230.

[7] Taylor, W. J., Jr. Safe Handling of Blasting Agents. Nat. Fire Protect. Assoc. Quart., v. 56, No. 3, January 1963, pp. 261-266.

[8] Maĉek, A. Sensitivity of Explosives. Chem. Reviews, v. 62, 1962, pp. 41-63.

of solid to gas phases in all cases except monolithic crystals, the shock wave primarily heats the gas in the interstices spaces to extremely high temperatures; the hot gas in turn ignites the solid particles which subsequently burn as individual grains. Other mechanisms, such as impact, friction, and shear involving the solid directly, may make important contributions to the generation of high temperatures as well as cause the original particles to break up. Fine crystals are more readily ignited than large ones, and will react faster because of a larger surface area for burning. Bulk density plays an important role as well; the lower the density the more readily the system can be brought to detonation. For example, cast trinitrotoluene (TNT) is very difficult to initiate compared to low-density, fine-grained TNT charges. Further, the initial shock need not have an amplitude adequate for immediate initiation of detonation, as the burning explosive can cause the pressure in the shock to increase leading to growth to steady state detonation which occurs some distance down the charge.[9] This concept is treated in more detail under "Discussion."

In contrast, liquids normally present no correspondingly large surface area and contain no air voids. In this case, initiation requires that the bulk liquid be heated by direct compression by the shock wave (liquids are quite compressible when pressures range from 10^4 to 10^6 psi). The liquid bulk temperature must be high enough to make the reaction self-sustaining. Detonation begins at the surface first subjected to the shock wave and the process becomes steady state. However, when some energetic liquid explosives are involved, a surface burning reaction can take place after weak shocks have caused the liquid to cavitate, leading to a low velocity detonation. In this case, the liquid behaves analogously to granular solids.

For both solids and liquids it is important that the charge diameter must be greater than some critical diameter for detonation to be initiated and for the detonation to propagate. Many liquids and solids have large critical diameters and thus fail to detonate in the test procedures. Although such results can be interpreted as indicative of low hazard potential, they should not be taken to mean that the material is incapable of detonation.

Raw AN[10 11] and AN-fuel mixtures have large critical diameters at ordinary temperatures and this property has tended to obscure their behavior under the impact of intense shock waves. But critical diameter is related to sensitivity, in the overall sense, as it is a function of the ease with which energy is released (activation energy), the amount of energy released per unit quantity, and the rate of energy release (reaction zone thickness). Materials like solid AN react partially and support the detonation wave with less than full energy release, when the charge diameter is greater than the critical diameter but less than the so-called ideal diameter at which detonation proceeds at maximum velocity. At the same time, the small-diameter charges

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[9] Griffiths, N., and J. M. Groocock. The Burning to Detonation of Solid Explosives. J. Chem. Soc., 1960, pp. 4154-4162.

[10] The term "raw AN" will be frequently used to mean any commercial prill (or Stengel process) grade of AN without added fuel.

[11] Winning, C. H. Detonation Characteristics of Prilled Ammonium Nitrate. Fire Technol., v. 1, 1965, pp. 23-31.

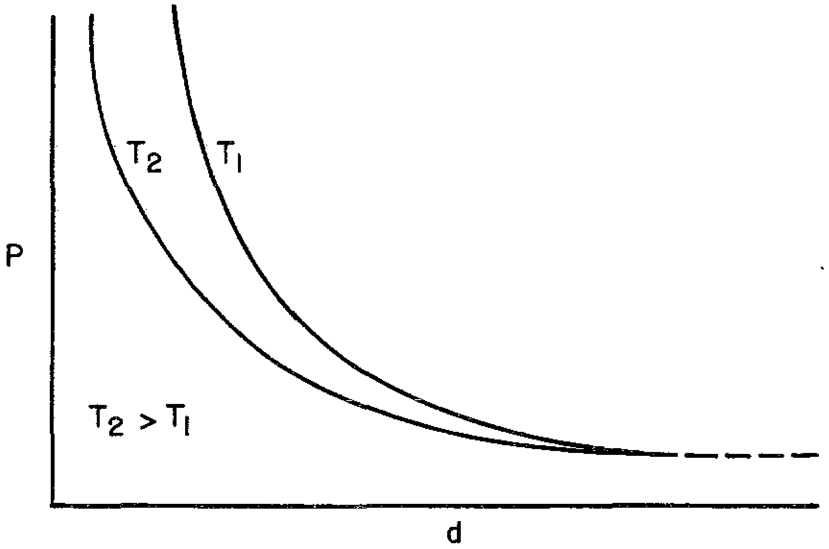

FIGURE 1. - Effects of Diameter (d) and Temperature (T) on the Pressure (P) Required for Initiation.

require higher amplitude shocks for initiation. A generalized relationship between shock pressure and charge diameter for two temperatures is given in figure 1. Thus for a given temperature there is a minimum diameter below which no shock is capable of initiating detonation (critical diameter); similarly, a minimum shock pressure is indicated for initiation of detonation at infinite charge diameters. A higher temperature reduces the required initiating pressure at a given charge diameter; or conversely, higher charge temperature leads to a lower critical diameter.

One commonly used technique for measuring ease of initiation of detonation is the card gap test.[12] With it, sensitivity is related to the ease of initiation of high velocity detonation in a test sample by an explosive-derived shock wave. The amplitude of the shock wave may be varied over the range of 5 to over 200 kilobars (1 kilobar approximately equals 1,000 atmospheres) by inserting a stack of cellulose acetate cards or polymethyl methacrylate disks between a standard explosive donor and the sample.

Because of the differences in initiation mechanisms, direct comparisons cannot be made between the gap values for liquid and for solid systems. Further, gap values serve reliably to differentiate the sensitivity of materials of the same physical state only when the charge size is substantially greater than the critical diameters of the materials and when experimental conditions are maintained as identical as possible. A complication for liquids is that they must always be in a container and experience has shown that the geometry of the container, its wall thickness and density as well as the nature of the material of construction may contribute materially to the results obtained. Thus, one cannot arbitrarily take the numerical results obtained in the gap test without considering the factors and experimental conditions.

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[12] Joint Army-Navy-Air Force Panel on Liquid Propellant Test Methods. Test No. 1, Card Gap Test for Shock Sensitivity of Liquid Monopropellants. John Hopkins University, Applied Physics Laboratory, The Liquid Propellant Information Agency, Silver Spring, Md., 1960.

DETONABILITY OF AMMONIUM NITRATE AND RELATED SYSTEMS

Shock sensitivity data are presented for AN prills at ambient and at elevated temperatures, molten AN, AN-fuel mixtures, solid mixtures of AN and urea, molten AN and urea, and certain hydrocarbon-nitric acid combinations, which all conceivably could have been involved in the explosion at Traskwood. The materials used in this program are described in appendix A.

Sensitivity to Explosives-Derived Shocks

The modified card gap test A, as described in appendix B, was used in the early investigations. Subsequently, a modified test B was used because this configuration gave more definitive results. With both configurations sensitivity is expressed in terms of a gap value; that is, the thickness of cards (cellulose acetate wafers) in the gap between the explosive donor and the material being tested for which there is a 50-percent probability that a sustained detonation will be initiated in the acceptor charge (test sample). This gap value is usually determined by an experimental design called the "up and down method" and described by Dixon and Massey.[13]

Solid Ammonium Nitrate

Earlier attempts to determine the shock sensitivity of solid AN prills by the modified card gap test A described in appendix B yielded only qualitative results. Thus AN prills showed increased ease of initiation at elevated temperatures and the liquid AN at 180° C was less readily initiated than the hot prills as anticipated. Clay-coated prills showed less sensitivity than uncoated prills under the same experimental conditions, although they too could be initiated at increased charge diameters and elevated temperatures.

The instrumented method, modified card gap test B described in appendix B, was used to evaluate the shock sensitivity of solid AN prills at various temperatures more precisely. At elevated temperatures the prilled AN and the steel containers were preheated in an electric laboratory oven for about 4 hours to allow the sample to equilibrate at the desired temperature. Four commercial prills were investigated (brands A, E, G, and H). Samples were contained in 1½-inch schedule 40 seamless steel pipe (1.61-inch id by 0.145-inch wall by 16-inch length) and 160-gram tetryl boosters (2-inch diameter by 2-inch length, density 1.57 grams per cubic centimeter) were used. The shock intensity was varied by an attenuator (cellulose acetate wafers) between the donor and acceptor charges, as described for the up and down method. Five trials were made at each temperature. Where detonation was observed, the 50-percent gap value was then determined with 20 trials at each point. Results are given in table 1.

As expected, the shock sensitivity of solid AN prills increased with increasing temperature--really a manifestation of critical diameter as suggested by figure 1; it varied somewhat from one brand to another. At elevated temperatures the most sensitive sample found was brand E, the least sensitive

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[13] Dixon, W. J., and F. J. Massey, Jr. Ch. 19 in Introduction to Statistical Analysis. McGraw-Hill, New York, 2d ed., 1957, pp. 318-327.

brand H. The average rates of detonation varied from 1,900 to 2,040 meters per second (6,230 to 6,690 ft/sec) and did not change significantly with increasing temperature or brand of prill. The pressure delivered to the transducer by the acceptor charge when a detonation was obtained was independent of the temperature of the sample or the brand of prilled AN. The recorded pressures developed in the AN varied from 18 to 22 kilobars, within the range of reproducibility expected for the transducers.

TABLE 1. - Shock sensitivity and detonation rate of ammonium nitrate prills as a function of temperature[1]

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

Type AN	ρ, g/cm^3	20° C	100° C	120° C	140° C
Brand A.................	0.79	0/5	0/5	0/5	[2]3/5
Brand E.................	.81	0/5	0/5	([3])	([4])
Brand G.................	.98	0/5	0/5	0/5	[5]3/5
Brand H.................	.79	0/5	0/5	0/5	1/5

[1] Zero gap unless otherwise shown. Contained in schedule 40 seamless pipe (1.61-inch id by 0.145-inch wall by 16-inch length) 160-gram tetryl donor.
[2] Average rate for 3 trials, 1,900 m/sec.
[3] Average rate for 5 trials, 2,020 m/sec. 50-percent value, 0.16-inch gap.
[4] Average rate for 5 trials, 2,040 m/sec. 50-percent value, 1.16-inch gap.
[5] Average rate for 3 trials, 1,960 m/sec.

Under these experimental conditions, particularly with the charge diameter used, a self-sustaining detonation was achieved only above 100° C for the more sensitive brands of prilled AN and only above 120° C for a less sensitive grade of AN (brand H).

In order to better determine the relationship between critical diameter, confinement, and temperature for AN prills, a series of charges of various diameters from 1½ to 12 inches were fired. Pressed tetryl pellets (density 1.57 grams per cubic centimeter) were used as boosters. The weight of tetryl was scaled with the diameter of the charge. For charges larger than 3 inches, composite boosters were formed by clustering pellets on the face of the charge, initiating these simultaneously by a single centered booster. The data are assembled in table 2. The effect of the heavier confinement in reducing the critical diameter is clearly shown by the shift of the curves to the left in figures 2 and 3. The effect of temperature in decreasing the critical diameter is also apparent.

TABLE 2. - The effect of temperature on the detonability of prilled ammonium nitrate at different diameters in a 24-inch charge

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

	Heavy confinement,[1] diameter and booster weight								Light confinement,[2] diameter and booster weight									
	1½ inch, 160 g		2½ inch, 360 g		4 inch, 320 g		6 inch, 640 g		3 inch, 360 g		4 inch, 320 g		6 inch, 640 g		8 inch, 1,280 g		12 inch, 1,440 g	
	° C	In.	° C	In.	° C	In.	° C	In.	° C	In.	° C	In.	° C	In.	° C	In.	° C	In.
Brand A prills:																		
Test 1..............	140	3/5	90	2/2	71	1/1	21	1/1	140	0/2	140	1/5	75	1/1	45	1/1	20	1/1
Test 2..............	120	0/5	80	1/1	50	1/1	-	-	120	0/1	130	0/1	[3]65	1/1	35	1/1	-	-
Test 3..............	100	0/5	75	1/2	40	1/1	-	-	-	-	90	0/1	54	1/1	-	-	-	-
Test 4..............	-	-	-	-	34	0/1	-	-	-	-	84	0/1	[3]45	0/1	-	-	-	-
Test 5..............	-	-	-	-	-	-	-	-	-	-	75	0/1	-	-	-	-	-	-
Brand E prills:																		
Test 1..............	140	5/5	70	1/1	35	1/1	20	1/1	140	0/2	130	1/1	50	1/1	30	1/1	20	1/1
Test 2..............	120	5/5	66	0/1	28	0/1	-	-	120	0/1	125	1/3	40	1/1	26	1/1	-	-
Test 3..............	100	0/5	65	0/1	-	-	-	-	-	-	120	0/1	35	0/1	22	0/1	-	-
Test 4..............	-	-	65	0/1	-	-	-	-	-	-	80	0/1	30	0/1	21	0/1	-	-
Test 5..............	-	-	-	-	-	-	-	-	-	-	74	0/1	-	-	-	-	-	-
Test 6..............	-	-	-	-	-	-	-	-	-	-	65	0/1	-	-	-	-	-	-

[1] Schedule 40 steel pipe.

[2] 24- to 28-gage stove pipe except as indicated by footnote 3.

[3] ¼-inch-wall cardboard tube.

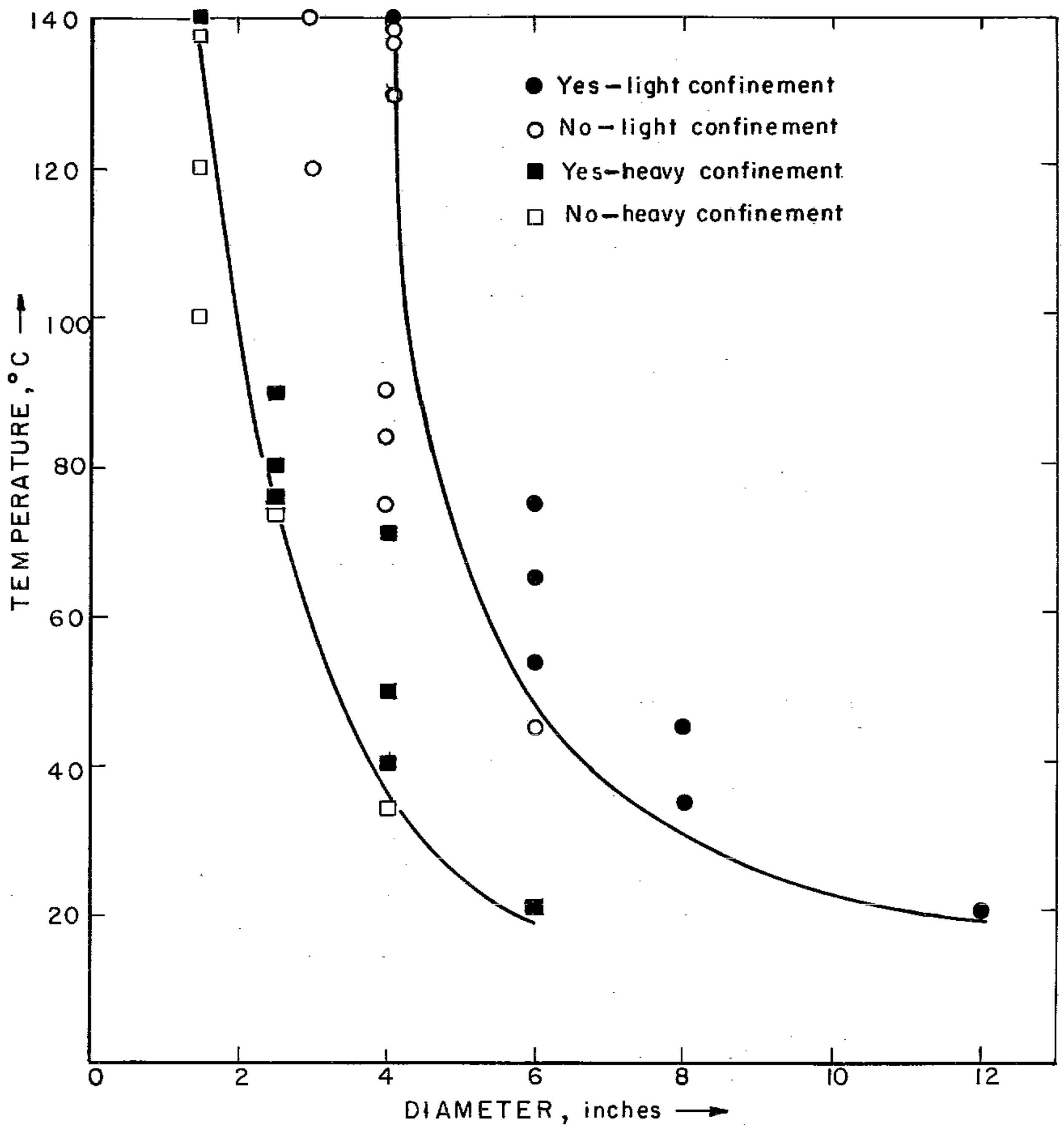

FIGURE 2. - Shock Sensitivity of Brand A Prills.

Ammonium Nitrate-Fuel Oil

The effect of water on the shock sensitivity of brand E AN-FO mixtures was determined using the card gap method. Samples contained in 1½-inch schedule 40 seamless steel pipe were shocked by 160-gram tetryl boosters. The addition of 5 and 10 percent water increased the sensitivity as shown by

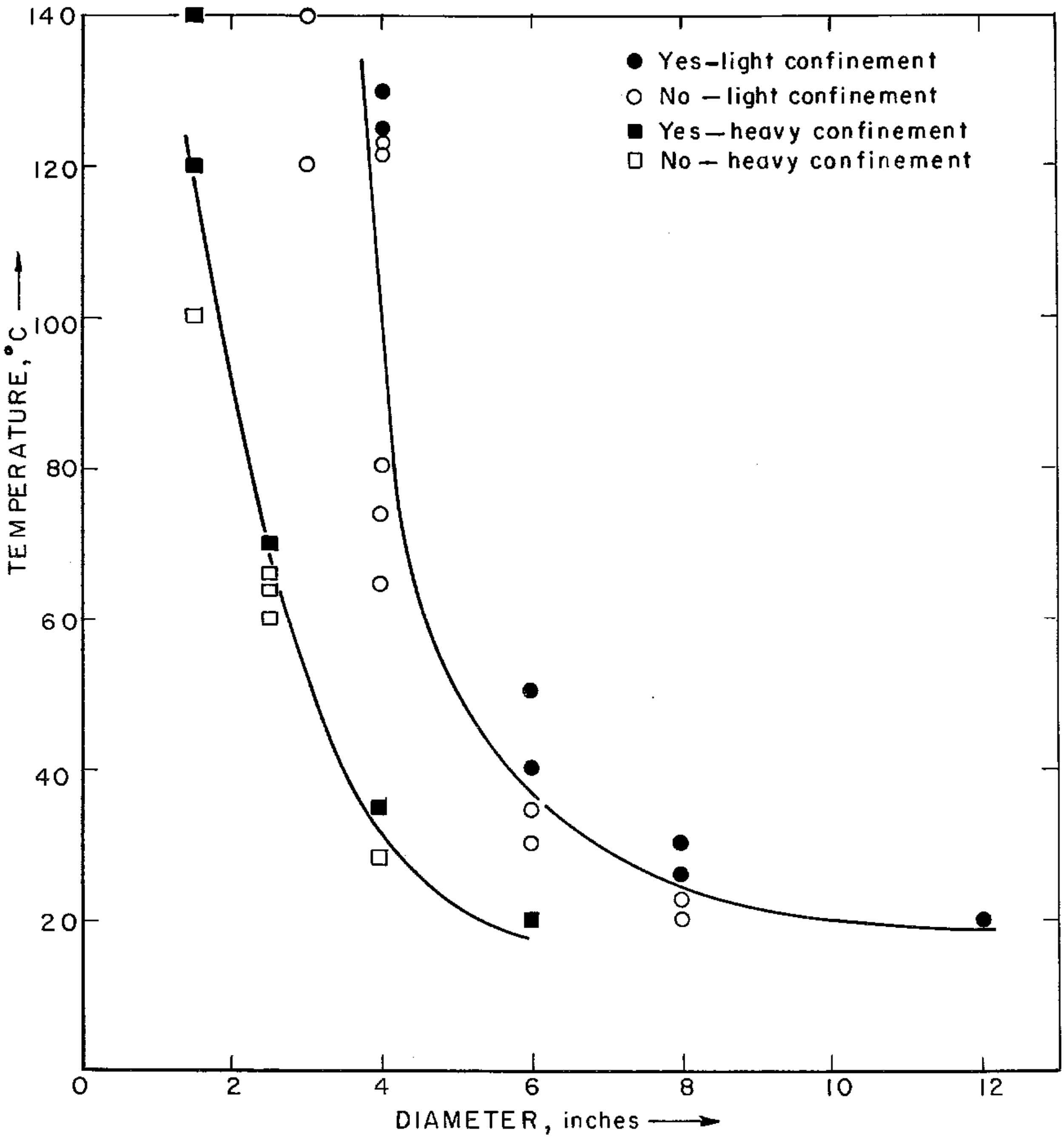

FIGURE 3. - Shock Sensitivity of Brand E Prills.

the increases in gaps of about one-quarter and one-half inch, respectively. Fifteen percent water desensitized the mixture beyond the range of the card gap test. The data are presented in table 3.

TABLE 3. - Effect of added water on shock sensitivity of ammonium nitrate-fuel oil[1]

H_2O, percent	Density	Gap, inches	Result	
			Initiation	No. of shots
0.0	0.85	1.50	Yes	10
		1.75	No	10
5.0	.89	1.75	Yes	5
		2.00	No	5
10.0	1.01	2.00	Yes	5
		2.25	No	5
15.0	1.39	.0	No	7

[1] Brand E prills (5 percent fuel oil) plus H_2O in schedule 40 seamless steel pipe, (1.61-inch id by 0.145-inch wall by 16-inch length) 160-gram tetryl donor (ρ = 1.57 grams per cubic centimeter).

In preparation for some related work on sympathetic detonation of AN and AN-FO[14] the maximum air gap over which brand E prills containing 5 percent fuel oil would transmit detonation from one charge to another was determined, using 2-inch, 4-inch, and 8-inch id cardboard containers. Donor charges with and without a 16-gage steel plate of the same diameter as the charge inserted on top of the donor were used (fig. 4). Inconsistent results were obtained at the 2-inch diameter, evidently because this diameter is below or near the critical diameter of prilled brand E AN-FO. With the 4-inch diameter, the air gap for 50 percent initiation without the plate was about 5 inches and with the plate initiation was observed for gaps up to and including 7 inches. In the 8-inch diameter the air gap without the plate was about 11 inches. With the plate inserted on top of the donor, detonation was observed in the acceptor up to and including 66 inches of gap, demonstrating that flying fragments are capable of initiating AN-FO at some distance. The data are shown in table 4.

Molten Ammonium Nitrate

To assist in evaluating the results with molten AN, the effect of the booster alone was determined on three steel containers filled with nondetonable liquids, water, and glycerin; table 5 shows the damage to containers caused by a 50-gram tetryl booster at a zero gap (no cards).

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[14] Van Dolah, R. W., F. C. Gibson, and J. N. Murphy. Sympathetic Detonation of Ammonium Nitrate and Ammonium Nitrate-Fuel Oil. BuMines Rept. of Inv. 6746, 1966, 34 pp.

TABLE 4. - Air gap initiation of AN-FO at 25° C

Tetryl booster, inches		AN-FO donor, inches		AN-FO acceptor, inches		Air gap			
						Without plate		With inserted plate	
Diam	Length	Diam	Length	Diam	Length	Inches	Initiation	Inches	Initiation
2	2	2	8	[1]2	16	0.5	Yes	-	-
						1	Yes	1	Yes
						1.25	No	1.25	No
						1.5	No	1.5	No
2	2	2	8	[1]2	16	.25	No	.25	No
						.75	No	.75	No
						1	No	1	No
						1.25	No	-	-
						1.5	No	-	-
3	2	4	8	4	8	2	Yes	5	Yes[2]
						3	Yes	5.5	Yes
						4	Yes	5.75	Yes
						5	Yes	6	No
						5.25	No	7	Yes
						5.5	No	-	-
4(3)	1	8.63	16	8.63	24	10	Yes	12	Yes
						12.5	No	13.5	Yes
						15	Yes	15	Yes
						-	-	18	Yes
						-	-	24	Yes
						-	-	42	Yes
						-	-	48	Yes
						-	-	54	Yes
						-	-	60	Yes
						-	-	66	Yes

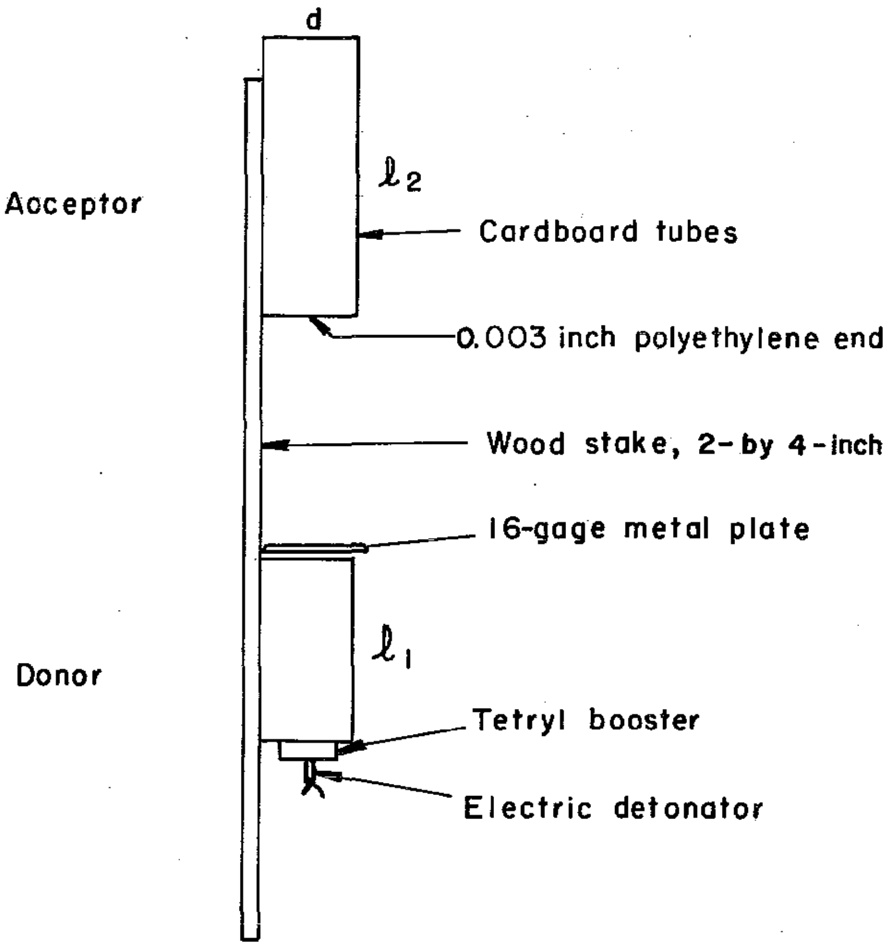
[1] 2 different batches showing inconsistency at 2-inch diameter.

[2] 4 trials.

TABLE 5. - Damage to container with inert material

Container	Damage to container, inches destroyed	
	H_2O, 25° C	Glycerin, 160° C
Steel, 1.05-inch id by 0.133-inch wall........	3	4
Steel, 1.61-inch id by 0.145-inch wall........	6	6
Steel, 2.07-inch id by 0.154-inch wall........	7	-

Initiation of molten AN at temperatures ranging from 180° to 220° C in steel and glass containers was attempted, using tetryl or pentolite boosters. Molten brand G AN at 180° C did not detonate in a 16-inch long container



d, inch	ℓ_1, inch	ℓ_2, inch
2	8	8
4	8	8
8	16	24

FIGURE 4. - Apparatus Used in Initiation of AN-FO Over Varying Air Gaps.

fabricated of steel tubing (1.63-inch id by 0.64-inch wall with a 100-gram tetryl booster, nor did it detonate in large diameter glass containers 4.6- and 5.6-inch id), using 175- to 570-gram pentolite boosters. However, at 220° C brand G was initiated in 1- and 1½-inch schedule 40 steel pipe by a 50-gram tetryl booster. In a 4.6-inch (1,500 cubic centimeters) glass beaker at 220° C, the sample did not detonate with a 100-gram tetryl booster but did detonate with a 175-gram pentolite booster. Since the melt (220° C) did not detonate in a 3.13-inch id (2,000 cubic centimeter) graduate cylinder, the critical diameter of molten AN at 220° C in glass appears to fall between approximately 3 and 4½ inches. This conclusion was confirmed with some trials with molten chemically pure AN (CPAN). Thus, at 220° C CPAN did not detonate in either 1- or 1½-inch schedule 40 steel pipe with 50 grams of tetryl but detonated (at approximately 1,900 meters per second) in three out of three trials in heavy wall (0.64-inch) steel tubing (1.63-inch id) with a 100-gram tetryl donor. In the 4.6-inch glass beaker the CPAN detonated at 220° C with 175 grams of pentolite as donor. In a 16-inch length of schedule 40 pipe CPAN did not detonate at 200° C in 2-inch and 3-inch diameters. In the 4-inch diameter no initiation was obtained at 200° C but at 220° C a velocity of about

1,900 meters per second was observed. Brands A, C, D, E, and H did not detonate at 180° C (molten) in 1-, 1½-, or 2-inch schedule 40 steel pipe (16 inches long) with a 50-gram booster.

Solid Ammonium Nitrate-Urea

Urea-AN mixtures have been proposed as high nitrogen fertilizers, but of immediate pertinence to this program was the suggestion that such mixtures might have been present at Traskwood following spillage and evaporation of the water and ammonia from some of the nitrogen solutions in cars that were involved in the derailment. Thus, the shock sensitivity of AN-urea was of interest. A series of synthetic mixtures was prepared from brand G AN and urea, both crushed to yield 50 percent through 325 mesh. Charges were prepared with a density about 0.6 gram per cubic centimeter, in 1-inch schedule 40 steel pipe containers (1.05-inch id by 0.133-inch wall by 16-inch length); 50-gram tetryl boosters were used in the card gap test described as the first modification A, appendix B. The fine particle-sized and low-density charges were used in order to reduce the critical diameter of all mixtures including straight AN to below the 1-inch diameter charges used. A sufficient number of trials was run on each mixture to give both failures and detonations so that an estimation could be made of the gap for 50 percent positive results, but an accurate determination of the 50 percent card gap value was not made. Mixtures containing up to 20 percent urea had about the same or perhaps somewhat less sensitivity than straight AN, but the sensitivity of mixtures with greater than 20 percent urea was significantly less. None of the mixtures was more sensitive than AN with the same particle size and bulk density (fig. 5).

Molten Ammonium Nitrate-Urea System

The shock sensitivity of molten mixtures of brand G AN and urea was determined by method A using a series of compositions in 1-inch schedule 40 pipe (1.05-inch id by 0.133-inch wall by 16-inch length) at 180° C. Detonability limits extend from approximately 10 to 30 percent urea. A peak sensitivity of approximately 2.4 inches of gap was obtained for the mixture near stoichiometric (80 percent AN - 20 percent urea; fig. 6). Again no attempt was made to determine the gap value precisely. The sensitizing effect of urea on molten AN is in sharp contrast to the desensitizing effect of urea on solid AN shown in figure 5.

To determine the effect of increased charge diameter or confinement on the limits of detonability of molten AN-urea mixtures (180° C), charges were fired in 1½-inch schedule 40 steel pipe 16-inches in length and in 1.63-inch id steel tubing (0.63-inch wall) 16 inches in length. Detonability limits for the AN-urea system at the zero gap level were not appreciably wider in 1½-inch schedule 40 pipe than in 1-inch schedule 40 pipe. However, in heavy walled Shelby tubing (1.63-inch id by 0.64-inch wall by 16-inch length), the limits extended from approximately 5 percent urea to approximately 40 percent urea, indicating that wider detonation limits would probably exist in substantially larger diameter charges.

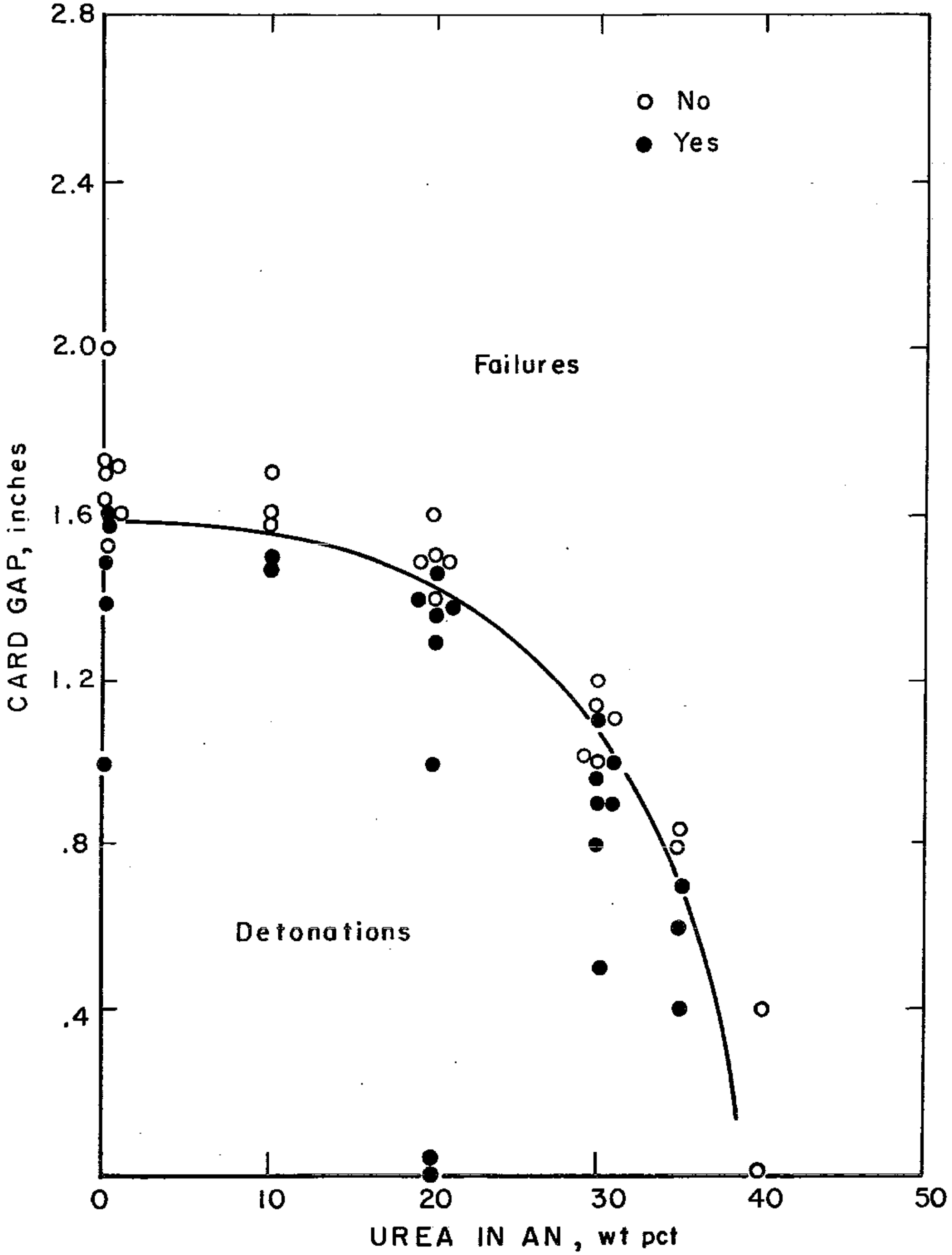


FIGURE 5. - Shock Sensitivity of Ammonium Nitrate (Brand G)–Urea System at 20° C. Sample: Finely divided components (approximately 50 percent through 325 mesh). Container: 1-inch schedule 40 seamless steel pipe, 1.05-inch id by 0.133-inch wall by 16-inch length.

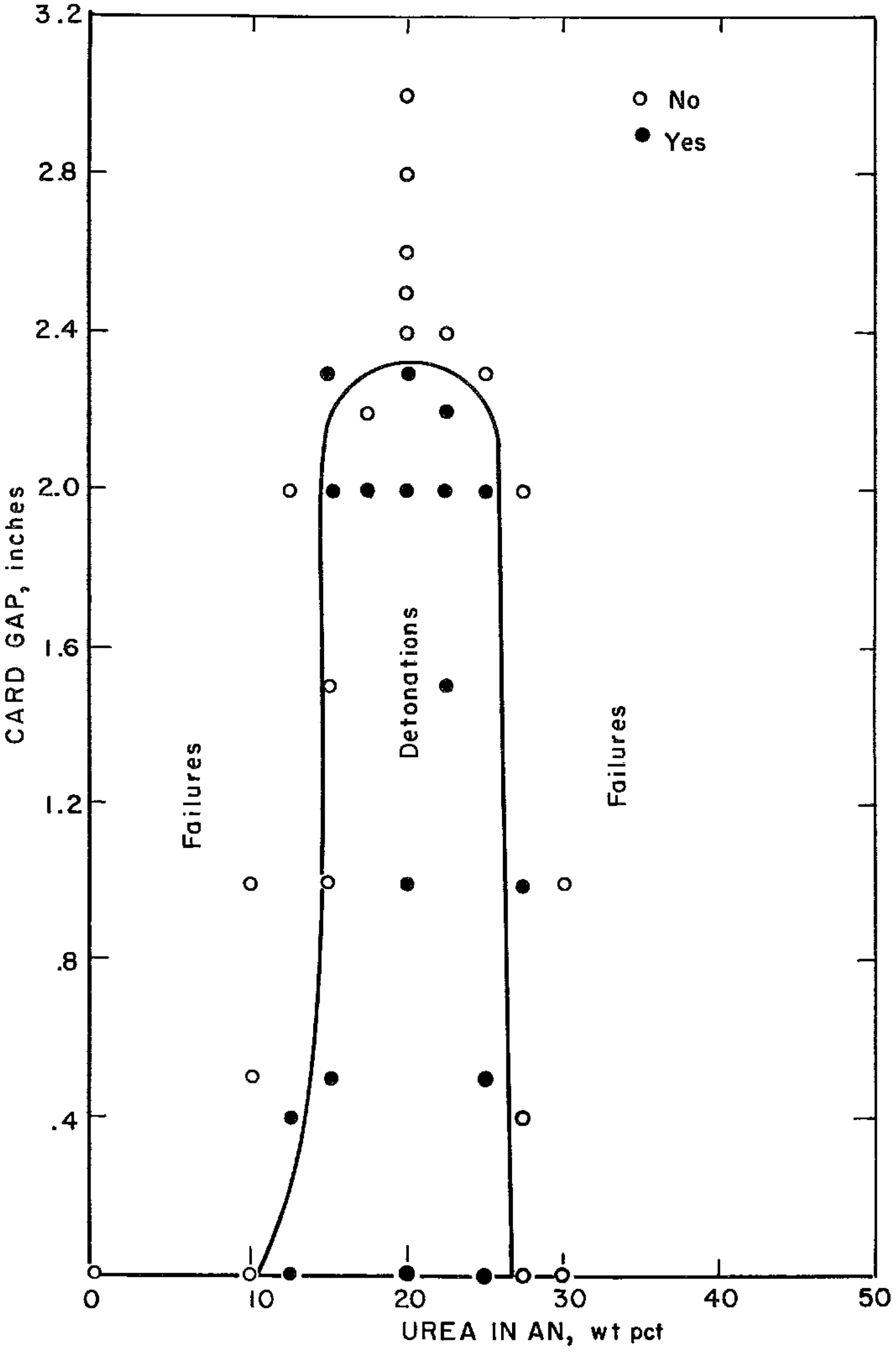


FIGURE 6. - Shock Sensitivity of Liquid Ammonium Nitrate (Brand G)–Urea System at 180° C. Container: 1-inch schedule 40 seamless steel pipe, 1.05-inch id by 0.133-inch wall by 16-inch length.

Nitrogen Fertilizer Solution

A solution was prepared containing 68.7 percent brand G AN, 16.3 percent urea, and 15 percent water. This liquid was not initiated (method A, appendix B) in four trials in 1-inch schedule 40 steel pipe by 50 grams tetryl donors at zero gap at temperatures ranging from 40° to 120° C. Neither could a sample at 120° C be detonated by a 100-gram tetryl donor in heavy wall 347 stainless steel tubing, 1.5-inch id by 0.5-inch wall by 6.5-inch length.

A sample of commercial nitrogen fertilizer solution containing 56 percent AN, 10 percent urea, 24.5 percent NH_3, and 9.5 percent H_2O was also examined. The material as received could not be detonated at 20° C in 1-inch schedule 40 pipe with a 50-gram tetryl donor, in 3-inch schedule 40 pipe with a 485-gram pentolite donor, in 4-inch schedule 50 pipe with an 848-gram pentolite donor, in 6-inch schedule 40 pipe with a 1,816-gram AN-FO donor, or in a 1-gallon paint can (6.5-inch id) by a 1,816-gram AN-FO donor. The donor diameter was the same as that of the acceptor in all cases. Samples of this solution were then evaporated to dryness to give a solid residue containing 15 percent urea and 85 percent AN (by analysis). The dry pulverized residue at 20° C (charge density was approximately 0.5 gram per cubic centimeter) detonated in 1-inch schedule 40 pipe with an average detonation velocity of 2,400 meters per second (7,870 ft/sec) at 1.3-inch gap and failed at a gap of 1.4 inches. The molten residue at 130° C did not detonate at zero gap but did detonate at 180° C with a 2-inch gap. The results at both 20° and 180° C are in accord with the results obtained with the previously described mixture of 15 percent urea in AN.

Detonation velocities (1.05-inch id schedule 40 iron pipe) were measured at 180° C for the molten residue from the evaporated nitrogen fertilizer solution using two pairs of rate stations. One-inch schedule 40 pipe containers were again used. In one trial with zero gap the detonation appeared to be accelerating from 2,910 meters per second to 3,220 meters per second. A clean hole in the witness plate was evidence of a complete detonation. With a 1.5-inch gap, the detonation velocity was fairly constant; 2,570 meters per second and 2,620 meters per second (8,430 and 8,600 ft/sec) were measured over two intervals. With a 2-inch gap, measured rates of 1,660 meters per second and 1,090 meters per second (5,400 and 3,600 ft/sec) were observed. In this trial the witness plate sustained no damage and only 15 inches of container was fragmented--evidence of a decaying reaction.

White Fuming Nitric Acid--Hydrocarbon Systems

In the train wreck at Traskwood, Ark., the fire which developed involved both petroleum products and nitric acid as well as AN and other materials. As part of an investigation seeking to determine possible initiation sources for the car of AN which detonated, the Spencer Chemical Company conducted a series of special burning tests involving gasoline and nitric acid. The company found that the introduction of 100 percent nitric acid into burning gasoline resulted in a vigorous reaction accompanied by a large fireball and some evidence of an explosion. It was of interest to determine if a condensed phase detonation could be initiated under these conditions.

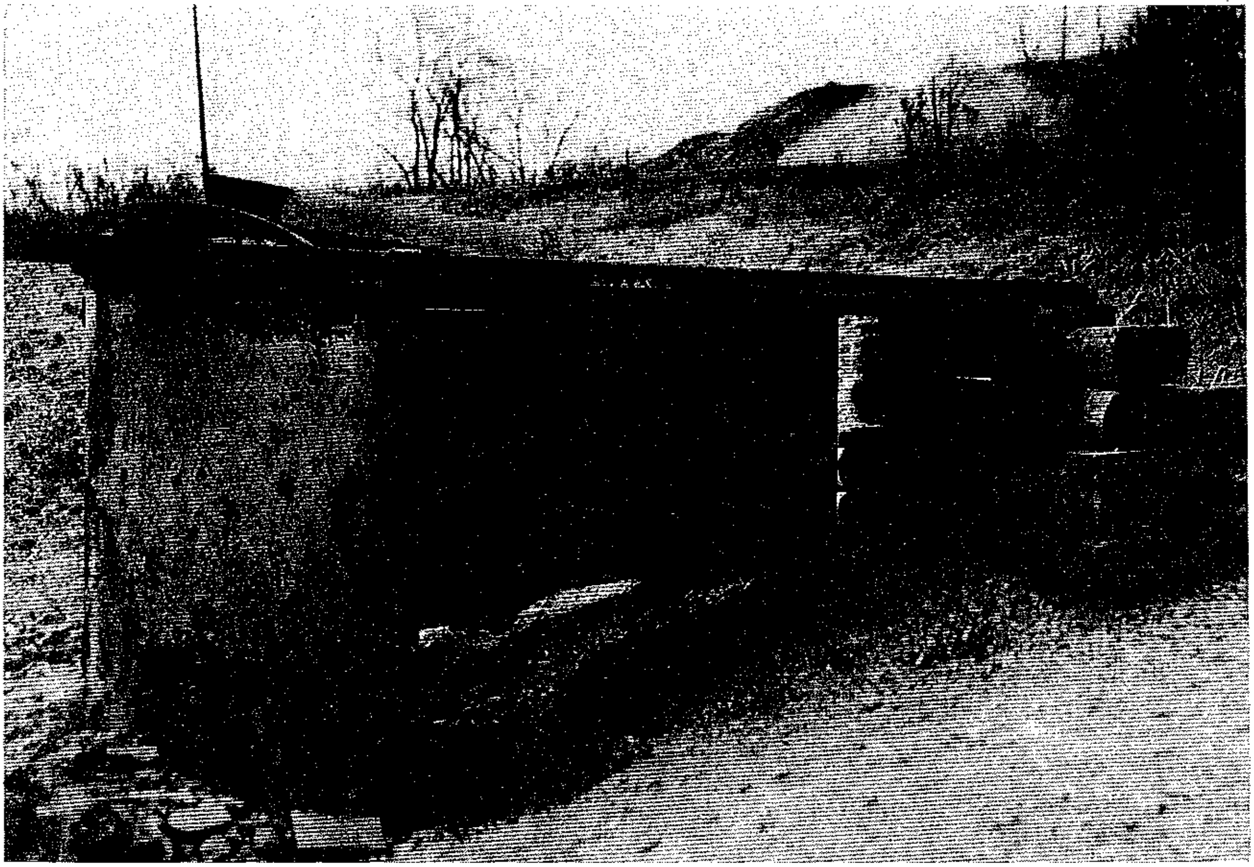


FIGURE 7. - Rough Enclosure for Explosives Testing.

In the first series of experiments, nitric acid contained in an aluminum tube closed at the bottom by a Teflon membrane was spilled into a container of gasoline. In a second series, the WFNA was contained in an Erlenmeyer or Florence flask and suspended by a wire about 2 feet above a container of gasoline or benzene. In order to break the flask and mix the nitric acid and hydrocarbon, the flask was dropped onto a breaker; this was a steel stud, ½-inch in diameter, mounted on a base, standing erect in the hydrocarbon and extending about 2 inches above the hydrocarbon surface.

Three types of results were obtained depending on the temperature of the hydrocarbon. With the hydrocarbon at ambient temperature and unconfined, a vigorous chemical reaction resulted and residues of nitrated hydrocarbon could be found spattered about afterwards. In a barricaded area with light confinement of the vapors and the hydrocarbon warmed to about 60° C, a gas phase explosion accompanied by a fireball and a perceptible pressure front was observed. When the gasoline was ignited and allowed to burn one minute before the acid was dropped in, a liquid phase detonation resulted. In one trial with 1,800 cubic centimeters of white fuming nitric acid (WFNA) and 1,800 cubic centimeters of burning fuel (regular gasoline) the condensed phase detonation leveled the barricaded area and created a crater 30 by 36 by 15 inches deep. Figures 7 and 8 show before and after views of this barricade. A liquid

FIGURE 8. - Destruction of Structure Shown in Figure 7 by Nitric Acid-Hydrocarbon Detonation.

phase detonation was also observed when 250 cubic centimeters of WFNA was spilled into 250 cubic centimeters of burning gasoline contained in a one gallon paint bucket resting on a 2-inch oak plank lying on a ½-inch steel plate. In this case, the bucket and the plank were destroyed and the plate was dented.

Further experimental work on spilling WFNA into burning gasoline established a technique with which detonation was achieved reproducibly, using as little as 250 cubic centimeters of each liquid. A schedule 40 steel tube 3-inch id by 7/32-inch wall by 12-inch length, was filled with 1,220 grams of 94 percent brand A AN and 6 percent fuel oil (AN-FO). A 1-gallon paint can was attached securely on top of the tube. Three hundred cubic centimeters of regular gasoline were placed in the can equipped with a four-legged breaker[15] that extended about 2 inches above the gasoline. Three hundred cubic centimeters of WFNA (18° C) in a 500 milliliter Florence flask were suspended 30 inches above the breaker in the can. After the gasoline was ignited and allowed to burn 1½ minutes, the flask of acid was dropped on the breaker. A liquid phase detonation resulted which initiated an apparent low order detonation in the AN-FO. The paint can was demolished and the schedule 40 pipe containing the AN-FO was fragmented into large pieces (of the order of 1 inch by 4 inches). In similar experiments using AN prills at ambient temperature and AN prills heated to about 120° C, both without added oil, the detonating acid-gasoline mixture failed to initiate the AN, a result now to be expected on the basis of the critical diameter results reported above. AN at 140° C in light 3-inch containers failed to be initiated by a tetryl donor.

Shock Sensitivity by Projectile Impact

Shock waves generated by projectile impact are effective in initiating detonation in solid explosives and offer some advantages over explosive generated shock waves. Recently, Brown and Whitbread[16] demonstrated that the controlling factor in the initiation by projectile impact was the amplitude of developed shock in the explosive acceptor. This conclusion was substantiated by Griffiths and Laidler.[17] Eldh and others[18] determined the relative sensitivity of a series of explosives in terms of the minimum projectile velocity necessary to initiate the explosive.

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[15] The breaker was made of four 4¼-inch pieces of 5/16-inch steel rod with a 60° bend 1 inch from one end. The 1-inch-long ends were welded together with the legs spread evenly.

[16] Brown, S. M., and E. G. Whitbread. The Initiation of Detonation by Shock Waves of Known Duration and Intensity. Ch. in Les Ondes de Detonation. (Waves of Detonation). Centre National de la Recherche Scientifique, Paris (France), September 1962, p. 69-80.

[17] Griffiths, N., and R. McN. Laidler. The Explosive Initiation of Trinitrophenylmethylnitramine by Projectile Impact. J. Chem. Soc., 1962, pp. 2304-2309.

[18] Eldh, D., B. Persson, B. Ohlin, C. H. Johansson, S. Ljungberg, and T. Sjolin. Shooting Test With Plane Impact Surface for Determining the Sensitivity of Explosives. Explosivstoffe, v. 5, May 1963, pp. 97-102.

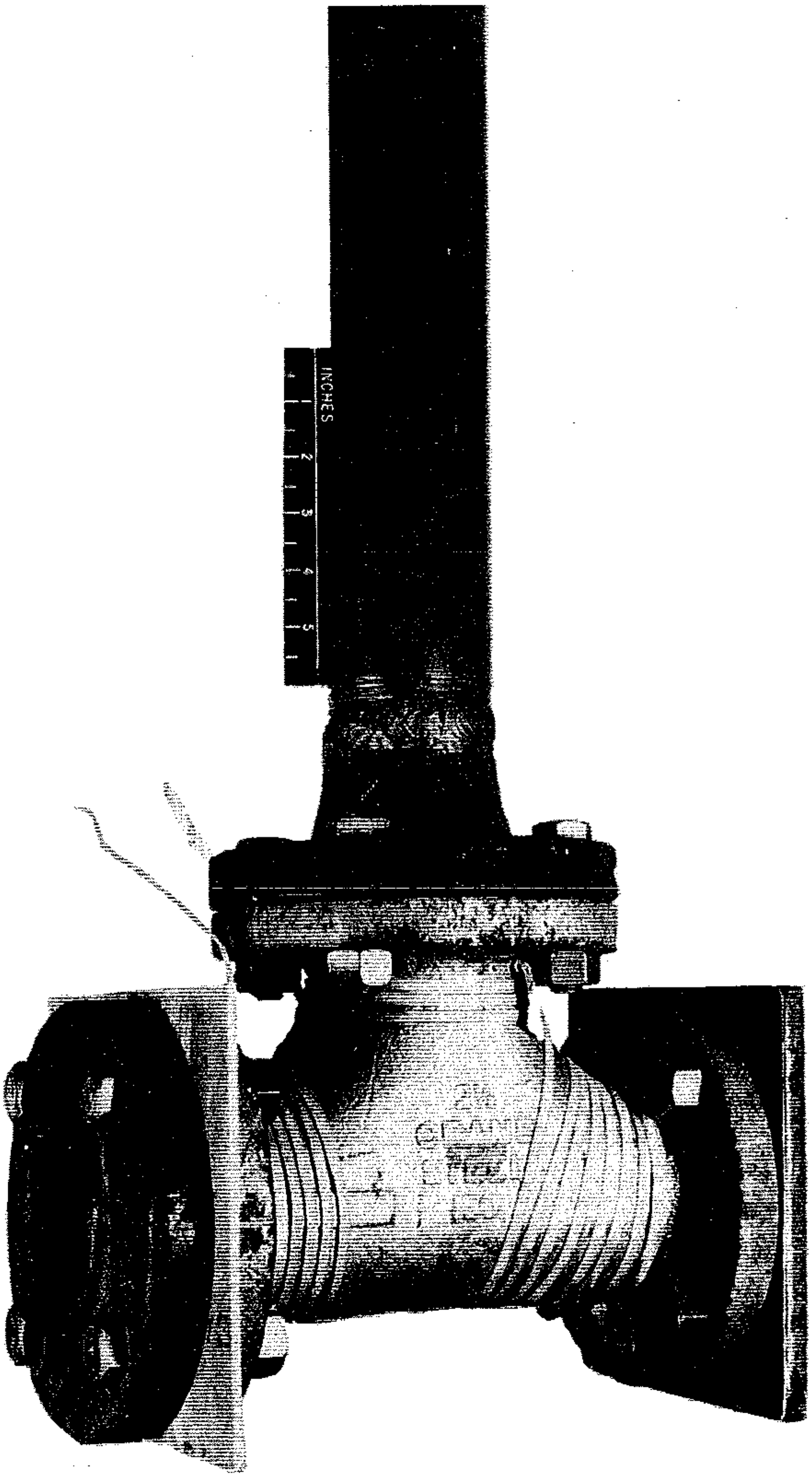

FIGURE 9. - Container Used in Projectile Impact Studies on Hot AN.

To obtain a preliminary estimate of the sensitivity of solid and liquid AN to initiation by projectile impact, three different rifles with five different bullets were used; these gave bullet velocities ranging from 800 to 1,080 meters per second. A 2½-inch flanged steel tee closed at the two arms with 1/8-inch thick aluminum sheet for a front plate and a 1-inch-thick steel blind flange (steel plate in one case) for a back plate was used to contain the AN. The side arm of the tee was open but a standpipe was attached when liquid chemically pure ammonium nitrate (CPAN) was involved. Figure 9 shows the latter container.

For solid AN, the tee without the standpipe was filled with 2 kilograms of prilled Brand G AN and placed in a heated oven whose temperature was increased slowly. When two thermometers placed in the sample near the front aluminum plate and at the neck of the tee agreed within 10° C, they were removed and the shot was fired within 3 minutes. A positive result was only obtained when the temperature was 140° C, using the maximum bullet velocity of 1,080 meters per second (3,540 ft/sec). Figure 10 shows the fragmented container after an apparent detonation of brand G at 140° C was initiated by the impact from a 110-grain bullet fired from a .300 Weatherby Magnum at 1,080 meters per second.

Molten CPAN, used because melted prills foamed excessively, was preheated and poured into the preheated vessel. The container and sample were then heated to the desired temperature by a gasoline burner; the temperature was recorded by two glass encased thermocouples placed in the sample 1 inch and 3 inches above the bottom. These were removed before firing. Figure 11 shows the result of an apparent detonation of liquid CPAN at 260° C. Detonations were observed at 260° C, using the .30 caliber bullet fired from the M-1 rifle (823 meters per second or 2,690 ft/sec), and at 220° C, using the .300 Weatherby Magnum (110-grain bullet, 1,080 meters per second or 3,540 ft/sec; fig. 12).

These preliminary results demonstrated that AN, as hot prills or liquid, could be initiated to an apparent detonation by bullet impact if the bullet had sufficient velocity. In order to make a more quantitative evaluation, a projectile impact method, adapted from the work of Eldh as well as others and described in appendix C, was used to determine the sensitivity of brand G and brand A prills as a function of temperature.

The AN was contained in schedule 40 aluminum pipe, 1.6-inch id by 1/8-inch wall, by 3-inch length, sealed at both ends by Teflon film. Up to 160° C, the samples were preheated in the containers to the desired temperature in an oven from which they were removed and tested immediately.

Over the range of 20° to 80° C, brands A and G prills could not be initiated with the maximum projectile velocity of 1,500 meters per second (4,920 ft/sec). In the temperature range of 100° to 140° C, the prills were initiated, and it was possible to obtain 50 percent velocities (table 6). The solid prills began to soften above 140° C and projectile velocities greater than 1,500 meters per second were required to initiate these samples between 140° and the melting point (170° C).

TABLE 6. - Projectile velocity data for ammonium nitrate in aluminum containers[1]

Temperature, ° C	Brand G prills, 1.6-inch id containers	Brand A prills, 1.6-inch id containers	Molten CPAN	
			1.6-inch id containers	3-inch id containers
20-80..........	>1,500	>1,500	-	-
100............	1,250	>1,500	-	-
120............	1,090	1,300	-	-
140............	1,000	1,100	-	-
180-240........	-	-	>1,500	>1,500
245............	-	-	>1,500	1,500
250............	-	-	>1,500	-
255............	-	-	1,500	-
280............	-	-	1,250	-

[1] Velocity, in meters per second, of a ½- by ½-inch brass projectile needed to obtain initiation in 50 percent of the trials; > indicates that no initiations were observed with projectiles at 1,500 meters per second.

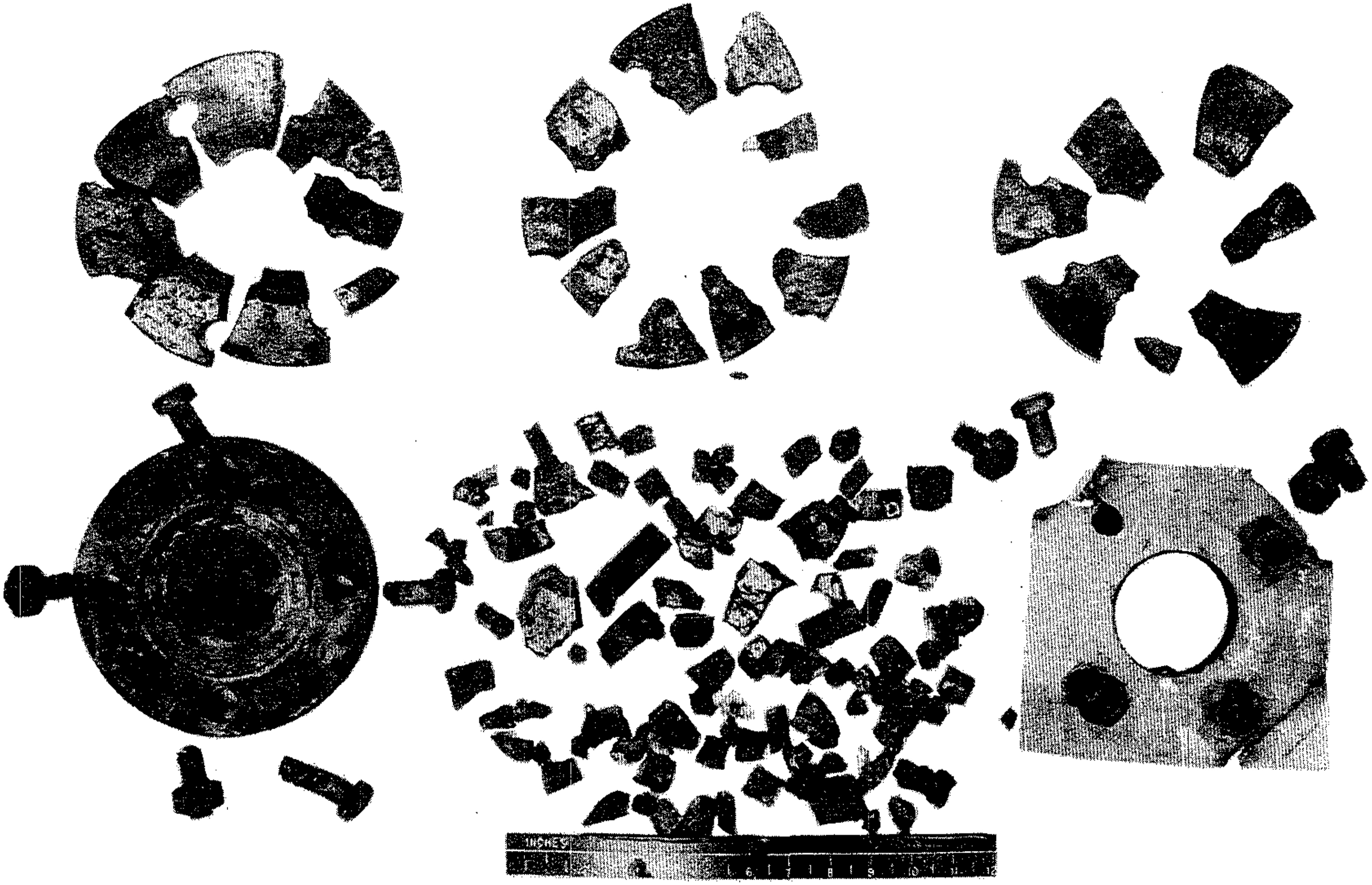

FIGURE 10. - Fragments of Container in Figure 9 From an Apparent Detonation of Brand G Prills at 140° C by 110-Grain Bullet From .300 Weatherby Magnum.

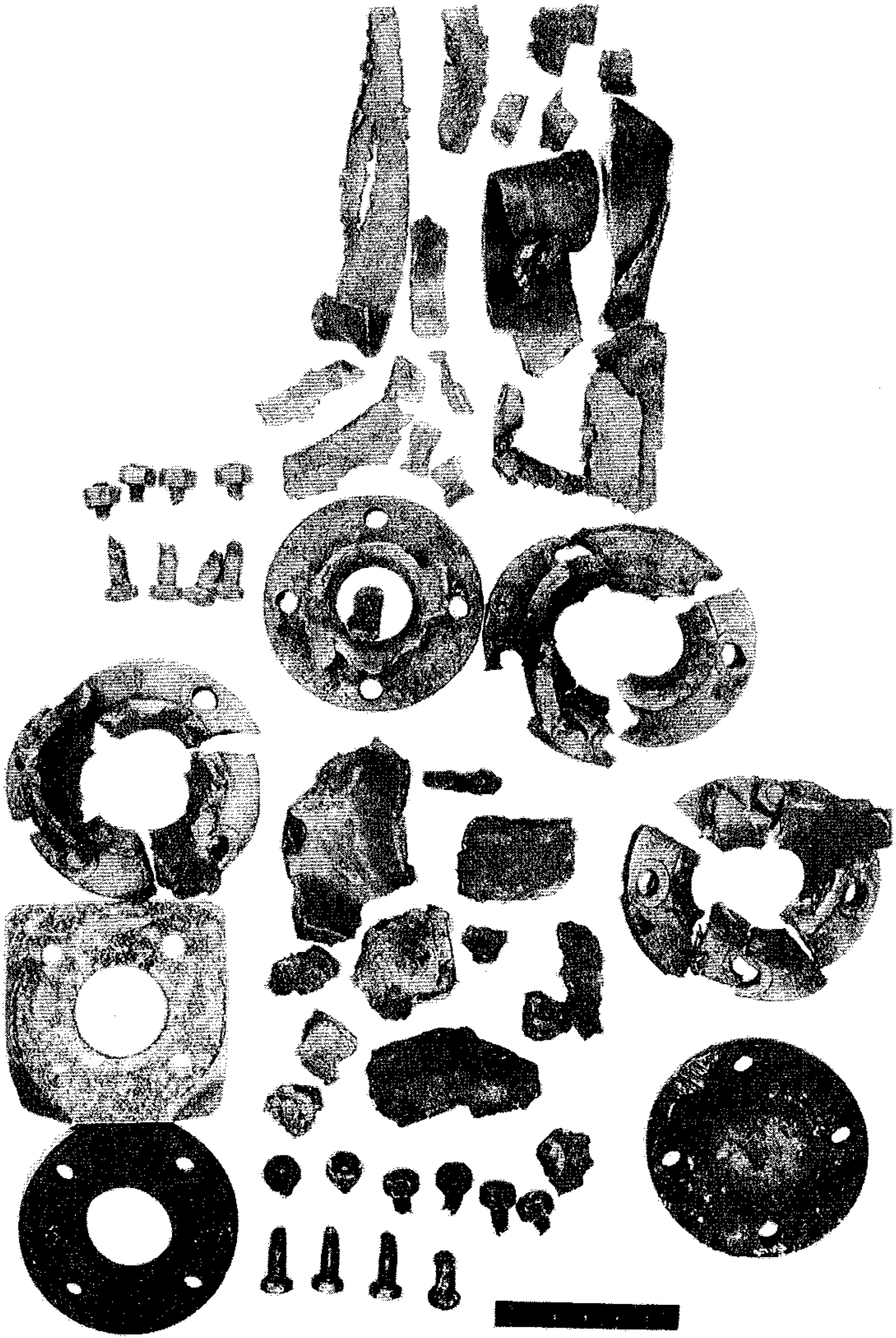

FIGURE 11. - Fragments of Container in Figure 9 From an Apparent Detonation of CPAN at 260° C by the M-2 Bullet From the M-1 Rifle. Note the impact of the bullet on the steel backing plate shown in the lower right-hand corner.

FIGURE 12. - Fragments of Container in Figure 9 From an Apparent Detonation of CPAN at 220° C by 110-Grain Bullet From .300 Weatherby Magnum.

The sensitivity of liquid AN to initiation by projectile impact was explored, mounting the gun to fire down into a pool of molten AN. Again CPAN was used to minimize frothing although at the high temperatures used, AN decomposes quite rapidly so that the liquid is full of bubbles. The molten AN was contained in 3-inch lengths of aluminum tubing, with the bottom sealed with asbestos paper. This container was set on a block of polyurethane foam. In a 1.6-inch id container at 255° C, the velocity for initiation 50 percent of the time (V_{50}) was 1,500 meters per second and at 280° C, 1,250 meters per second. In a 3-inch id container V_{50} was 1,500 meters per second at 245° C (table 6).

The initiation of solid and liquid AN by rifle bullets at lower velocities in the preliminary trials than in these latter trials resulted from the use of heavy-walled steel containers and a steel backing plate. These provided greater confinement and the impact of the bullet on the backing plate gave much higher pressures than impact on AN. Although the containers used in the two series of experiments were much different, a comparison of results shows the increase in sensitivity with increasing temperature for both solid and liquid AN.

Initiation of Detonation in Ammonium Nitrate by Gas Detonation

Gas phase detonations have been frequently suggested as the cause of detonation in AN despite the inadequacy of the shock amplitude as shown by theoretical calculations. The maximum shock pressure produced in the most energetic gas phase detonation starting at one atmosphere pressure is about 100 atmospheres. Detonating gas-air mixtures deliver much lower pressures. These pressures are to be compared with the 5,000 to 20,000 atmospheres shock pressure necessary to initiate detonation in AN. However, in order to substantiate this conclusion with experimental evidence, AN was subjected to the shock from detonating hydrogen-oxygen mixtures which deliver a peak shock pressure of about 40 atmospheres and to the shock from detonating acetylene-oxygen mixtures which deliver a peak shock pressure of about 100 atmospheres.[19]

Stoichiometric mixtures of hydrogen and oxygen at atmospheric pressure and 20° C were fed into an aluminum tube 1.93-inch id by 0.035-inch wall by 10½-foot length. The mixed gas, fed through a stopper at the top of the tube, was sparked after the tube was purged of air, approximately 10 minutes. The lower open end of the shock tube was either in contact with or extended under the surface of the test sample contained in 3-inch schedule 40 pipe. Ionization probes stationed 25 centimeters apart at the lower end of the detonation tube were used to measure the detonation rate in the gas mixture. An average detonation velocity of 2,810 meters per second was observed.

Whole and pulverized AN prills at a density of 0.80 at temperatures ranging from 140° to 160° C were subjected to hydrogen-oxygen detonations. No initiation was observed in two trials each at 140° C and at 160° C. Similar results were obtained when AN-FO (6 percent oil) at 20° C was substituted for the AN. A molten mixture, containing 20 percent urea (180° to 190° C) in AN, was not initiated nor was even a relatively sensitive gelatin dynamite.

When using the more powerful acetylene-oxygen mixtures (C_2H_2-O_2), a gas detonation tube 21 feet long and 3 inches in diameter was filled with a stoichiometric ($5O_2 + 2C_2H_2$) mixture at one atmosphere initial pressure. The tube was flushed at least four times with the C_2H_2-O_2 mixture in order to ensure a well-mixed system free of air. Gas samples were taken to ensure that the desired mixtures were obtained. The detonation rate of the C_2H_2-O_2 was also checked each time to be sure that the expected pressure was delivered to

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[19] This value is based on experiments conducted by Elton Litchfield and coworkers of the Explosives Research Center.

the AN. When using a PZ-14 Kistler[20] pressure transducer located in the downstream end of the detonation tube, the measured detonation pressure averaged 100 atmospheres in three trials. The resistance pressure transducer located in the same position gave the same value.

In one experiment the downstream end of the detonation tube was connected to a 12-inch-long by 3-inch-diameter pipe, containing pulverized Brand E AN at a loading density of 0.5 gram per cubic centimeter and heated to 100° C. This AN, at this density and temperature, has a critical diameter for detonation below 3 inches. The container was preheated in order to prevent the AN from cooling during the experiment. The sample had a resistance pressure transducer mounted in the bottom and rate stations in the side wall of the container so that both the pressure and the reaction rate could be determined. There was no evidence of burning or decomposition; the only result was compression of the AN from the original depth of 12 inches to a depth of 7 inches. The experiment was repeated with pentaerythritol tetranitrate (PETN) at 30° C in place of AN. The PETN (low density) sample was 7 inches long and three-quarters of an inch in diameter. The PETN was compressed to 3½ inches by the detonating gas but no evidence of decomposition was observed.

As the C_2H_2-O_2 detonation delivers a higher pressure than is to be expected from any gas-air detonation when the initial pressure of the mixture is one atmosphere and since low-density, granular PETN is one of the most sensitive secondary explosives, these results indicate that initiation of detonation of AN by a gas detonation should not occur in an AN fire.

COMBUSTION OF AMMONIUM NITRATE IN POROUS BEDS

It has been known for many years that AN heated under confinement will develop a rapid accelerating decomposition that can culminate in an explosion or detonation,[21] but the question of whether a similarly accelerating decomposition can be established in AN under fire conditions has never been answered adequately. Such a reaction should only be possible if sufficient pressure can be developed in a bed of AN.

It is convenient to consider the one dimensional case, that is, the pressure at the bottom of a pile of large enough dimensions so that pressure losses to the side can be neglected. Four pressures can be associated with a bed of bulk AN prills. The first pressure is the (hydro) static pressure defined by the height and the bulk density of the bed. Thus, for AN prills of bulk density 0.85 gram per cubic centimeter, the pressure at the bottom of the pile is 0.37h psi, where h is the height in feet. The second pressure is the fluidization pressure; this pressure is again defined primarily by the bed height and density. The third pressure is the gas pressure in excess of the fluidization pressure which will cause the bed to lift as a coherent mass,

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[20] Reference to specific trade names is made to facilitate understanding and does not imply endorsement of such items by the Bureau of Mines.

[21] An explosion is defined here as the sudden release of pressure by rupture of the vessel. A detonation is a shock-initiated reaction that propagates through the medium at greater than local sound velocity.

or slug; the magnitude of this excess pressure will define the acceleration given the slug. Finally, a fourth pressure would occur on collapse of a column (or pile) of AN prills. Here the magnitude of the pressure at the base of the column is defined by $P = \rho v U_s$, where ρ is the density; v is the impacting velocity, defined by the height of fall; and U_s is the velocity of sound in the bed. Of these quantities, the latter, U_s, is yet to be determined satisfactorily, the difficulty lying in the very great attenuation of sound by a bed of AN.

Thus, static pressures in the bed are much too low for accelerated decomposition leading to a deflagration to detonation transition (DDT) to be expected. A 20-foot-high bed would have a static pressure at the bottom of only about 8 psi. However, inertial pressures can be very much greater. These inertial pressures are related to the acceleration given the bed by the equation:

$$P = \rho h a,$$

where ρ is the density, h the height of a pile having a length and width much greater than h, and a is the acceleration. For example, a pressure of 1,000 psi would impart an acceleration of 4,000 ft/sec^2 to a bed 20 feet high, and the bed would move its own height in but 100 milliseconds. Should there be a rapid increase in decomposition rate with increased pressure, then it is conceivable that an explosion or a transition to detonation could occur; however, the increase would have to be very great to compensate for the movement of the bed.

This problem has been approached both experimentally and analytically; this section deals with the experimental approach. Investigation of the conditions which can lead to DDT is difficult for several reasons. The experiment must be scaled down to the limits of the laboratory, and if means can be found to effect deflagration to detonation transition, the variables which affect the transition must be determined and evaluated in order to relate the model results to actual conditions existing in large piles of AN.

When AN is heated without confinement, decomposition usually results in the two reactions:

$$NH_4NO_3 \rightarrow N_2O + 2H_2O, \tag{1}$$

$$NH_4NO_3 \rightleftarrows HNO_3 + NH_3. \tag{2}$$

Reaction (1) is exothermic and reaction (2) is endothermic, and the rates and thermal effects are such that the system is in thermal balance at 291° C at one atmosphere pressure, if no additional heat is supplied externally. Other possible reactions are:

$$NH_4NO_3 \rightarrow 2H_2O + 1/2\ O_2 + N_2, \tag{3}$$

$$NH_4NO_3 \rightarrow 2H_2O + 1/2\ NO_2 + 3/4\ N_2, \tag{4}$$

which are considerably more exothermic than (1). For example, reaction (3) has about three times the heat release of reaction (1) and is believed to be the reaction of greatest importance in a detonation and presumably in transition to detonation. It was of interest to explore this concept experimentally.

Gaseous Products From the Decomposition of Ammonium Nitrate

The Crawshaw-Jones apparatus[22] was used to estimate the reaction products of AN decomposing under high pressure and to compare these products to those from AN detonations. The Crawshaw-Jones apparatus consists of a heavy steel cannon attached to a receiver 7 inches in diameter and 10 feet in length. Each end of the receiver is flanged. One end is closed by a 2-inch steel end plate; the cannon, which is bolted to the other end, has a borehole 2 inches in diameter and 17 inches long. Means are provided for evacuating the receiver, measuring the temperature and pressure, and sampling the gases.

Preliminary attempts to burn AN under pressure in the cannon, using an electric match and ANP propellant,[23] were unsuccessful as the ignited propellant simply pushed the AN into the receiver with very little decomposition occurring. To correct this problem, the AN was confined in a heavy steel tube 1-3/4-inch id and 42-inch-length, which was sealed at one end and closed at the other end with a burst disk. The steel tube was supported inside the Crawshaw-Jones receiver. The AN was ignited at the sealed end by ANP propellant which in turn was ignited by an electric match. At the pressure determined by the burst disk, usually about 10,000 psi, the decomposition products were released into the evacuated receiver. Most of the AN was decomposed by burning under these conditions; material balances accounted for 95 percent or more of the AN used in each run. The results in table 7 show that nitrogen is consistently the principal gaseous product, with N_2O being a minor product; only one exception involving one sample of brand G was noted. These results indicate that reaction (3) best represents the decomposition of AN under pressure.

To determine comparable products of detonation, AN loaded in the steel cannon was initiated by a detonator and PETN booster. Nitrogen was again the principal product as shown in the last two columns of table 7.

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[22] Crawshaw, J. E., and G. W. Jones. An Apparatus for Studying the Gases of Explosives Detonated Under Confinement. Eng. and Min. J., v. 120, 1925, pp. 965-967.

[23] ANP is an ammonium perchlorate, aluminum, and polyurethane binder rocket propellant. In chopped form it provided an intensely hot ignition source and some prepressurization.

TABLE 7. - Gaseous products from burning under pressure and detonation of ammonium nitrate

(20 grams ANP except as indicated)

Pressure--psig[1]	2,000	10,000	10,000	10,000	10,000	10,000	(2)	(3)
AN:								
Brand	A	A	A	G	G	C.P.	A	E
Grams	240	240	300	300	300	300	240	300
Percent reacted	44.0	100.0	97.0	92.0	98.0	94.0	90.0	96.0
Gaseous products, volume-percent:								
N_2	73.5	76.5	75.9	61.4	75.9	75.0	72.7	68.2
H_2	1.4	1.6	0.02	0.2	2.1	3.2	0.02	0.3
O_2	-	13.5	10.8	0.7	8.0	-	-	-
CO_2	14.0	5.6	6.0	7.7	8.9	10.5	18.3	18.0
CO	3.8	0.6	0.2	1.9	2.1	2.0	1.0	0.8
NO	1.0	-	-	4.1	-	0.8	6.1	10.9
N_2O	6.0	2.2	7.1	24.0	2.8	6.5	1.9	1.8
NO_2	.1	-	-	-	-	2.0	-	-

[1] Burst disk.
[2] 20 grams PETN booster instead of ANP igniter.
[3] 30 grams PETN booster instead of ANP igniter.

Ignitability of Ammonium Nitrate Mixtures

To find the best fuel (or worst contaminant), differential thermal analysis was used to determine the ignitability of various AN fuel mixtures. A 2-liter beaker wound with nichrome ribbon and containing hot 66 percent KNO_3 + 34 percent $LiNO_3$ was used for the heating bath. A stirrer and two 25-millimeter-diameter by 200-millimeter-long test tubes were immersed in the hot liquid. One test tube contained the sample and the other the reference (66 percent KNO_3 + 34 percent $LiNO_3$). Thermocouples were immersed in the test tubes to which 10 grams of AN mixture and reference were added. The temperature of the bath was raised about 2° to 3° C per minute, and the differential temperature was recorded.

Different AN samples, mixed with 6 percent polyethylene (PE), showed marked exothermic reactions, beginning in the temperature range of 189° to 231° C. With brand G and PE an ignition resulted as shown in figure 13. AN coated with about 11 percent resin also ignited. AN coated with petrolatum-resin-paraffin (PRP),[24] the coating used in the AN involved in the Texas City disaster, gave an exothermic reaction at the lowest temperature--185° C. The higher differential temperatures obtained with the PE mixtures result from the

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[24] Miller, P., G. A. Lenaeus, W. C. Saeman, and M. N. Dokken. Production of Grained Ammonium Nitrate Fertilizer. Ind. & Eng. Chem., v. 38, July 1946, pp. 709-718; PRP is a mixture of petrolatum, rosin, and paraffin, 1:3:1, used to coat the AN grains. The coating represents about 1 percent of the total weight.

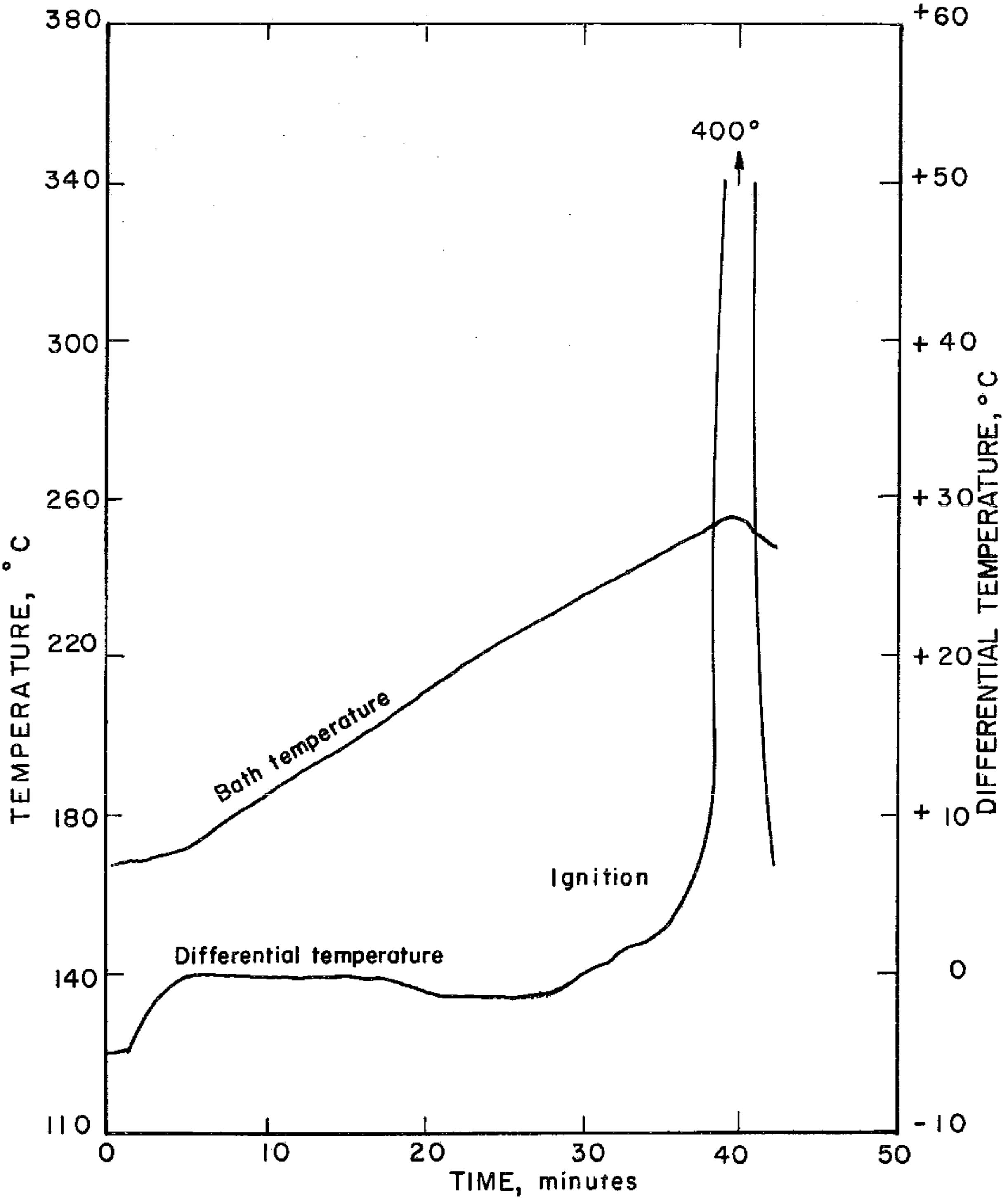

FIGURE 13. - Differential Thermal Analysis of 94 Percent Brand G AN + 6 Percent Polyethylene Versus 66 Percent KNO_3 + 34 Percent $LiNO_3$.

larger amount of fuel available than present in the PRP mixtures (table 8). In eight trials, 80 percent AN + 20 percent urea (both CP and fertilizer grade) did not exhibit noticeable exothermic reactions. This result agrees with the observations of Rozman and Borodkina[25] that urea is effective in stabilizing AN decomposition.

TABLE 8. - Differential thermal analysis of ammonium nitrate mixtures

Ammonium nitrate	Polyethylene additive, percent	Initial exotherm, ° C	Highest differential temperature reached, ° C
CP	6	221	45
Brand A	6	189	44
	6	260	30
	6	259	14.5
Brand C	6	210	15
Brand D	6	230	52
Brand E	6	256	32
	6	260	25.5
Brand G	6	231	Ignition
	6	237	[1]271
	6	246	[1]271
	6	259	[1]263
<0.5 percent PRP coated (granulated dynamite grade).	-	185	6
5.3 percent paraffin-coated prills.	-	205	11
11 percent resin-coated prills	-	190	Ignition

[1] Ignition occurred at this temperature.

Burning in Beds of Prilled Ammonium Nitrate

A one-dimensional experimental design was used to scale a bed of AN to a size within the weight limitations of the Bureau of Mines Explosive Research Center facilities. A section of pipe closed at the bottom and open at the top was used to contain the AN. The experiment assumes that the pipe represents a central core of a large pile and that no confinement exists except that provided by the static head and inertia of the bed. The assumption that the pipe wall does not interact to change the reaction is recognized as not being entirely valid as some heat losses are sure to occur. Also, in actual practice the bed was not always free-moving as some of the beds tended to plug the pipe, thus converting this experiment to one of a closed vessel.

In a series of experiments which varied in minor details as the work progressed, AN or a mixture of AN and fuel was ignited at the bottom of

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[25] Rozman, B. Yu, and L. I. Borodkina. Inhibition of the Thermal Decomposition of Ammonium Nitrate. J. Appl. Chem. of the U.S.S.R. (English translation of Zhurnol Prikladnoi Khimii), No. 32, January-June 1959, pp. 291-294.

heavy-walled 3-inch id steel pipes, 6 to 21 feet in length. The AN, typically ½ to 2 kilos in amount, was usually topped with prilled urea as an inert burden of approximately the same physical characteristics as the AN prills. In some cases, denser materials were used to simulate even higher beds. Since the 3-inch diameter is usually below the critical diameter of AN prills at room temperature, trials were made at elevated temperatures with fueled samples and with micropulverized material of low density. Figure 14 is a general schematic of the arrangement used. Pressures were measured in the earlier trials with a quartz piezoelectric transducer[26] limited to 3,500 psi. In later work, a quartz transducer[27] was used which could measure up to 70,000 psi. The pressure gages were first connected to the bottom of the pipe through the oil-filled length of high pressure tubing shown in figure 14 and were protected by a blowout disk assembly designed to rupture at 24,000 psi. The slow response time of the oil-filled line was later eliminated by mounting the gages in a special holder directly in the wall of the heavy steel cap shown on the bottom of the pipe in figure 14. The output of the pressure transducers was fed through amplifiers[28] directly to a recording oscillograph.[29] The overall response of the system was limited to about 8 kilocycles per second, which was the response of the galvanometers in the recording oscillograph. This system will respond to rates of pressure rise of about 10^6 psi per second, limited by the writing speed of the recorder.

The AN and AN-fuel mixtures were ignited by a small quantity (25 to 60 grams) of ANP propellant,[30] which in turn was ignited by an electric match. A series of trials with inert loads above the ANP established the maximum pressure developed by the gases from the igniter. Urea was first tried as an inert load but this often resulted in incomplete combustion of the propellant, presumably due to quenching by the urea. When 500 grams of rock salt were inserted between the urea and the ANP, the ANP burned completely. The ANP was varied from 20 to 40 grams in the 6-foot beds and 25 to 80 grams in the 12-foot beds. The pressure generated in 5 trials by 20 grams of ANP in the 6-foot bed was never sufficient to eject any appreciable quantity of material from the container and no measurable pressure was recorded. With a weight of ANP greater than 25 grams, the pressure increased rapidly to a peak value and then declined. Figure 15 shows typical pressure time traces for 25 and 40 grams in a 6-foot bed. The maximum pressures obtained are plotted in figure 16 for 6-foot beds and in figure 17 for 12-foot beds. These pressures represent reasonable estimates of the maximum pressure which may be attributed to the ANP igniter when used with AN or AN-fuel mixtures.

The technique used in studying the combustion of AN and AN-fuel mixtures was first to establish a set of conditions in which the ANP would ignite the sample. The quantity of ANP used was usually the minimum needed to initiate sustained combustion in the AN. A resin-coated AN (RCAN) first was selected

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[26] Kistler PZ-14 quartz pressure transducer.

[27] Kistler 617A ballistic pressure transducer.

[28] Kistler Calibrator Amplifier, Model 568 and (galvanometer) amplifier, Model T6GA.

[29] Visicorder Recorder, Model 906-B.

[30] Work cited in footnote 23.

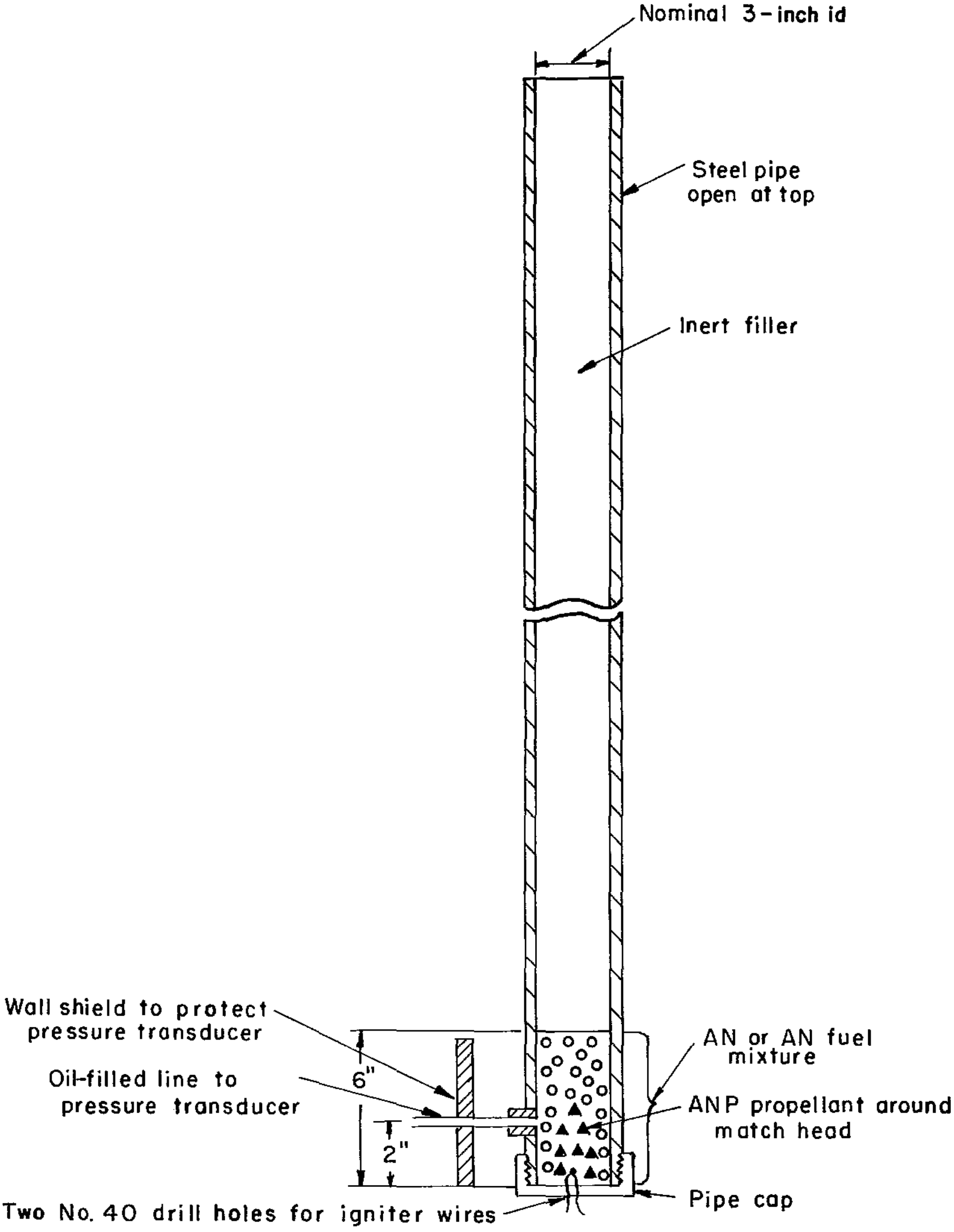

FIGURE 14. - Container Used in AN Combustion Experiments.

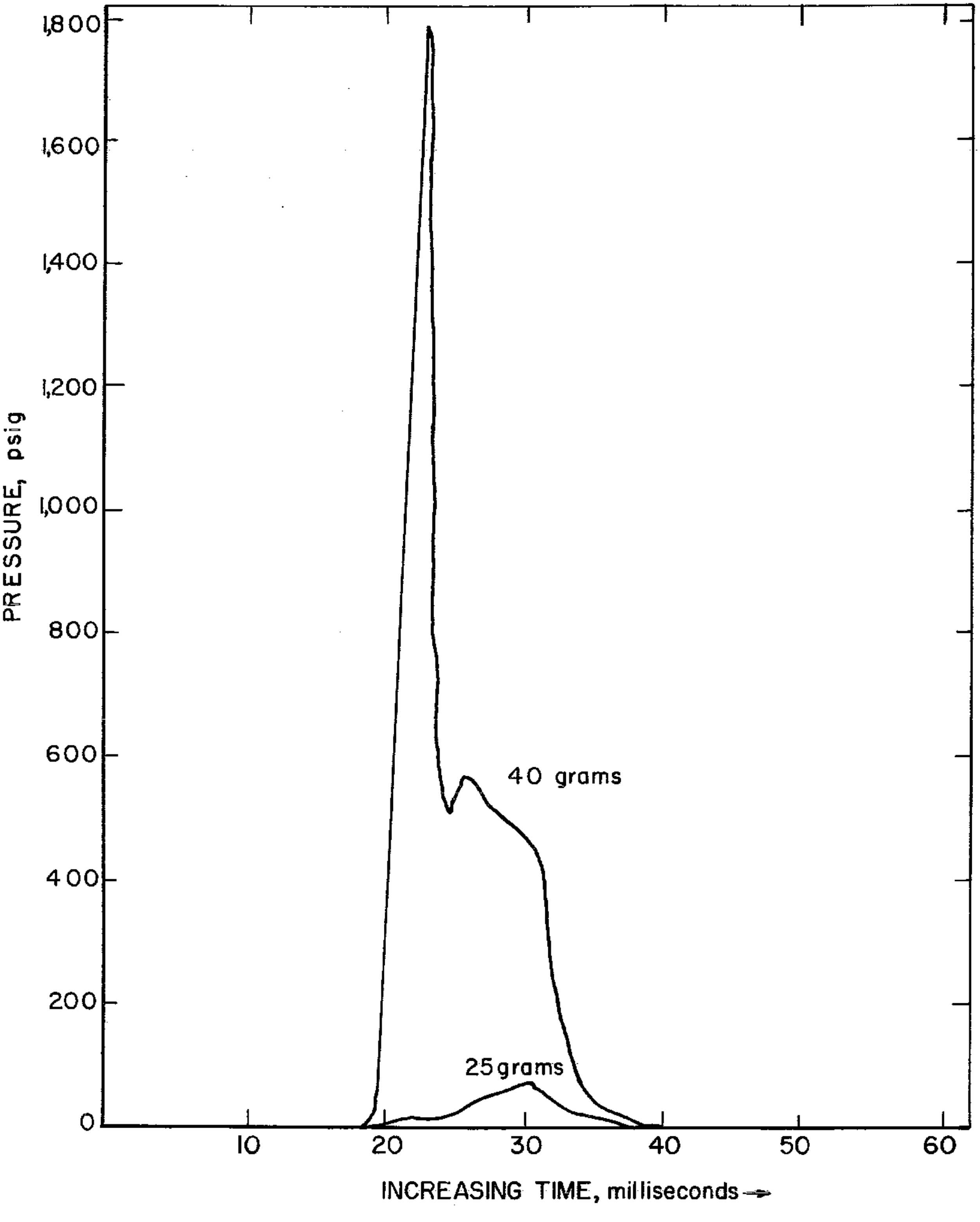

FIGURE 15. - Pressures Developed by ANP Burned at the Bottom of a 6-Foot Inert, Porous Bed.

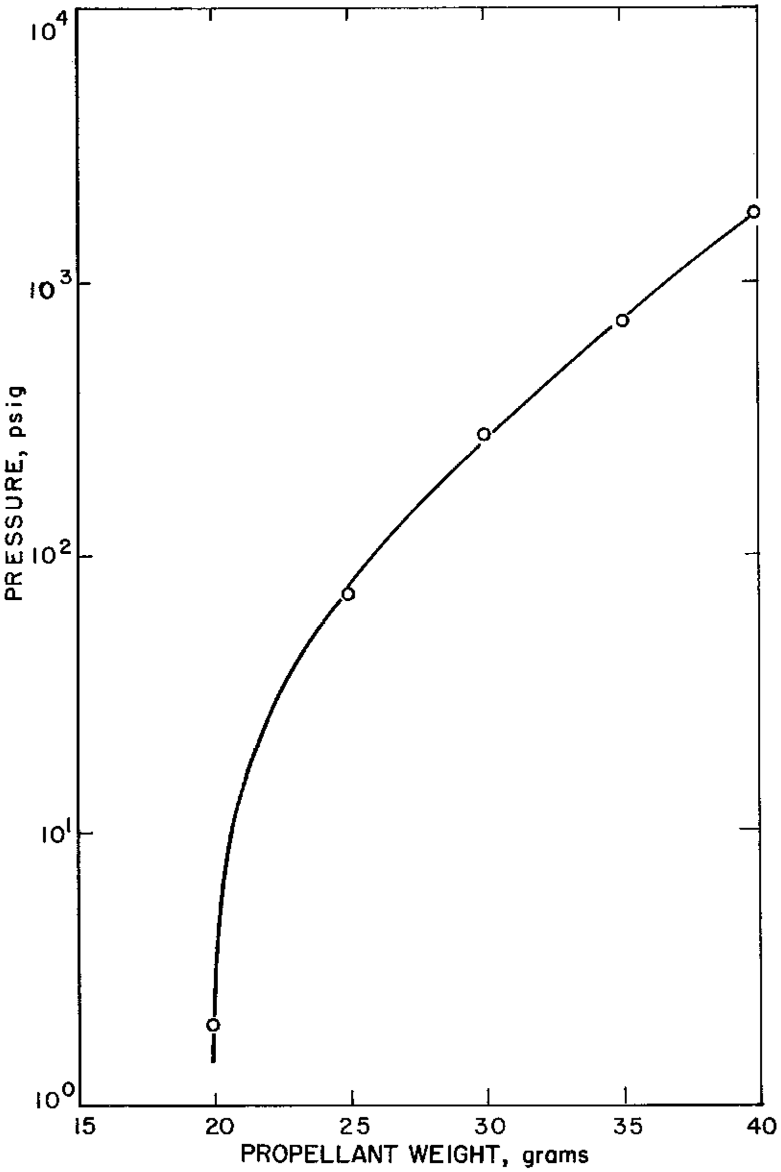

FIGURE 16. - Maximum Pressures Generated by ANP Igniter at the Bottom of a 6-Foot Inert, Porous Bed.

to determine the feasibility of using a 3-inch pipe with no vertical confinement other than that supplied by the inertia of a 6-foot porous bed. Five hundred grams of RCAN were carefully placed around 20 grams of ANP in the bottom of a 6-foot-high, 3-inch schedule 40 pipe. The pipe was then filled to the top with prilled urea to simulate prilled AN. About 300 milliseconds after the start of ignition of the ANP the pressure rose in 50 milliseconds to 3,400 psi. At this point a very rapid pressure rise (10^6 psi per second) resulted. The bottom 3 feet of the pipe was broken into large fragments. (The pressure time trace is shown in fig. 18.) With 600 grams of RCAN in a similar experiment (all other factors being unchanged), almost identical results were obtained.

In other preliminary trials, a comparison was made between the pressure developed by 500 and 1,000 grams of brand A AN ignited at the bottom of a 6-foot bed. The AN was placed above 30 grams of ANP igniter, and the 6-foot pipe was filled to the top with urea prills. The AN depth was about 3.5 inches for the 500 grams and 7 inches for the 1,000 grams. The average maximum pressure generated in four trials was 2,700 psig for both 500 and 1,000 grams of AN (table 9). Allowing for the 300 psig which can be developed by the ANP, about 2,400 psig was developed on the average by the AN prior to ejection from the pipe.

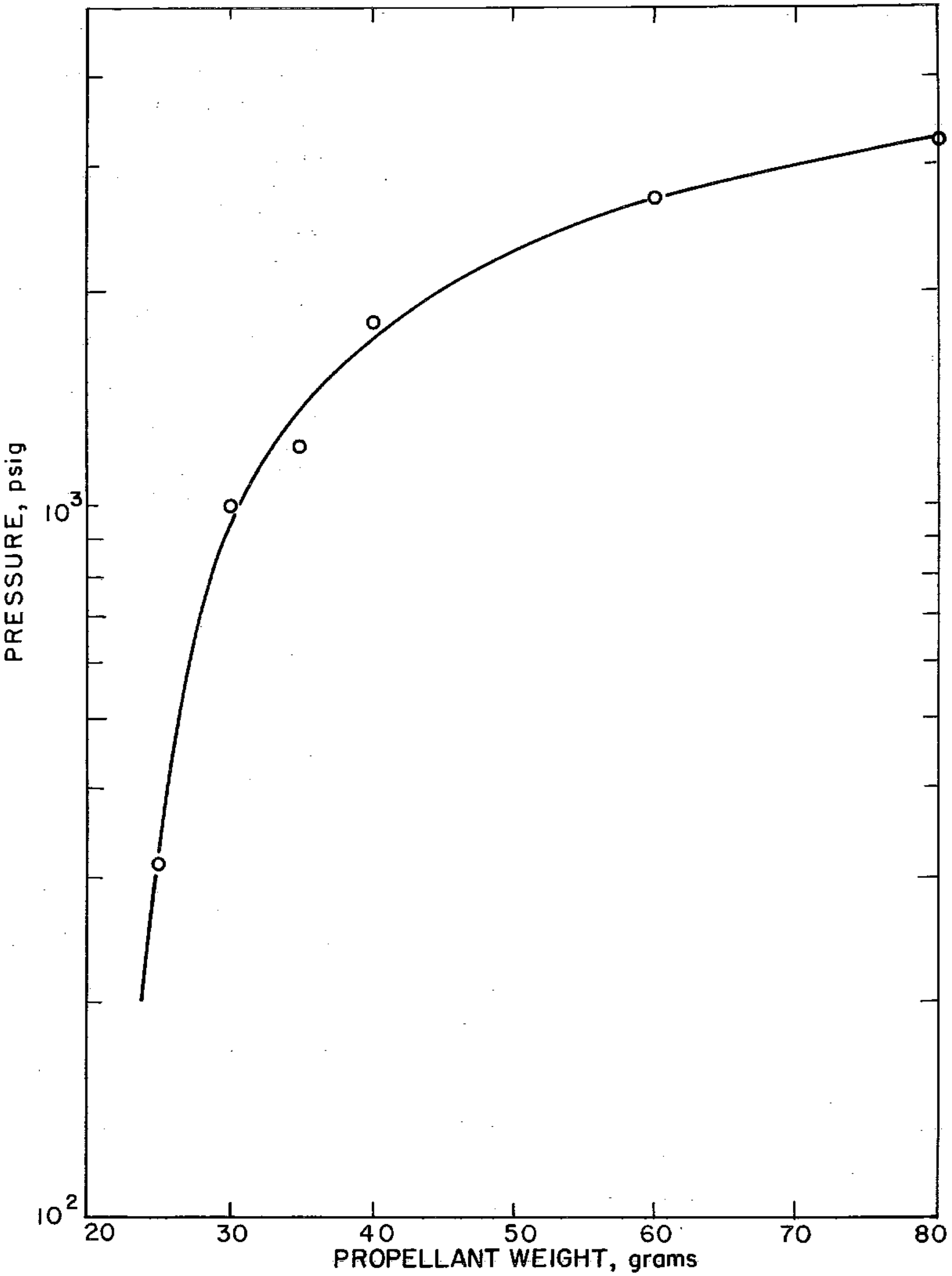

FIGURE 17. - Maximum Pressures Generated by ANP Igniter at the Bottom of a 12-Foot Inert, Porous Bed.

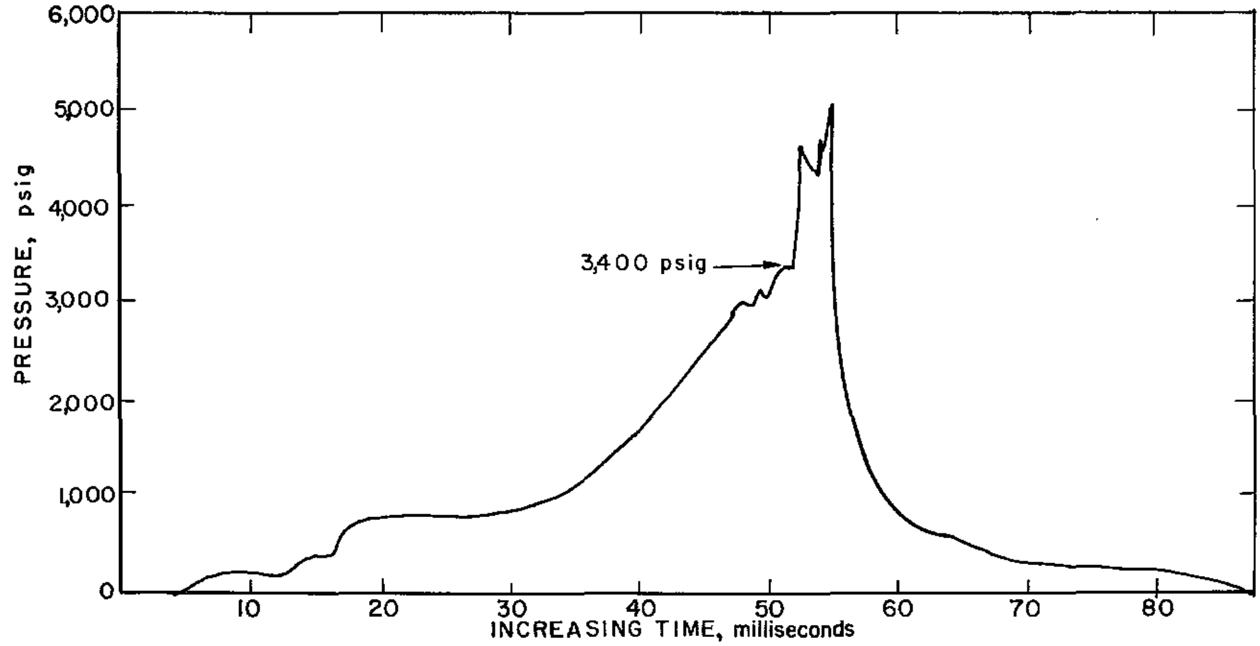

FIGURE 18. - Pressure Developed by 500 Grams of RCAN Prills in a Simulated 6-Foot Deep Bed.

TABLE 9. - Maximum pressure (in thousands of psig) generated by ammonium nitrate (brand A) ignited by 30 grams of a rocket propellant at the bottom of a 6-foot bed 3.4 inches in diameter

	500 grams AN	1,000 grams AN
	1.7	3.8
	3.0	2.5
	3.8	3.2
	2.2	1.3
Average value	2.7	2.7

In an attempt to reduce the variation in the maximum pressures developed and to ignite the AN better, the ANP was supplemented in some trials with resin-coated AN (RCAN) since RCAN had been found to be more readily ignited than AN prills. To study the decomposition of AN with more severe confinement, a series of runs was made with 12- and 21-foot beds. The technique used differed from that used in the 6-foot beds only in the depth of the prilled urea burden. The results suggest that the minimum pressure necessary to initiate sustained decomposition is about 300 psig. With an igniter mixture of 100 grams of RCAN and 25 grams of ANP, there was no increase in pressure with increase in height of bed. The 21-foot bed gave a maximum peak pressure of 4,200 psig, which was less than the maximum measured for the 12-foot bed (6,200 psig) and not significantly different from the maximum measured in the 6-foot bed (4,900 psig). The data, together with data from 6-foot beds of the same diameter, are assembled in table 10. As described later in this section the formation of a plug or partial blocking of the bed in the pipe appears to be responsible for the pressure variation observed.

TABLE 10. - Maximum pressure generated by 1 kilogram of ammonium nitrate (brand A) ignited by different igniters at the bottom of 6-, 12-, and 21-foot-high beds, 3.4 inches in diameter

Bed height, feet	Igniter		Maximum pressure, thousand psig	Maximum igniter pressure, thousand psig[1]
	ANP, grams	RCAN, grams		
6	20	100	0	-
	20	150	0.4	-
	25	100	2.2	-
	25	100	4.9	-
	25	150	2.5	[2]2.2
	25	150	2.6	-
	25	150	2.9	-
	30	0	1.3	0.3
	30	0	3.8	-
	30	0	2.5	-
	30	0	3.2	-
12	25	0	2.3	0.3
	25	0	5.0	-
	25	0	4.9	-
	25	0	3.7	-
	25	0	3.7	-
	25	100	6.2	-
	25	100	5.0	-
	30	0	4.5	1.0
	35	0	4.5	1.2
	40	0	4.9	1.7
	40	0	5.0	-
21	25	100	4.2	([3])
	25	100	3.4	-

[1] Taken from figures 16 and 17.
[2] Measured directly.
[3] Not determined.

As the critical diameter for detonation decreases with temperature, the temperature of the AN was increased to facilitate transition to detonation in the simulated one dimensional case. AN at about 120° C (1- and 5-kilogram samples) was ignited by 60 grams of ANP in 12-foot pipes. The simulated bed height was increased to 17 feet by using pea gravel for the inert burden. However, it was found that pea-gravel tended to jam and crush under pressure and to form plugs. These plugs effectively contained the AN in a closed vessel, leading to rupture at about 10,000 psi. In some cases when no plugs formed, ejection rates as high as 400 feet per second were observed by means of high speed movies.

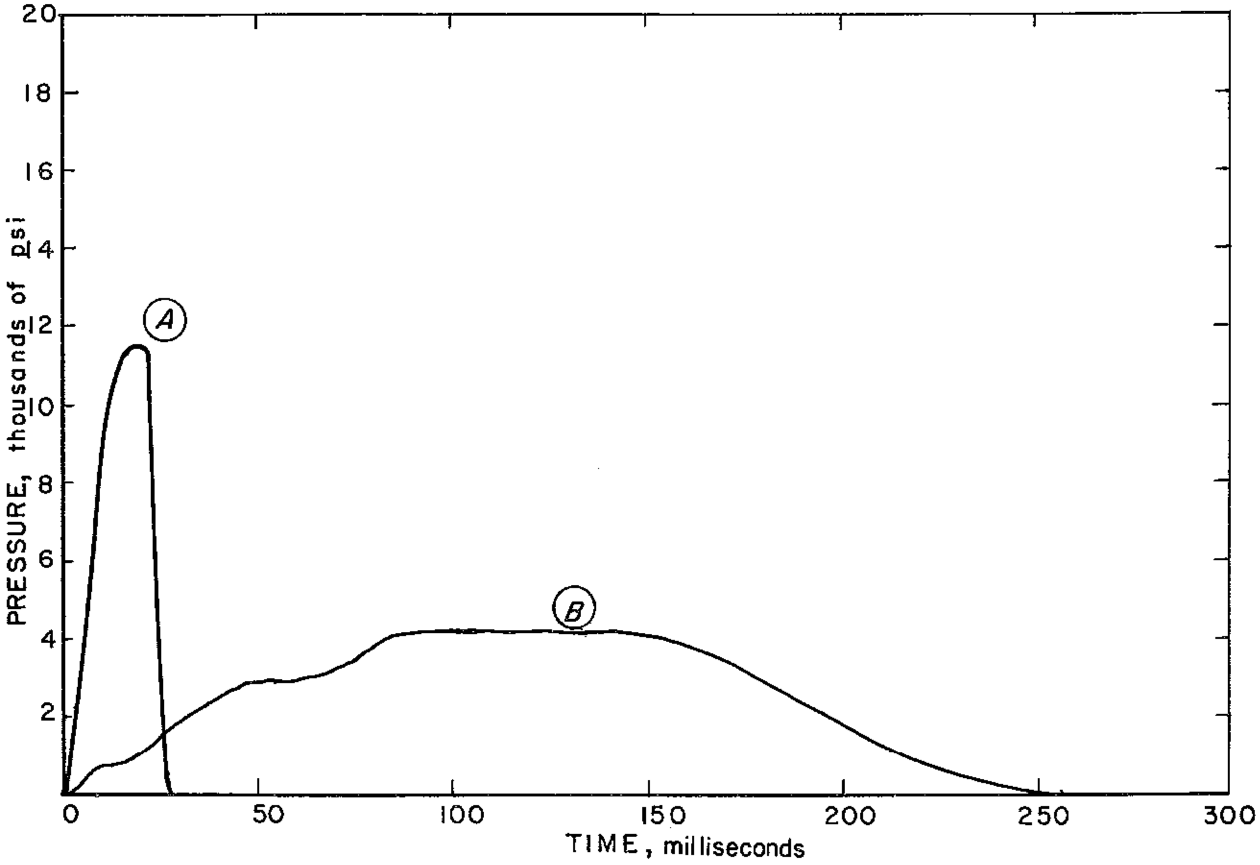

FIGURE 19. - Representative Pressure Time Traces for AN Decomposition in Which the Pipe Ruptured, *A*, and One in Which There was Bed Ejection, *B*.

The data can be separated into two groups, distinguished by whether or not the bed formed a plug in the pipe. In three runs, for which a typical pressure time trace is shown as A in figure 19, a plug formed and the pressure rose steadily and rapidly at a rate in excess of 10^6 psi per second; the vessel ruptured in about 10 milliseconds at a pressure in excess of 10,000 psig. In a fourth run (fig. 20), where a plug also formed, the pressure rose at about 120,000 psi per second for 50 milliseconds, and then it accelerated rapidly to 10,000 psig. The AN decomposed at 10,000 psig for 30 milliseconds, venting the product gases through the holes provided in the bottom of the cap for the introduction of the igniter wires.

In the other runs, for which a typical trace is shown as B in figure 19, there was free ejection of the bed from the pipe. The pressure rose less rapidly than in the first four runs, averaging about 40,000 psig per second, to reach a maximum of about 4,200 psig in 100 milliseconds. The peak pressure was sustained for about 60 milliseconds and then decreased. The maximum pressures and the times to attain them, starting from atmospheric pressure, are assembled in table 11. The trials are listed in order of decreasing pressure generated.

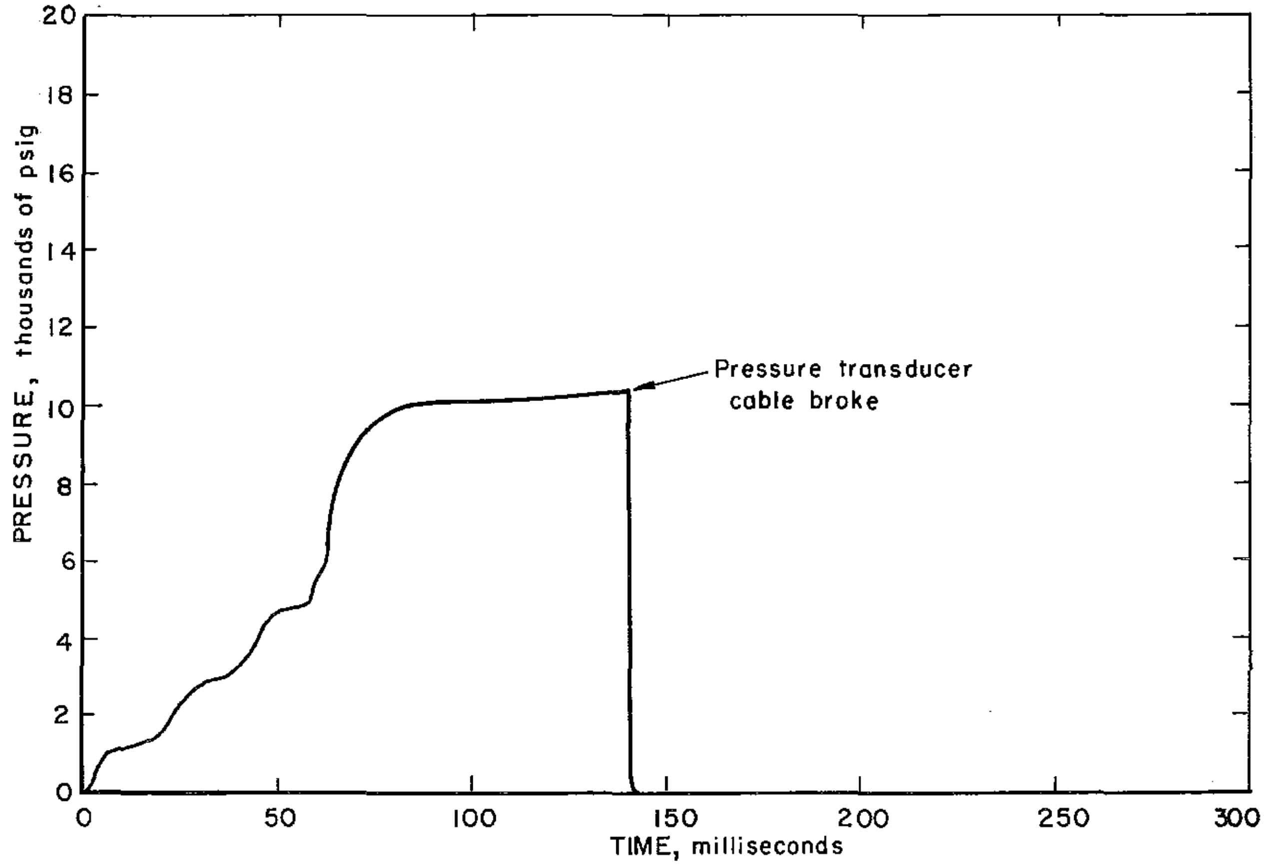

FIGURE 20. - Pressure Time Trace for AN Decomposing Steadily at 10,000 psi. The vessel ruptured after 140 milliseconds and severed the pressure transducer cable.

The pressure time traces obtained for decomposing AN samples (in the five runs where the bed did not plug) have the following average properties: Peak pressure, 4,300 psig; time for peak pressure to develop starting from atmospheric pressure, 93 milliseconds; length of time for which pressures over 1,000 psig can be measured, 213 milliseconds; and the total time for a measurable pressure pulse (that is, more than 200 psig), 231 milliseconds. In no case did a catastrophic pressure rise, such as might lead to a DDT, occur.

The lack of detonation observed in these experiments may be attributed to the charges being near critical diameter. The critical diameter for initiation by an explosive-derived shock (figs. 2 and 3) for AN prills at 110° C under the confinement typical of these experiments is between 2 and 2.5 inches, not much less than the 3.4-inch diameters used here. However, the answer lies most likely in the fact that the shocks developed by accelerating combustion have a much lower amplitude than shocks from explosive boosters.

TABLE 11. - Maximum pressure generated by hot ammonium nitrate (brand A) prills ignited by 60 grams of propellant (ANP) at the bottom of a porous bed contained in a 12-foot-long pipe 3.4 inches in diameter

AN weight, kg	Temperature, ° C	Height[1] of bed, ft	Maximum pressure, thousands of psig	Time to attain maximum pressure, msec	Remarks
1.0	110	11	>10.0	15	1 kg brand A (9 inches) topped with 15 kg of pea gravel. Hard plug formed 7 inches thick starting 2 feet up from the bottom.
1.0	120	11	>11.6	16	1 kg brand A (9 inches) topped with 15 kg pea gravel. Hard plug formed 7 inches thick starting 1½ feet up from the bottom with 2 feet of loose gravel on top.
1.0	112	16	>9.3	273	1 kg brand G (9 inches) on top of ANP--9 kg brand H (6.5 feet) above this and topped with 13 kg pea gravel. Pipe was cleared out but broken loose at lower cap and ejected from bombproof. Probably formed a plug.
5.0	130	11	>10.0	140	5 kg brand A (3½ feet) topped with 11 kg pea gravel. Hard plug formed 3 inches thick starting 3½ feet up from the bottom.
5.0	128	8	6.6	120	5 kg brand A topped with 7 kg pea gravel. No plug evident.
5.0	125	8	5.0	45	5 kg brand A topped with 7 kg pea gravel. No plug evident.
5.0	115	13	4.2	110	5 kg hot brand A topped with 8.3 kg cold AN. Small isolated pieces of AN stuck to the pipe wall.
5.0	125	17	3.4	90	Brand A topped with 6.8 kg gravel. Upper 4 feet of pipe glazed with a thin layer of molten AN.
5.0	115	12	2.5	110	5 kg hot brand A topped with 13 kg of cold brand A.

[1] Effective height of the bed calculated as AN prills.

Combustion of Ammonium Nitrate-Fuel Mixtures in Beds

Since some combustibles seem to accelerate AN decomposition and may be present in a fire situation, the studies of decomposition at the bottom of an AN bed were extended to include paper and polyethylene as fuels. Three kilos of AN, mixed with 5 percent polyethylene, were ignited by 30 grams of ANP propellant at the bottom of a steel pipe 3.4 inches in diameter, 6 feet in length. Approximately 3 kilos of raw prilled AN was used as burden above the fuel mixture. The ignition method and pressure measuring system were as described in the section on burning in beds of prilled ammonia nitrate. In two trials in which a micropulverized mixture of brand G prills and 5 percent polyethylene at 38° C was used at a loading density of 0.5 gram per cubic centimeter, the burden was ejected from the pipe by the burning AN-fuel mixture and a pressure of 2,000 psi was developed in 50 milliseconds. In a third trial under identical conditions, the result was identical except that 3,000 psi was reached in 20 milliseconds.

In other trials the column height was increased to 12 feet. One kilo of brand E AN prills was mixed with 2 percent paper (plugs from punched-card holes), warmed to 94° C, and ignited by 60 grams of ANP propellant. The resulting combustion developed a pressure of 4,800 psi in 39 milliseconds with subsequent ejection of the burden. A similar mixture heated to 122° C before ignition developed a pressure of 3,000 psi in 15 milliseconds with subsequent ejection of the burden. A mixture of 1 kilo of brand E prills with 2 percent PE fines warmed to 50° C and ignited, developed a pressure of 4,000 psi in 19 milliseconds before ejection of the burden. One kilo of brand E was micropulverized with 5 percent PE. When this mixture was ignited at 22° C, a pressure of 4,600 psi was developed in 34 milliseconds before ejecting the burden from the pipe. One kilo of brand G AN was mixed with 5 percent PE and micropulverized. At a temperature of 32° C with 30 grams of ANP igniter, this mixture developed 3,800 psi in 80 milliseconds before ejection of the burden (table 12).

The average pressure (4,100 psi) developed by fueled mixtures of AN was about the same as that developed by raw AN but the average time to peak pressure, using 60 grams of ANP igniter, was 27 milliseconds, about one-third of that for raw AN (table 11). In no case was detonation observed.

Decomposition in Inverted Models of Ammonium Nitrate Beds

The experiments described in the previous paragraphs demonstrated that pressures as high as 4,000 psi could be reached in free moving beds for a few milliseconds prior to appreciable movement of the bed. Because of the experimental difficulties imposed by bed and pipe movement, the question of the minimum pressure at which transition from deflagration to detonation would occur still remained unanswered. To overcome these problems, AN and AN mixtures were burned in 3-inch id pipes closed at the top except for an orifice to control the pressure. This inverted bed still simulates a real bed, except for movement of the overall bed. Again, elevated temperature, small particle size, low density, and addition of fuel were used to reduce the critical diameter. Ignition was at the top, just beneath the orifice by means of ANP propellant.

Preliminary work was done in pipes 2 feet in length. These were subsequently lengthened to 4 feet to provide sufficient length of bed for a transition to occur.

TABLE 12. - Maximum pressure generated by ammonium nitrate-fuel mixtures ignited by 60 grams of propellant (ANP) at the bottom of a 3.4 inches in diameter porous bed contained in a 12-foot-long pipe

AN weight, kg	Fuel, percent	Maximum pressure, thousands of psig	Time to attain maximum pressure, msec	Remarks
3	2	4.8	39	1 kg brand E with 2 percent paper at 94° C (9 inches), topped with 2 kg brand H (16 inches) and 14 kg urea prills. Pipe cleared out by ejection of burden.
3	2	3.0	15	1 kg brand E with 2 percent paper at 122° C (9 inches), topped with 2 kg brand H (16 inches) and 14 kg urea prills. Pipe cleared out by ejection of burden.
3	2	4.0	19	1 kg brand E with 2 percent polyethylene fines (11 inches) at 50° C, topped with 2 kg brand H (18 inches) and 14 kg urea prills. Pipe cleared out by ejection of burden.
3	5	4.6	34	1 kg brand E with 5 percent polyethylene fines pulverized together, ambient temperature (11 inches). Topped with 2 kg brand H (16 inches) and 13 kg urea prills (9.75 feet). Pipe cleared out by ejection of burden.
3	5	3.8	80	ANP reduced to 30 grams. 1 kg brand G with 5 percent polyethylene micropulverized together (11 inches) and topped by 2 kg brand H (16 inches) and 13 kg urea prills. Pipe cleared out by ejection of burden.

The 4-foot containers were equipped with pressure pick-ups at the center and top and an expendable pressure transducer capable of measuring detonation pressures located at the bottom of the charge. Rate measuring stations were positioned 10 centimeters apart, the lower station being 10 inches above the bottom of the pipe. The container shown in figure 21 was constructed of 4-inch schedule 120 steel pipe, 4.5-inch od by 3.15-inch id, capped with 3,000-pound standard pipe caps. Calibration runs were made to determine the igniter pressure developed for different orifice diameters using cast iron shot as an inert filler. The pressure developed by the ANP igniter is designated as the "ANP pressure."

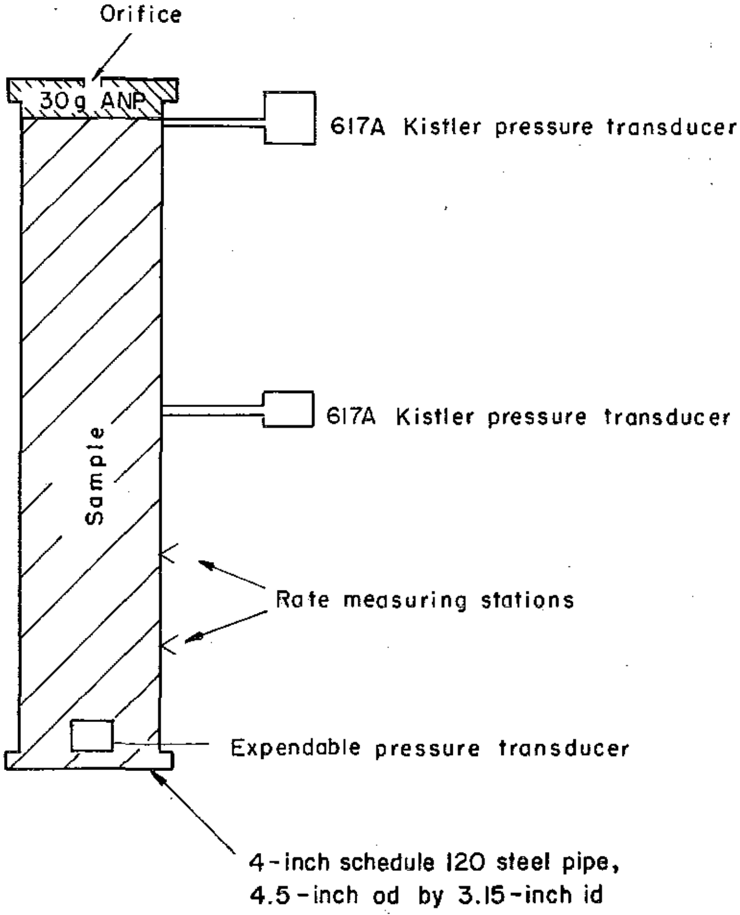

FIGURE 21. - Container Used to Study Pressure Required for Transition to Detonation of AN-Fuel Mixtures.

In the 2-foot container with a 1/8-inch vent, a mixture of brand E prills with 5 percent fuel oil, when ignited with 30 grams ANP, fragmented the container, giving some indication that a DDT had occurred. A micropulverized mixture of brand G with 5 percent polyethylene reached a pressure in excess of 50,000 psi and apparently underwent transition to detonation. Raw prills ignited with 30 grams of ANP did not burn to completion even though a pressure of 1,250 psig was recorded. With larger weights of igniter much higher pressures developed and the container ruptured but no DDT was indicated. The pressure-time trace for a run with raw brand A prills, ignited by 30 grams of ANP, is shown in figure 22 and shows that the pressure rose continually for about 140 milliseconds, reaching an ultimate pressure of about 8,000 psi. This maximum pressure of 8,000 psi was sustained for about 10 milliseconds prior to rupture of the vessel. The data for the 2-foot pipes are given in table 13. When raw brand A prills were burned in the 4-foot-long container with the same weights of igniter, lower peak pressures were obtained. The pressures were 1,950, 3,000 and 3,400 psig when the 30, 45, and 60 gram igniters were used.

These experiments were continued using a longer 4-foot container to allow more time for the run-up of the deflagration to detonation. Some samples were heated to 100° C before ignition. By varying the orifice size, the effect of pressure on the burning behavior of prilled and pulverized brand E AN alone and mixed with polyethylene (PE), paper, or fuel oil was determined. A constant igniter weight of 30 grams was used.

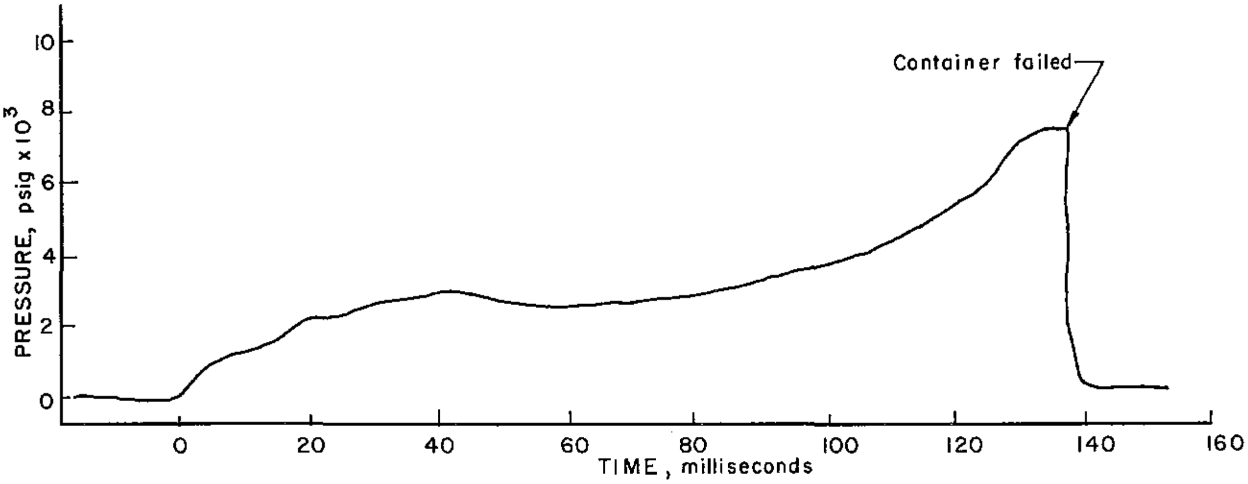

FIGURE 22. - Pressure Time Record for the Decomposition of Brand A Prills Ignited by ANP.

TABLE 13. - Burning behavior of ammonium nitrate systems in 2-foot container

Sample	Grams ANP	ANP pressure	Developed pressure, psig	Remarks
Brand E + 5 percent FO prills.	30	160 psig	-	Pipe fragmented.
Brand G pulverized[1]	30	160 psig	10,000	Decomposed all of AN but 4 inches. No vessel damage.
Brand G + 5 percent PE[1] pulverized.	30	160 psig	>50,000	System presumably detonated.
Brand A prills.....	30	160	1,250	1,500 grams high density prills recovered.
Brand A prills.....	45	220	8,000	Both caps pulled off, 10 percent decomposed.
Brand A prills.....	60	300	6,200	Cap pulled off pipe, 100 percent decomposed.

[1] 2,000 grams of the pulverized mixtures were used in these runs; 2,400 grams in all other runs.

A micropulverized mixture of AN and 5 percent PE was the most rapid burning of the materials tried; a DDT occurred with a 7/16-inch vent. A similar mixture but one containing only 1 percent required a 5/16-inch vent. Prills mixed with 5 percent polyethylene underwent a DDT with a 1/4-inch vent. One out of two trials with prills and 5 percent fuel oil gave a DDT with a 1/8-inch vent. AN pulverized with 15 percent paper (approximately a stoichiometric mixture) yielded a DDT with a 3/8-inch vent, apparently a mixture nearly as reactive as the AN-PE mixture. Again raw prills failed to show a DDT although a pressure of 1,700 psig was recorded. Pulverized AN with a 1/8-inch vent in the container burned for approximately one-half second at 1,000 psig, after which the pressure rose to 6,400 psig, causing the container to fail. The data are summarized in table 14.

TABLE 14. - Burning behavior of brand E systems in 4-foot vented vessels

Orifice, inch	ANP pressure, psig	100° C									
		AN + 5 percent PE, micro-pulverized		AN + 1 percent PE, micro-pulverized		Prills + 5 percent PE		Prills + 1 percent PE		Prills + 4.2 percent FO[2]	
		Psig	Result[1]	Psig	Result[1]	Psig	Result[1]	Psig	Result[1]	Psig	Result[1]
1/8	180	-	-	[3] 9,000	Yes[3]	-	-	1,500	No	-	-
1/4	160	-	-	-	-	1,000	Yes	700	No	-	-
5/16	140	-	-	1,200	Yes	-	-	-	-	800	No
3/8	110	-	-	700 750	No[4]	700	No	-	-	-	-
7/16	85	1,200	Yes	-	-	-	-	-	-	-	-
1/2	50	700	No	-	-	-	-	-	-	-	-
9/16	-	500	No	-	-	-	-	-	-	-	-
3/4	-	<150	No	-	-	-	-	-	-	-	-
		30° C									
		Prills		Prills + 5 percent FO, No. 1		Prills + 5 percent FO, No. 2		AN + 15 percent paper, pulverized, dry		AN + 15 percent paper, pulverized, 4 percent water	
		Psig	Result[1]	Psig	Result[1]	Psig	Result[1]	Psig	Result[1]	Psig	Result[1]
1/8	180	1,700	No	1,000	No	1,700	Yes	-	-	1,000	Yes
1/4	160	-	-	800	No	-	-	1,100	Yes	700	No
5/16	140	-	-	800	No	-	-	1,100	Yes	650	No
3/8	110	-	-	450	No	-	-	950	Yes	-	-
7/16	85	-	-	-	-	-	-	900	No	-	-
1/2	50	-	-	-	-	-	-	-	-	-	-
9/16	-	-	-	-	-	-	-	-	-	-	-
3/4	-	-	-	-	-	-	-	-	-	-	-

[1] Yes indicates that, at the 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.
No indicates that the pressure is the maximum pressure measured during the experiment.

[2] By analysis of sample taken just prior to ignition.

[3] In contrast to all other runs, pressure rose continuously after ignition until disintegration of the vessel.

[4] 2 trials.

Only fast burning was observed when the pressures developed by the AN mixtures were less than about 1,000 psig. When burning took place at pressures higher than 1,100 to 1,200 psig, the combustion continued over a period of 100 to 150 milliseconds with a relatively slow rise in pressure to about 2,200 to 3,000 psig, after which a very rapid rise in pressure occurred, causing fragmentation of the vessel. Detonation rates of 2,000 meters per second (6,560 ft/sec) were measured and

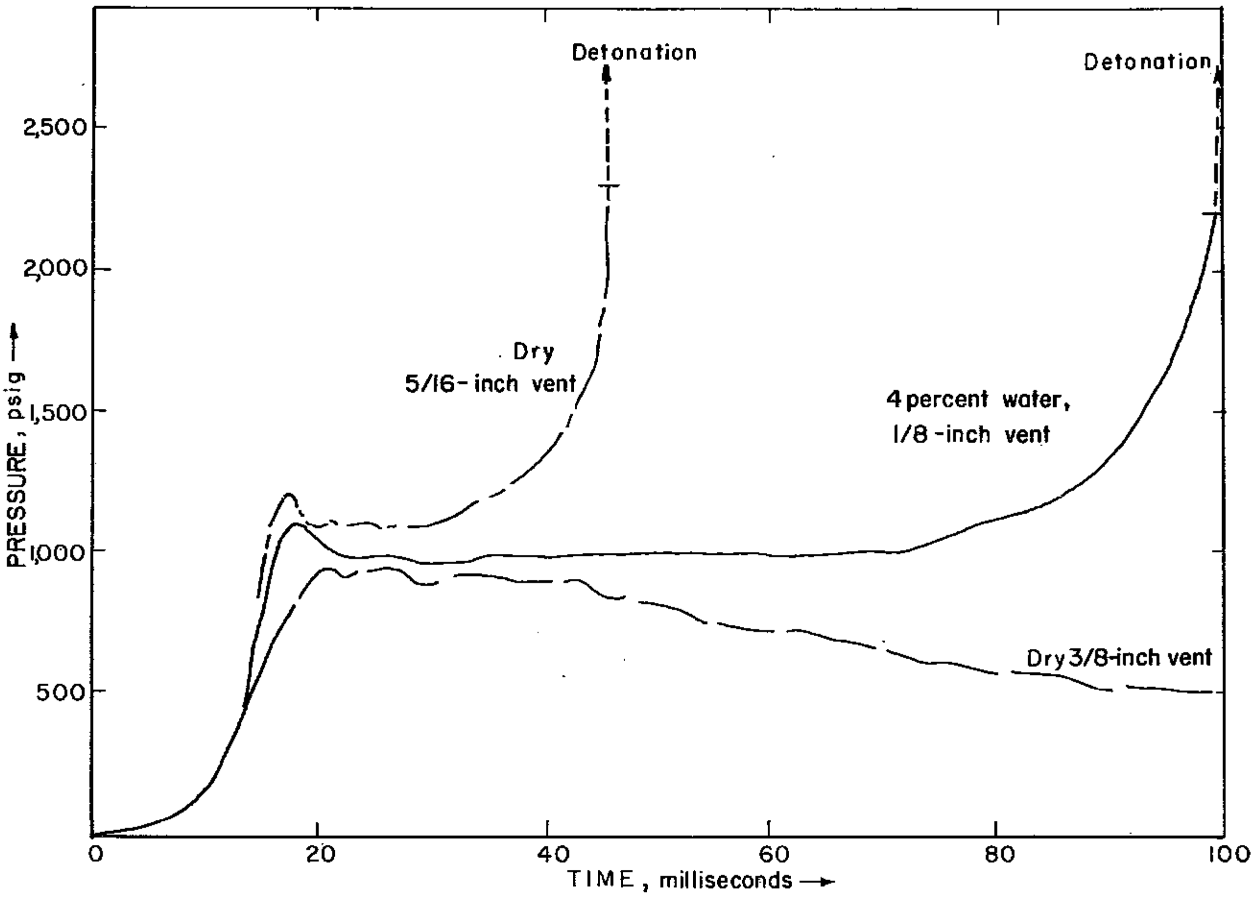

FIGURE 23. - Pressure Time Curve for Wet and Dry Pulverized Brand E AN With 15 Percent Paper Decomposing in a Vented Vessel, 3.15-Inch id by 4-Foot Length.

pressures of over 50,000 psi were recorded by the expendable pressure transducer at the bottom of the pipe, clear evidence of a detonation.

Compressed plugs of AN were recovered from several runs where only partial burning occurred. The AN had been compressed from a density of about 0.5 gram per cubic centimeter to 1.5 grams per cubic centimeter. This packing presumably occurs in all runs and may be responsible for the ultimate, sudden rise in pressure from the plateau of 1,000 to 1,200 psi to pressures of 2,000 to 3,000 psi from which catastrophic pressure rises commence.

The effect of water on the burning rate of mixtures was briefly examined. Pulverized brand E AN mixed with 15 percent by weight pulverized paper was either ignited as prepared (less than one-half percent H_2O), or purposely mixed with 4 percent water. Figure 23 shows the pressure time curve for three of these runs, two samples containing no water, and the other containing 4 percent water. The sample containing 4 percent water underwent DDT when the vent size was one-eighth of an inch or about 9 times smaller in area than the minimum required for the identical dry sample.

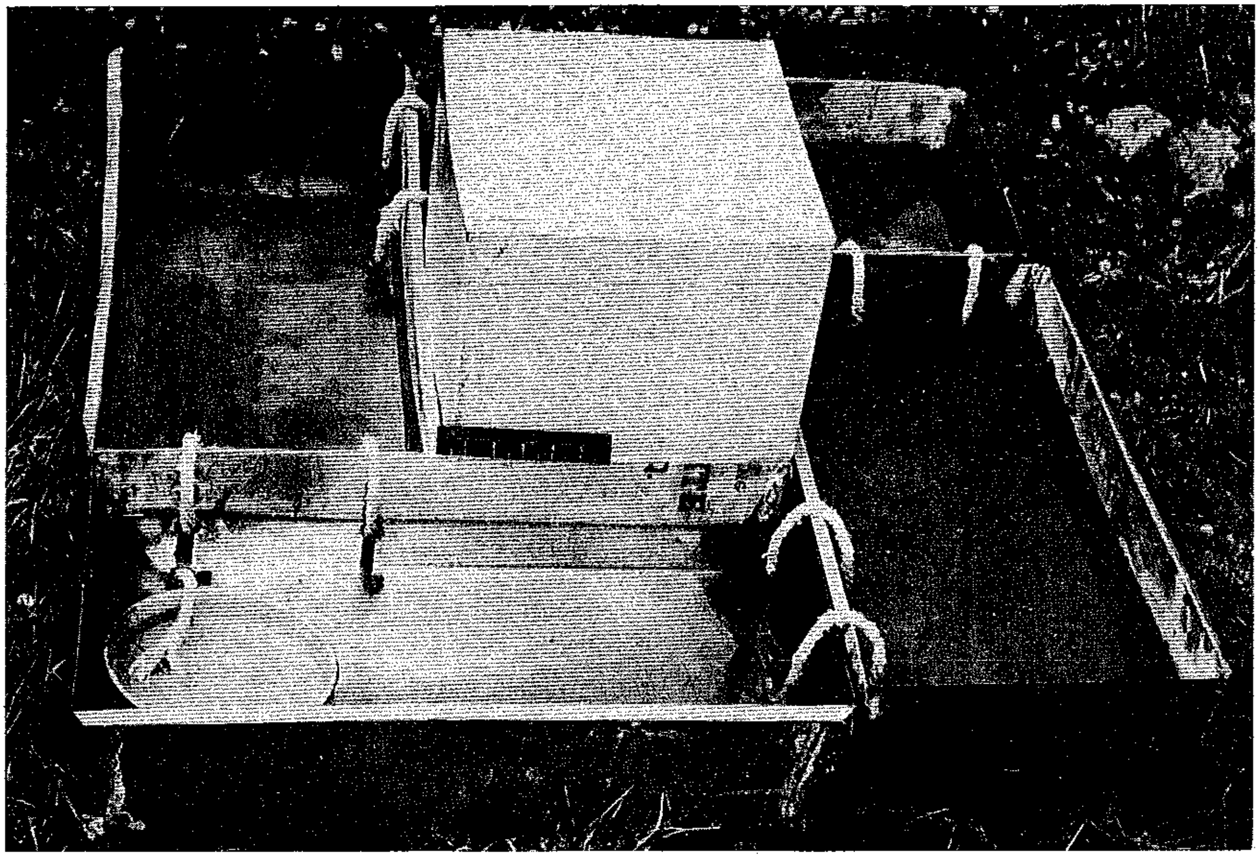

FIGURE 24. - Arrangement of Container and Oil Pans for Burning Studies. Container is filled with 48.4 pounds of brand C ammonium nitrate prills.

FIRE TESTS ON AMMONIUM NITRATE

On December 27, 1961, a fire and explosion destroyed an AN-FO mixing plant in Norton, Va.[31] This incident and the finding that certain molten urea-AN mixtures were readily detonable suggested the desirability of conducting relatively large-scale fire tests of these mixtures rather early in the program.

A preliminary series of fires, designed primarily to test instrumentation, was conducted in a strip mine near Clearfield, Pa. The experimental scheme was to envelop samples of AN or of AN mixtures in a fire so as to simulate exposure to a much larger fire. The arrangement, shown in figure 24, consists of a central steel container 1 foot by 1 foot by 1 foot in depth filled to the top with prilled AN or AN mixtures and surrounded by four trays 1 foot by 2 feet by 6 inches deep, containing 22 gallons of diesel oil. Stainless steel thermocouple wells were inserted through the bottom of the AN container; the thermocouple leads were conducted underground to a cold junction and recorder.

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[31] Van Dolah, Robert W., and Joseph S. Malesky. Fire and Explosion in a Blasting Agent Mix Building, Norton, Va. BuMines Rept. of Inv. 6015, 1962, 12 pp.

Fifty-pound quantities of AN, AN-urea, and AN-FO were burned in these tests. The first fire involving 48.4 pounds of prilled AN was uneventful. For the second trial, 41 pounds AN were premixed with 10 pounds technical grade urea. The solids dropped from sight after 9 minutes; at the same time there appeared to be a flame burning at the mouth of the container. Extensive foaming occurred after 14 minutes and a large flame lasting for several seconds appeared at 17 minutes. The mixture was found completely consumed, except for reddish-brown residue. For the final experiment on this scale 46 pounds AN and 2.3 pounds diesel oil were premixed and allowed to stand overnight. The burning of AN-FO was very vigorous and lasted for about 39 minutes even though the surrounding oil was burned away in about 35 minutes. Very little residue was found.

Large-scale fires of AN-urea and AN-FO were conducted at a diatomite mine made available by the Aquafil Corporation near Fernley, Nev. Eight AN mixtures, ranging from 100 to 5,000 pounds were burned with surrounding diesel oil fires used again to simulate much larger scale fires. No unusual behavior was observed in any of these fires.

The AN mixtures, contained in 50- and 80-pound paper bags, were stacked in roughly cubical piles surrounded by oil contained in 2-foot by 5-foot by 6-inch-deep trays. Efforts were made in several instances to increase convective exposure to the oil flame with channels in the pile of bagged material made by building the pile on a latticework of timbers or by putting oil under the pile as well as around it.

For one fire, 800 pounds of brand A mixed with 200 pounds of prilled urea was piled (in 20 50-pound paper bags) on top of a single layer crib of 4- by 4-inch by 3-foot timber. The pile was held together by vertical posts of 4- by 4-inch by 3-foot timber. The mixture burned rapidly but uneventfully, being completely consumed in 20 minutes. Examination of the site after the fire showed that considerable material had melted and run away from the fire zone.

The experiment was repeated with 800 pounds of brand G mixed with 200 pounds of prilled urea. The twenty 50-pound bags were piled in a metal pan 2 feet by 5 feet by 6 inches deep, which rested on top of the pans containing the oil. Under these conditions the fire eventually surrounded a pool of molten 80 parts of AN and 20 parts of urea several inches deep. About 5 minutes after ignition a bag was observed to break and spill the AN-urea mixture into one of the pans of burning oil. All the AN-urea appeared to be consumed in 30 minutes.

In a third fire, 1,300 pounds of brand A in 50-pound bags, 2,960 pounds of brand G in 80 pound bags, 600 pounds of prilled urea in 100-pound bags, 50 pounds of a mixture of 80 parts of AN and 20 parts of urea and about 75 empty paper bags were randomly stacked in a pile 56 inches square by 76 inches high (fig. 25). This pile contained a total of 4,910 pounds of material containing about 12 percent urea. In the course of the fire some of the bags fell off the pile into and beyond one of the pans. However, the spilled material was not entirely consumed and some prills were found intact under a crust

FIGURE 25. - Arrangement of 4,910 Pounds of Mixed AN, Paper Bags, and Urea. The urea content is about 12 percent.

after the fire (fig. 26). The heated AN prills appeared to melt on the surface forming a cover of molten AN that could not penetrate the interior of the pile; in turn the pile did not heat appreciably because of the low heat transfer of the solid AN.

This observation was confirmed by subsequent work on a laboratory scale. Four-inch glass tubes 12 inches long were closed at the bottom by a rubber stopper through which were placed thermocouple wells extending up into the tube. The end of the first well was placed 1 inch below the top of the tube and the others were in descending 1-inch steps. Thermocouples were also placed on the outside of the glass container opposite those inside to observe the heat conduction through the glass walls. The tube was filled with AN prills and heat was applied to the surface from above by means of a burner using natural gas and compressed air.

With brand A prills, the melt on top was only one-quarter of an inch thick (fig. 27) and the size of the flame from the torch seemed to have little effect on the depth of melt. After 80 minutes in one trial, the surface of the AN was down 4 inches from the top of the container. One inch below the lower surface of the melt the temperature was 50° C whereas at 2 inches below the surface the AN was at ambient temperature (30° C). When 80 percent AN (brand A) + 20 percent urea (technical) were used, the material ignited easily and burned slowly. The temperature was only 40° C, three-quarters of an inch below the surface of the melt, while 1-3/4 inches below the surface the mixture was still at ambient temperature.

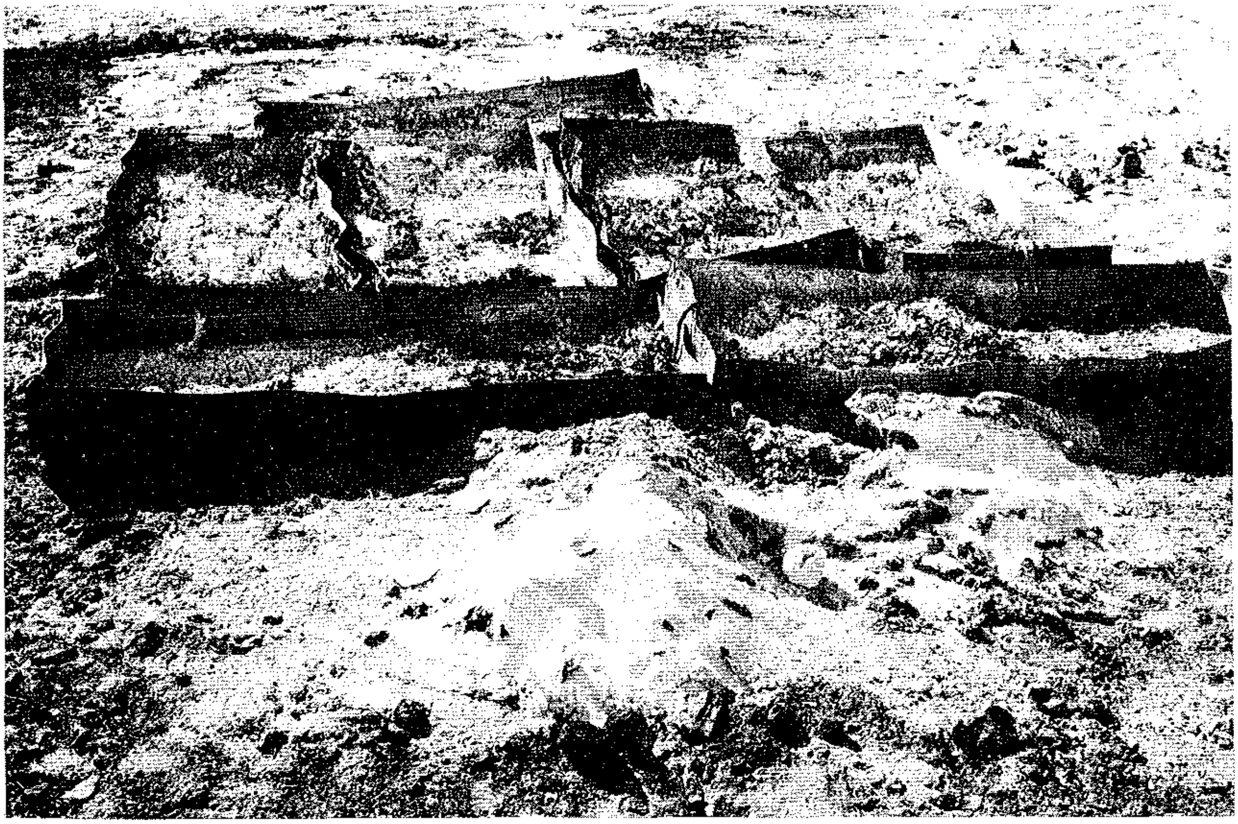

FIGURE 26. - Residue From Fire Involving 4,910 Pounds of Mixed AN and Urea. Note the unchanged prills in the foreground from which the fused crust has been scraped away.

Because of the rather vigorous burning of AN-FO observed in the preliminary fire at Clearfield, two somewhat larger but similar fires were made at Fernley using 100 pounds AN-FO (brand A). A steel box 1 foot by 1 foot by 2 feet deep was used to contain the AN-FO. In the first fire, the box rested on the ground so that the lower 6 inches of sidewall were protected from the flame by the sides of the oil trays. During this fire there was a continuous, audible ejection of particles that left trails of white smoke until the oil in the surrounding trays was consumed. The AN-FO burned down to about the 6-inch level leaving residue of prills covered by a thin crust of resolidified AN. In a second similar trial the container was supported above the oil trays. The burning was again very vigorous with many sprays of particles; all of the AN-FO was consumed within 30 minutes; very little residue remained in the container.

Three large-scale fires were burned with AN premixed with 6 percent fuel oil. In one fire, 960 pounds of brand A_x AN-FO in 80-pound bags were piled on two layers of cribbed timber 4- by 4-inch by 3 feet long, and the pile was surrounded by pans of oil. In another fire, 1,000 pounds of brand A AN-FO in 50-pound bags were piled on a cribbing of 4-inch by 4-inch timbers 3 feet long, one layer high. The pile was held in place by 4- by 4-inch wooden stakes

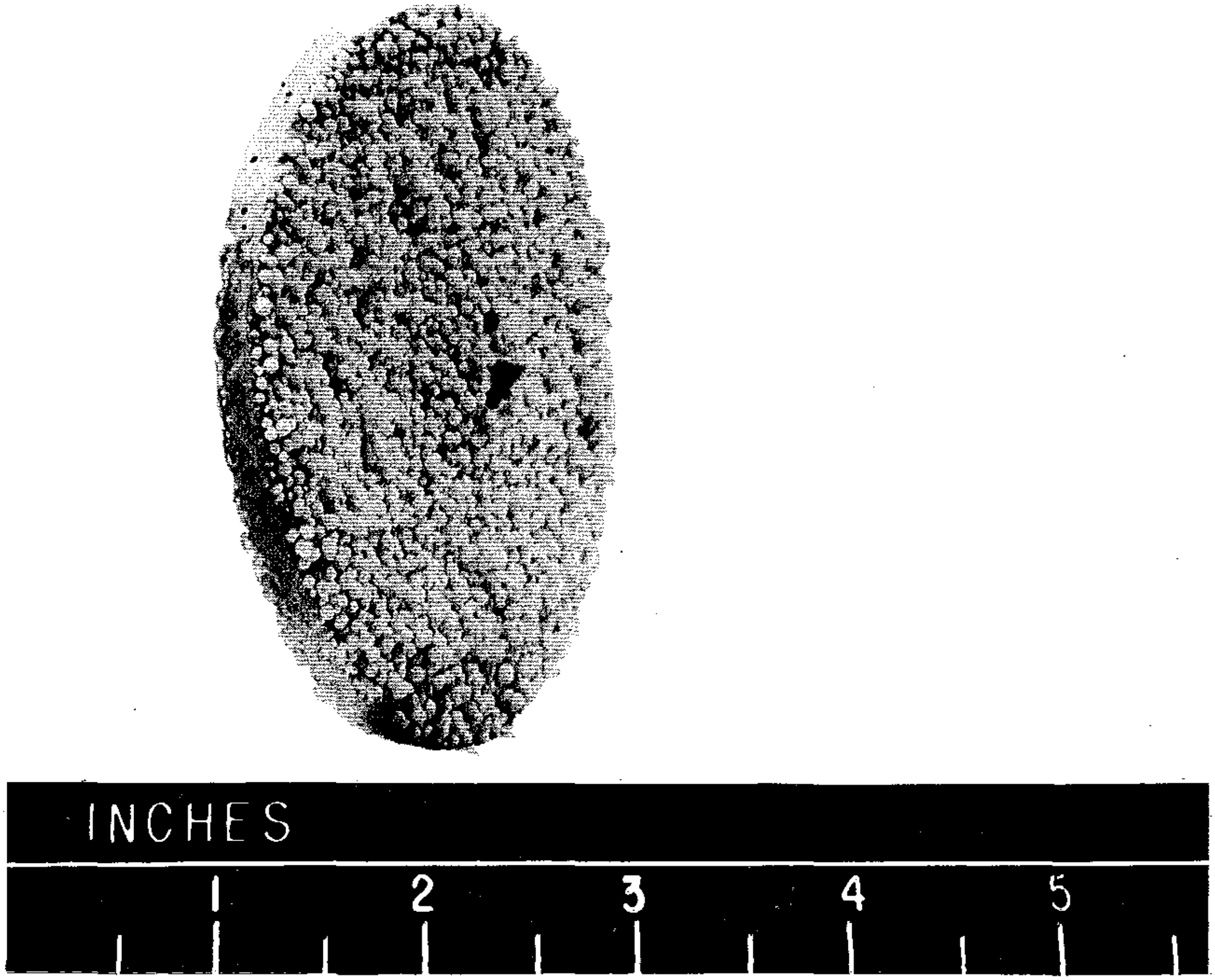

FIGURE 27. - Crust Formed After Exposing a Column of AN Prills Contained in a Glass Pipe to a Gas Flame.

secured by iron wire. The third fire of the AN-FO series, involved 1,000 pounds of Brand G mixed with 6 percent fuel oil. In this case the material was stacked on trays to retain the molten AN.

Radiation measurements were found to be about as expected from diesel oil fires indicating that the decomposing AN samples made little if any contribution to the overall fires.

A more important aspect of the surrounding oil fire is the severity of the fire exposure on the AN mixtures. Despite nearly constant winds that sometimes were rather high, the surfaces of the piles were exposed to a more or less constant radiant flux of about 3 watts per square centimeter, a figure derived from the evaporation rate of oil in the surrounding trays. The fires described were characterized by a complete lack of confinement and it must be emphasized the still larger-scale fires may introduce problems of internal confinement. The vigorous reaction of the AN-FO in steel containers demonstrates the potential danger of confining a gas-producing reaction under a thick bed of granular material.

MATHEMATICAL ANALYSIS OF THE POSSIBILITY OF A DEFLAGRATION TO DETONATION TRANSITION

Fertilizer-grade AN has been shown to be detonable by shock without resort to such modifications as pulverization, addition of fuel, or strong confinement, although it is weak and insensitive and has a very large critical diameter (~100 times that of ordinary explosives) under normal conditions.[32] In the absence of strong shock sources, detonation can only be initiated by a deflagration-to-detonation transition (DDT). The possibility of such an event is examined analytically in this section.

The basic difference between deflagration and detonation is that in the former the reaction propagates mainly via thermal conduction, while in the latter the propagation is by hydrodynamic shock with a reaction rate correspondingly greater (by a factor of about 10^5). Still another mechanism must be operative in the transition process in order to span this range of rates; this mechanism is the forced convection of the hot products of reaction through the unreacted material.

In the transition process, as the reaction rate and consequent pressure rise are accelerated, the material begins to be compressed and to flow. If the acceleration is sufficiently rapid, a shock wave will form, and if the shock becomes strong enough, the associated heating of the material will of itself cause sufficiently rapid reaction to maintain the shock. This is the detonation rate.

Ordinarily, two conditions must be satisfied for such an accelerated deflagration to occur: (1) The reaction rate $\frac{dn}{dt}$ must increase with the pressure for example, as $\frac{dn}{dt} = AP^k$, where A and k are constants and $k>0$) and (2) gas must be generated faster than it can escape. Condition (2) may be satisfied in various ways depending on the environment:

(a) In a closed vessel there is no release of pressure up to the failure stress of the vessel; under this condition it is necessary only that $k>0$ for the reaction to accelerate.

(b) In a vented vessel gas escapes at a rate proportional to the pressure; in this case it is necessary that $k>1$ for acceleration to occur.

(c) Under inertial confinement (that is, where an increase in the volume available to the gas requires an acceleration of the material by the pressure), the volume will increase at a rate proportional to the impulse (that is, the time-integrated pressure); under this condition accelerated reaction requires that $k>2$.

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[32] Work cited in footnote 11.

As most structures used to contain AN may be expected to fail at no more than a few tens of psi, at which the reaction rate will still be very small, only (c) need be considered. In order to understand how the corresponding required reaction rate can occur, it is necessary to consider two types of propagative burning:

(1) In the usual so-called propellant burning, the energy released in the reaction zone is transmitted to the surface of the unreacted material by thermal conduction (and to some extent radiation and mass diffusion); the surface regresses at a rate r_s given roughly by $r_s = AP^k$, where A is a constant and k is equal to or slightly less than one. (Occasionally observed indices greater than unity are believed to be due to increasing area of the burning surface.)

(2) In a bed of loose material the reaction can also propagate via the ignition of new surfaces by the hot gaseous products of adjacent burning material. If ignition occurs deep within the bed, this propagation need not be merely diffusion-controlled, as the gases will be driven into the bed (forced convention).

In this type of burning, it is possible to speak of a burning front (ahead of which no grain surfaces are ignited and behind which all surfaces are ignited) advancing through the bed with a velocity r_b dependent on the pressure differential across it (that is, as $r_b = BP^{\ell}$, where B and ℓ are constants). If the bed is fairly homogeneous, the total area S of the burning surfaces will be proportional to the volume enclosed by this front, and if the latter originated from a localized center so that spherical symmetry applies,

$$\frac{dN}{dt} = \text{Const} \cdot r_b \cdot \left(\int r_b \, dt\right)^2 .$$

The rate of propagation of this front is particularly important. If $r_b << r_s$, the burning grains will be consumed too fast in relation to the number of new ones being ignited, with the result that the reaction zone will be reduced to a thin layer moving slowly through the bed. If on the other hand $r_b >> r_s$, equivalent to simultaneous ignition of all surfaces, too little pressure will be generated during the period of maximum acceleration, and thereafter the rate will not increase sufficiently. Thus it is important that r_b be matched to r_s, and it is evident that among the most important factors in the DDT problem are those which determine r_b.

Unfortunately, it is just this aspect about which the least is known. In principle the problem is simple: The equations describing the flow of gas through a porous bed must be coupled to those describing the ignition characteristics of the bed material, that is, the heat transfer and chemical kinetic equations. This would be a complex problem even if the high-temperature, high-pressure kinetics of AN were well in hand. But since this is by no means the case, its solution would be a purely academic exercise and certain assumptions must be made in its stead:

(1) The ignition delay time will be assumed to be negligible at the temperatures and pressures under consideration, that is, the time elapsed between contact of a grain surface by hot gas and the reaction of material derived from this surface is much less than the time scale of the overall event. (As an example, if L is 10 meters and if the average r_b is 1,000 meters per second, the ignition delay must be <<10 milliseconds.) The validity of this assumption is difficult to assess, though it probably leads to overestimation of the chance of a DDT. It is made here because of its simplicity and the lack of positive evidence for an alteranative. Its consequences are that r_b equals the streaming velocity of the gas at the burning front and that negligible gas escapes from the burning zone as the gas "carries the zone with it."

(2) This gas velocity is assumed to be proportional to the gas pressure; the constant of proportionality μ, a measure of the bed permeability, will have a large range of possible values depending on compaction, fluidization, the presence of fine particles, softening of the grains by heat and moisture, etc., so that meaningful treatment must account for all reasonable values.

A computation based on the foregoing ideas is presented in the outline of computation in appendix D. Since the current state of knowledge concerning DDT mechanisms (particularly with reference to AN) leaves much to be desired and especially since numerical values of many of the quantities involved are scarcely known to an order of magnitude, the main value of such a calculation is to indicate: (1) The relative importance of the various factors and (2) the areas in which research is necessary for a more definitive treatment. Before referring to the results of this computation, the remaining inherent assumptions should be discussed:

(1) Localized ("point") ignition is assumed to occur deep within the bed, specifically at the bottom, a distance L from the nearest free surface, so that the product gases are confined by the bed. Only the portion of the bed contained in a hemisphere of radius L centered at the ignition point is considered.

(2) It should be noted that ignition of propellant-like deflagration of AN is probably not possible at atmospheric pressure but requires an ambient pressure of the order of 100 psi. This pressure need not be the static pressure of the bed and in fact need only be sustained by extraneous causes long enough for the attainment of a sufficient reaction rate by the burning AN; this may be only a few milliseconds. It is quite easy to attain such pressures dynamically; for example, a mass of AN falling 20 centimeters (8 inches) will generate a pressure of 300 psi on impact, assuming that the velocity of sound of AN is about 1,000 meters per second. This is developed in appendix D under Impact Shock Pressures in AN due to Free Fall.

(3) AN will be assumed to obey the simplest form of propellant burning law in which the rate of regression of a burning surface is proportional to

the pressure: $r_s = A \cdot P$. The constant A will be taken to be 1.3 times 10^{-4} cm/sec/psi, a value consistent with the measurements of Andersen and others.[33]

(4) It is assumed that there is no significant pressure gradient in the reaction zone.

(5) It is assumed that the covolume of the gas produced is compensated by the volume of condensed phase consumed in its formation. This assumption, traditional in internal ballistics, reduces the Nobel-Abel equation of state to the Ideal Gas Law.

(6) The volume available to the product gases is equal to the interstitial volume in the reaction zone plus the volume made available by the displacement of the surrounding bed due to the gas pressure.

(7) It is assumed that when the driving pressure becomes sufficiently large, a shock wave of comparable magnitude will have formed and that when a pressure of about 5 kilobars is reached, detonation will be initiated. (Although shock initiation thresholds of about 20 kilobars are observed for AN in small samples, there is some evidence that the lower figure applies to large samples.)

The results of the mathematical development of the foregoing, given in appendix D, are listed in table 15. Values are given for R_T versus the bed permeability parameter μ and effective bed radius L, where R_T is the distance from the point of ignition to the position of the burning front at the instant transition occurs. Within the limitations imposed by the many assumptions, a transition may be possible for a bed whose height L (or other controlling dimension) appreciably exceeds the tabulated R_T.

TABLE 15. - Calculated transition distance R_T versus effective bed radius L and "permeability" μ for deflagration-detonation transition[1]

L		$\mu \times 10^5 \ \frac{cm^3}{dyn\text{-}sec}$								
meters	feet	1	1.5	2	2.5	3	4	5	6	8
12.5	41.0	-	12.5	-	-	-	-	-	-	-
15.0	49.2	-	15.0	10.7	10.4	10.9	12.6	14.5	-	-
20.0	65.6	17.7	8.0	7.9	8.6	9.4	11.4	13.5	15.7	20.0

[1] Values in body of table are the distances (in meters), from the point of ignition, at which transition to detonation occurs.

The values calculated in the table are strongly affected by the assumed values of the parameters. The critical size will be smaller for larger values of A, S, and T, and for smaller values of f_v. The parameter A may be much greater than the value used here, according to some measurements whose validity is however somewhat doubtful; S will increase if the prills are shattered;

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[33] Andersen, W. H., K. W. Bills, E. Mishuck, G. Moe, and R. D. Schultz. A Model Describing Combustion of Solid Composite Propellants Containing Ammonium Nitrate. Combustion and Flame, v. 3, 1959, p. 301.

T will be greater in the presence of fuel; and f_v will decrease with compaction of the bed. Compaction of the bed and shattering of the prills will also decrease μ, a factor which may decrease or increase the critical size. In view of the great uncertainty involved in these parameters, it is felt that more extensive calculations made at this time would not be meaningful.

DISCUSSION

The large-scale fire tests conducted rather early in this program demonstrated that AN, even contaminated with urea and fuel oil, did not burn very rapidly. This behavior is typical of that noted in the accidental fires in warehouses and transportation incidents in recent years. The Traskwood incident, however, resulted in detonation of one rail car of AN--possibly through fire exposure. Thus, the major problem in this investigation was an attempt to define the conditions that could lead to a detonation of AN when subjected to fire exposures, if indeed such a consequence is possible.

One important result of the investigation was the demonstration of a marked reduction in the critical diameter for detonation of raw AN at elevated temperatures. Typical fertilizer-grade AN at ordinary temperatures will have a critical diameter in the range of 10 to perhaps 40 inches.[34] In contrast the same AN, when heated to near its melting point, may have a critical diameter in the order of only 4 to 5 inches under light confinement and as small as 2 inches under heavy confinement. Similarly, contamination with fuel substances, particularly finely divided solid fuels or liquid fuels, effects a reduction in the critical diameter as well as producing more energetic systems. Another result was the confirmation of reports from Canada[35] that a small amount of water would increase the shock sensitivity of AN-FO. Although these data were obtained using explosive-derived shocks, they are significant to the fire problems because of the possibility of fragments being projected into the hot AN by adjacent explosions resulting from the fire. A smaller critical diameter means that a smaller fragment or one traveling at a lower velocity may be capable of initiating the AN; this possibility is enhanced by multiple fragments. This fact was confirmed by the results on projectile initiation of AN at elevated temperatures.

In the absence of adjacent explosions with associated projectiles, a detonation can occur in AN or contaminated AN only as a result of a transition from deflagration to detonation (DDT). Much effort was expended in attempting to effect this transition in free-flowing beds contained in heavy pipe and in inverted beds in which deep beds and associated inertial pressures were simulated by discharging the gaseous products of combustion through an orifice plate. In raw AN, no DDT could be accomplished even when hot AN was used. Pressures as high as 4,000 psi with hot AN or even as high as 8,000 psi in AN at ordinary temperatures failed to yield reaction rates that were rapid enough to effect a transition to detonation. Although, as indicated earlier, the charge diameter was not very much above critical, such pressures as these are very unlikely to occur in beds that are only self-confined.

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[34] Work cited in footnote 11.

[35] McCreedy, J., and J. H. Dewey. INCO Steps Up AN-FO Uses. Min. Eng., v. 16, No. 11, November 1964, pp. 56-60.

In the experiments using an inverted bed with an orifice plate, DDT's were obtained with AN contaminated with fuel materials but not with uncontaminated AN. It was found that ignition and sustained combustion occurred at about 100 psi and that a critical pressure of the order of 1,000 to 1,200 psi under these experimental conditions was necessary for the reaction to proceed ultimately to a detonation. Fueled AN burning at pressures no higher than 700 to 800 psi routinely burned out without accelerating to detonation. In those cases in which detonations were ultimately obtained, the final acceleration in burning rate probably came as a result of compaction of the bed and crushing of the prills to yield a denser bed and additional surface area. Pressures of the order of 2,000 to 3,000 psi were recorded before the reaction became truly runaway.

Water, added in small proportions to AN-paper, made the DDT more difficult, in contrast to the finding that water increased the shock sensitivity of AN-FO. These results suggest that the early stages of combustion are hindered by the water slowing the acceleration of burning, but the later reactions, those brought about by shock pressures, are not influenced by water. The increased shock sensitivity may derive from the easier crushing of the prills made softer by the water.

These results may be related to the fire hazard problem in the following way. The minimum pressure of 100 psi, necessary to effect ignition and bring about burning at a reasonable rate in AN and fueled-AN, may be attained in many ways--by falling roof or timbers or by collapse of the floor or the pile itself. Thus, a pile of AN falling only about 1 inch would develop 100 psi on impact (appendix D). The burning rate at this pressure is very low, but a pressure of 1,000 psi or more may develop under the inertial confinement provided by a high pile. However, at a pressure of 1,000 psi the associated acceleration would cause a 20-foot deep pile to be lifted a height equal to its depth in about 100 milliseconds. Thus, the decomposition would have to proceed extremely rapidly in order to maintain the pressure during movement of the pile, let alone cause a further acceleration of the pressure to much higher values necessary for a runaway reaction leading to a transition to detonation.

An attempt to approach the problem of DDT in a pile of AN analytically led to a minimum pile height of about 40 feet, below which no transition should be possible, given ignition at the bottom of the pile. The treatment suffers from the large number of assumptions that were necessary and the many variables for which values are not available, so little trust can be placed on the figure of 40 feet although this value probably is very conservative. However, this type of treatment tends to illuminate the areas of ignorance and point the way toward the work that should be done to resolve some of the unknowns.

Consideration of the pressure required for a transition to detonation to occur leads to strong arguments in favor of bulk storage of AN and even of AN-FO over bag storage. A pile of bagged material, usually on pallets, will have many channels for the fire to penetrate into the center of the pile. Subsequent collapse of the pile could give momentary surges of pressure and, with the material already ignited, sufficient reaction rates could possibly be attained to lead ultimately to a transition to detonation if the pile were large enough. Such a transition would seem more probable in the case of fueled AN rather than raw AN because of the perhaps threefold increase in energy which is available from the former, but it must be recognized that the bags and wooden pallets and particularly their pyrolysis products can serve as fuel. In contrast, a pile of bulk material on a solid foundation is impervious to the penetration of fire into the center of the pile. External fire exposures, even with contaminants such as tar from the roof, etc., would result in only a slow decomposition of the surface layers of AN and reaction at the surface with the contaminants. Neither the hot gases from the decomposition reactions nor the contaminants can penetrate the pile to affect the interior significantly. An obvious hazard that must be considered, of course, is the possibility that under radiant and convective heating, considerable AN may be melted. If this molten AN runs into an area where it may be trapped and subsequently heated under confinement, the consequences are well known. Puddles of AN of any reasonable depth, however, do not appear to present any significant hazard in the open.

The kinetics of decomposition of liquid AN was examined rather briefly in the course of the work; however, it was decided that the kinetics of the nitrous oxide reaction are sufficiently well known as the result of the work of Feick and Hainer,[36] Keenan and Dimitriades,[37] and Rosser, Inami, and Wise.[38] What is more important, it was shown in this work that the nitrous oxide reaction is not the one that is involved in rapid decomposition and detonations of AN. Rather, it is the reaction leading to nitrogen, oxygen, and water, a much more energetic reaction but one for which no kinetic data are available. Thus, it would appear that the predictions of Sykes, Johnson, and Hainer[39] and Hainer,[40] which are based on the nitrous oxide reaction, may not be relevant to the actual runaway decomposition of AN. Sykes, Johnson, and Hainer proposed a model for the self-acceleration of the thermal decomposition of a mass of molten AN in which the fume-off products burning at the liquid surface develop a reaction pressure (analogous to the reaction of a rocket motor). The authors suggest that this pressure increases with the reaction rate which in turn increases with the temperature of the melt. The equilibrium temperature of the melt increases with the applied pressure, a fact which these authors use implicitly in writing the reaction rate directly as a function of pressure. According to this treatment the reaction rate

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[36] Feick, G., and R. M. Hainer. On the Thermal Decomposition of Ammonium Nitrate. Steady-State Reaction Temperatures and Reaction Rates. J. Am. Chem. Soc., v. 76, 1954, pp. 5860-5863.

[37] Keenan, A. G., and B. Dimitriades. Differential Rate Method for Kinetic Measurements. Thermal Decomposition of Ammonium Nitrate. Trans. of the Faraday Soc., v. 57, No. 462, pt. 6, June 1961, pp. 1019-1023.

[38] Rosser, W. A., S. H. Inami, and H. Wise. The Kinetics of Decomposition of Liquid Ammonium Nitrate. J. Physical Chem. v. 67, 1963, pp. 1753-1757.

[39] Sykes, W. G., R. H. Johnson, and R. M. Hainer. Ammonium Nitrate Explosion Hazards. Chem. Eng. Progressing, v. 59, No. 1, January 1963, p. 66.

[40] Hainer, R. M. The Application of Kinetics to the Hazardous Behavior of Ammonium Nitrate. Fifth Symp. (International) on Combustion. Reinhold Publishing Corp., New York, 1955, pp. 224-230.

accelerates without limit if a critical depth of liquid is exceeded. This analysis greatly overestimates the hazard for the following reasons:

(1) Since the fume-off products originate in the bulk of the liquid, not at the surface, there will be a flux of bubbles rising in the liquid. Near the surface this flux is very large. For example, to maintain an overpressure of 1 atmosphere, a flux of $\sim$30,000 cm^3/cm^2-sec is required. The consequent violent ebullition, foaming, and entrainment of liquid implicit in such a high flux would result in rapid loss of liquid; this loss cannot be sustained due to the slow time scale of the buildup of reaction rate (see item (2)).

(2) The relationship between equilibrium temperature and applied pressure cannot be used for instantaneous changes. As the pressure is increased, the liquid seeks a new equilibrium temperature rather slowly. Even under infinite pressure, which completely suppresses the endothermic dissociation reaction, the rate of temperature rise is limited by the rate of the decomposition to N_2O and H_2O. At the normal fume-off temperature (292° C for one atmosphere pressure), this corresponds to about 0.8° C per second, whereas the half-life of the melt at the same temperature is only about 250 seconds. Thus, much of the liquid will be removed by decomposition if not by mechanical entrainment in the product gases while the process is in the early stages.

The above authors also give a qualitative model involving the effects of violent foaming and inertial confinement by the liquid itself. Although this model is not developed mathematically (and it is quite difficult to do so), it is intrinsically more plausible than the model explicitly discussed. However, a very approximate mathematical development of this notion leads to estimated critical pool dimensions of many tens of meters, so that it appears to be an unlikely source of hazard in even the largest fires which can reasonably be anticipated.

Gas detonations were demonstrated to be an improbable cause of detonation of raw AN as much more sensitive explosives could not be initiated by detonation of acetylene-oxygen, a more energetic system than the usual fire gases.

In summary, it would appear that although the initiation of detonation in AN as a result of fire exposure cannot be ruled out completely, a direct DDT in raw AN would appear to be possible, if at all, only in a pile of extremely large dimensions with the ignition at the bottom or center of the pile. Projectiles derived from nearby explosions can initiate runaway reactions, particularly in hot AN. However, ordinary sporting arms bullets are incapable of initiating raw AN under normal storage conditions.

Thus, in the case of the Traskwood incident the possibility that a DDT did occur in the boxcar of bagged AN cannot be ruled out a priori, but another possibility would appear to be shocks derived directly, or from projectiles, associated with a detonation of a petroleum-nitric acid mixture. Spontaneous initiation of detonation in such a mixture was shown to be possible, and the detonating mixture was found capable of initiating AN-FO. Undoubtedly, the detonating mixture would be capable of initiating raw AN if the area first shocked were substantially greater than the critical diameter and particularly if the explosion hurled projectiles at high velocity against the AN.

In the case of the Norton, Va., explosion, both raw AN and AN-FO were present in large quantities. The floor of the building was constructed of oak planks spaced to provide ventilation, but access of fire to the bottom of the pile was also thus possible. The floor was a few feet above grade. Collapse of the floor could have caused a momentary pressure surge with the resulting increase in burning rate that might have led to a transition to detonation. Other possible causes cannot be completely ruled out. Mixing was by means of an auger turning in a pipe. This mixer was reportedly cleaned of material, but if it had not been adequately cleaned the confinement provided by the pipe and auger to any contained AN-FO could cause it to decompose explosively when heated. Projectiles from this explosion could have initiated detonation in either the raw AN or, more readily, in the AN-FO.

Despite an intensive program seeking to define the conditions under which AN and contaminated AN can undergo a transition to detonation, many questions remain unanswered. These questions relate mainly to the penetration of fire through a bed of AN, the burning rate of AN prills as a function of pressure and temperature and contamination, the behavior of a bed under acceleration and compression, and the kinetics of decomposition reactions other than the one producing nitrous oxide. Research is continuing in an attempt to define some of these variables to allow an even better prediction of the behavior of AN under fire exposures.

SUMMARY

This program has sought to define the potential explosion hazards of AN when involved in fire. Particular attention was paid to the question of why AN detonated in the derailment incident at Traskwood, Ark., and AN or AN-FO in the mix-house incident at Norton, Va., despite the extensive experience of explosion-free fires involving AN in the post-Texas City and post-Brest period.

The intrinsic sensitivity of AN and AN systems was investigated by means of card gap techniques. Attention was directed to the effects of temperature and charge size, as other work has demonstrated that the lack of reaction of AN in commonly used test procedures may result from the use of too small a charge, a charge below the critical diameter. Fertilizer-grade AN can be detonated, but at ordinary temperatures very large charges and strong explosive donors must be used to obtain a detonation. It was found that the critical diameter of raw AN decreased significantly at elevated temperatures. This implies an increase in apparent sensitivity. Prills coated with about 3 percent clay were less sensitive than prills with only about 0.5 percent parting agent. Water in small amounts increased the shock sensitivity of AN-FO.

Raw and fueled AN was burned under pressure in numerous experiments designed to simulate the burning of these materials in deep beds where high pressures may exist by virtue of the inertia of the bed. In simulated free-flowing beds, no transitions to detonation in AN systems were observed, even with pressures as high as 8,000 to 10,000 psig. An inverted vented vessel technique was used to overcome the experimental limitations of the free-flowing beds and to develop more rigorous burning conditions. Using this technique, transitions to detonation were obtained with AN intimately mixed with fuel oil, polyethylene, or paper. Transitions were most readily accomplished with pulverized AN-fuel systems but were also obtained with prilled AN systems. AN without added fuel, however, did not undergo transition to detonation under the most rigorous conditions used. For the fueled systems, pressures greater than 1,000 psig had to be sustained for 50 to 100 milliseconds before an acceleration in pressure developed, leading to detonation. Under experimental conditions that gave lower pressures, smooth burning occurred until the charge was consumed. The final acceleration to detonation, that occurred after rather long sustained burning at pressures in the order of 1,000 to 1,200 psi, may have resulted from the burning front reaching a region of compressed material. An overall evaluation of the burning data suggests that a similar burning to detonation in free-flowing beds, even with ignition at the bottom of the bed, is quite unlikely in bed sizes that are typical of those to be found in storage and transportation. The same considerations favor bulk storage over bag storage because of the difficulty, if not impossibility, of penetration of the bed by the burning front.

Gas detonations, even those involving stoichiometric acetylene-oxygen, were shown to be incapable of initiating AN systems or even dynamite and PETN. However, hot AN was shown to be capable of initiation to detonation by a high-velocity bullet or projectile impact, and AN-FO was sensitive to initiation by fragments from another AN-FO charge some several diameters away. These results were confirmed with larger-scale trials conducted under another program.

The difficult requirements for transition to detonation in raw AN or even fueled AN under free-flowing bed conditions and the ready initiation of hot AN or contaminated AN by high-velocity projectiles suggest that the latter may be the most probable cause of detonation in the Norton and Traskwood incidents. Particularly in the case of Traskwood another Explosive system could have been a contributing factor. This program has demonstrated that detonation could be reproducibly caused by the injection of fuming nitric acid into burning gasoline--two materials that were present in the pile of derailed cars. The detonation of this system was also shown to be capable of initiating AN-FO directly, although the sensitivity of hot AN to high-velocity projectiles would not require that the detonating gasoline-nitric acid be in immediate contact with the car of AN that detonated.

Additional work remains to be done before the explosion hazards of AN can be fully elucidated. These questions mainly concern the burning of beds of AN prills and the kinetics of decomposition reactions other than the one leading to nitrous oxide. This reaction has been shown to have little relevance to the explosive decomposition of AN.

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Commercial Solvents Corporation,
Consolidated Mining & Smelting Company of Canada, Ltd.,
E. I. du Pont de Nemours & Company, Inc.
Hercules Powder Company,
Monsanto Company,
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APPENDIX A.--MATERIALS USED

The materials used are listed in the table. Photomicrographs of the samples are shown in figures 28 to 34, where each superimposed square is 1 millimeter in each dimension.

CPAN - Chemically pure ammonium nitrate--Fisher Scientific Company catalog No. A-676 (certified grade).

WFNA - White fuming nitric acid--General Chemical Company 99+ percent grade.

Gasoline - A lead-free, high-aromatic, premium grade.

Fertilizer-grade ammonium nitrates:

Brand A - Prilled ammonium nitrate with small amount of surfactant and about 0.5 percent clay or diatomaceous earth coating.

Brand C - Prilled ammonium nitrate with about 3 percent clay or diatomaceous earth coating.

Brand D - Stengel process ammonium nitrate.

Brand E - Similar to Brand A but from a different manufacturer.

Brand F - Similar to Brand C but from a different manufacturer.

Brand G - Uncoated prills stabilized against the 32° C phase transition.

Brand H - Similar to Brand C but from a different manufacturer.

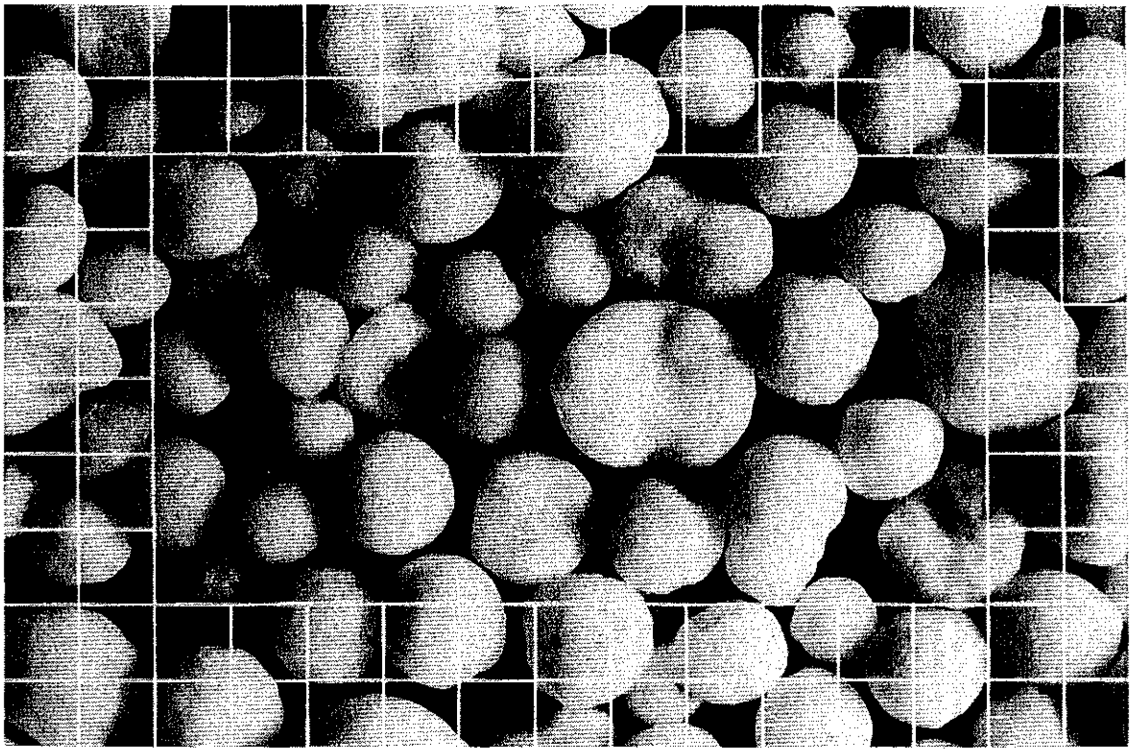

FIGURE 28. - Photomicrograph of Brand A (X 10).

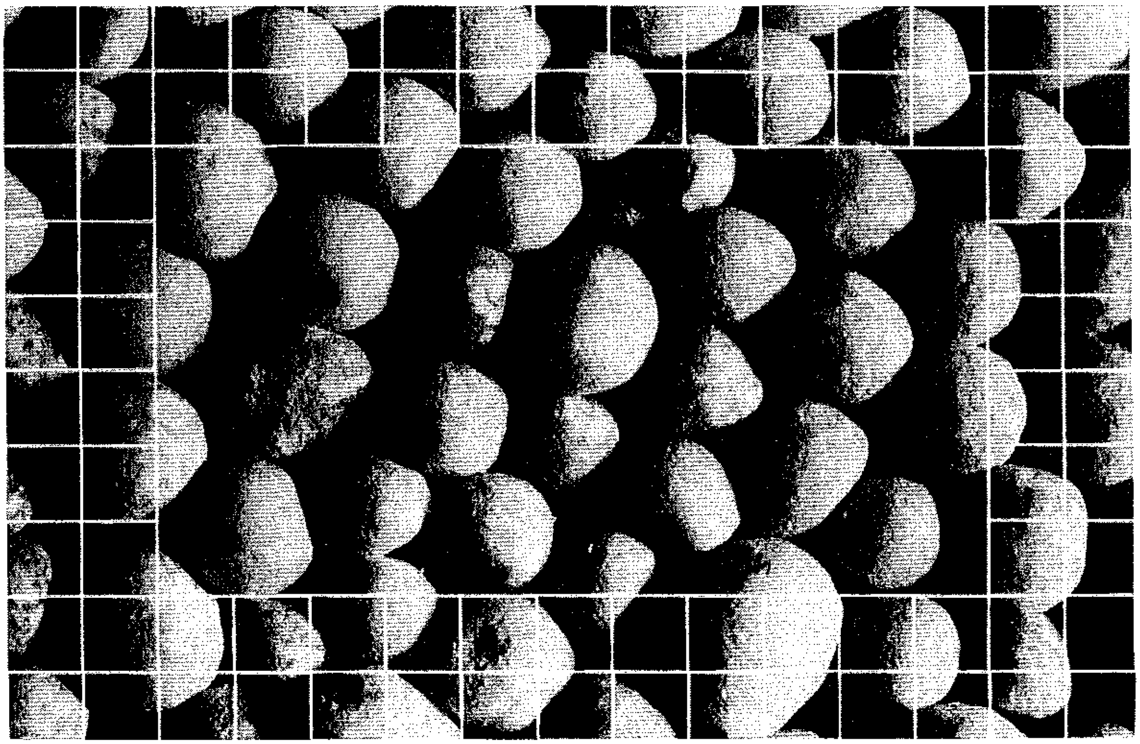

FIGURE 29. - Photomicrograph of Brand C (X 10).

FIGURE 30. - Photomicrograph of Brand D (X 10).

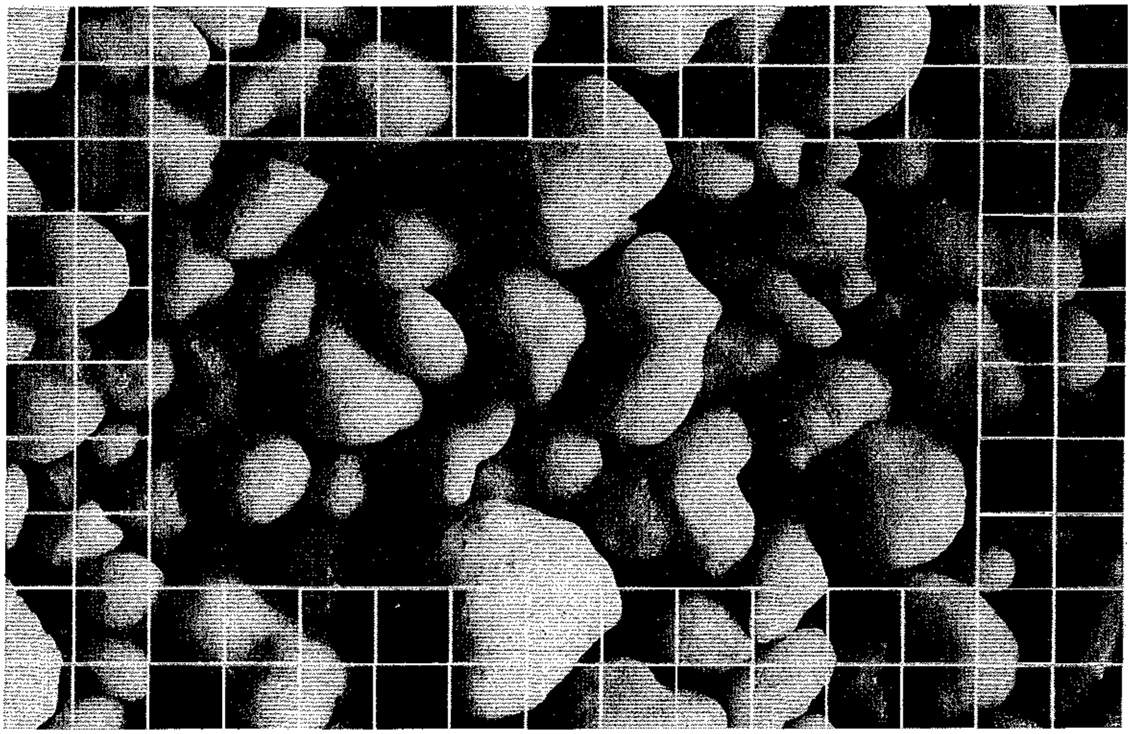

FIGURE 31. - Photomicrograph of Brand E (X 10).

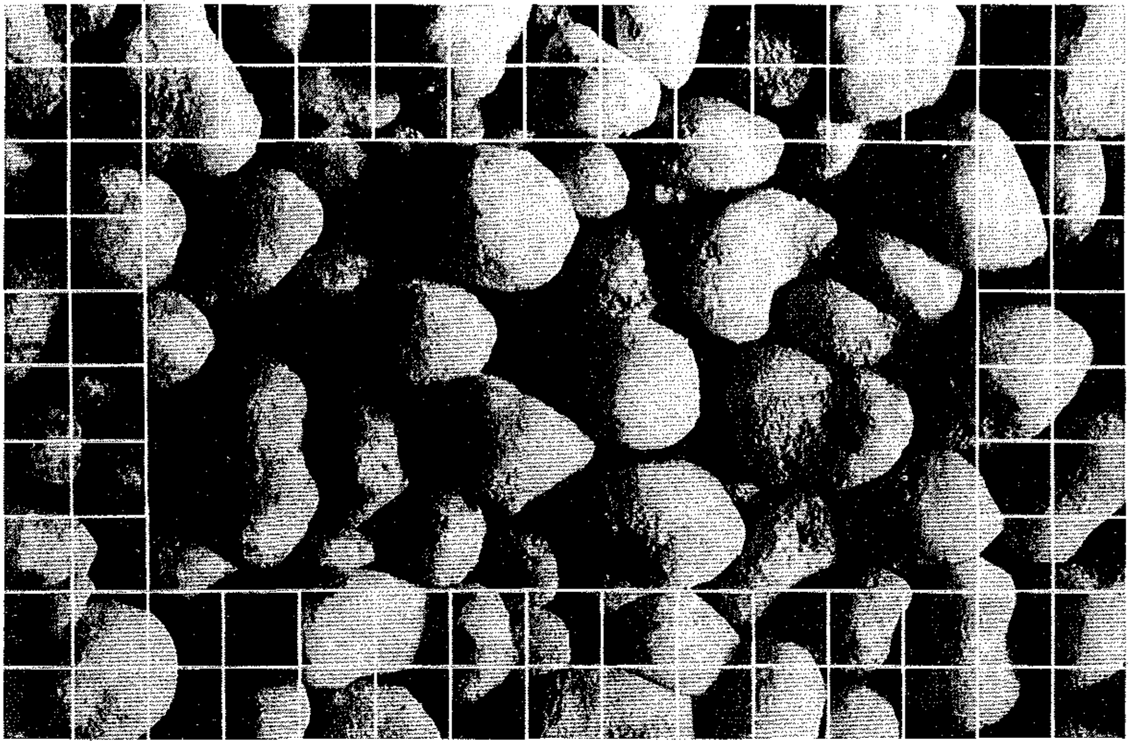

FIGURE 32. - Photomicrograph of Brand F (X 10).

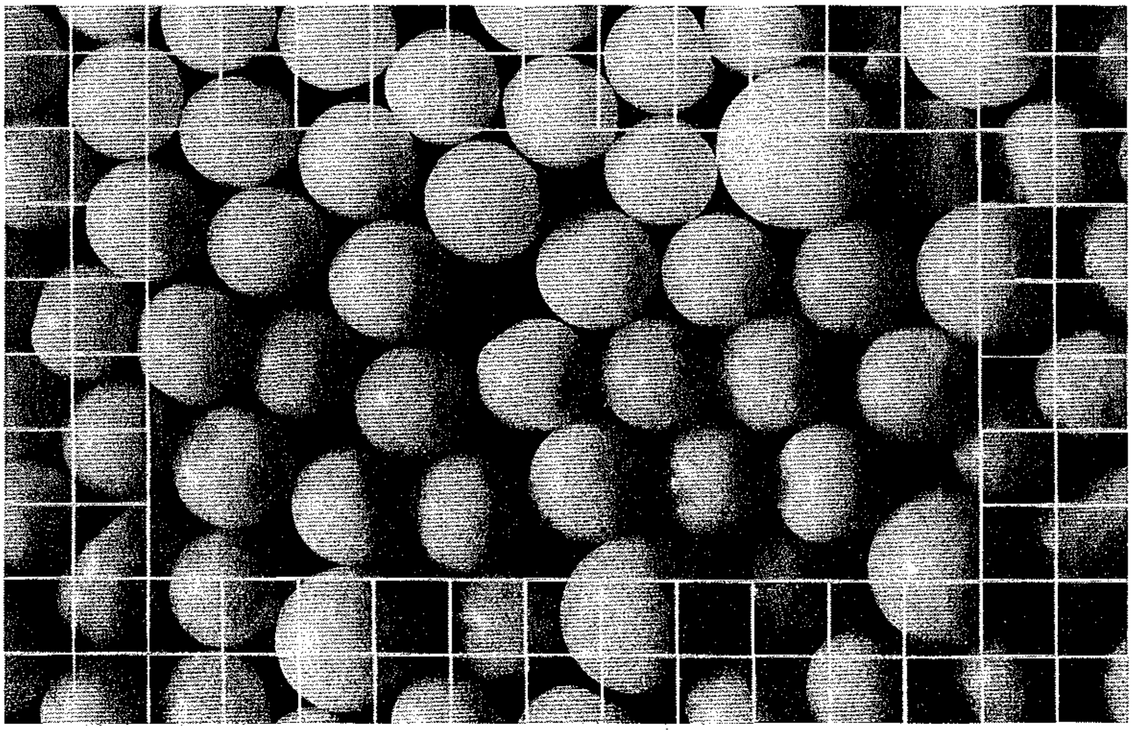

FIGURE 33. - Photomicrograph of Brand G (X 10).

FIGURE 34. - Photomicrograph of Brand H (X 10).

APPENDIX B.--MODIFIED CARD GAP TESTS

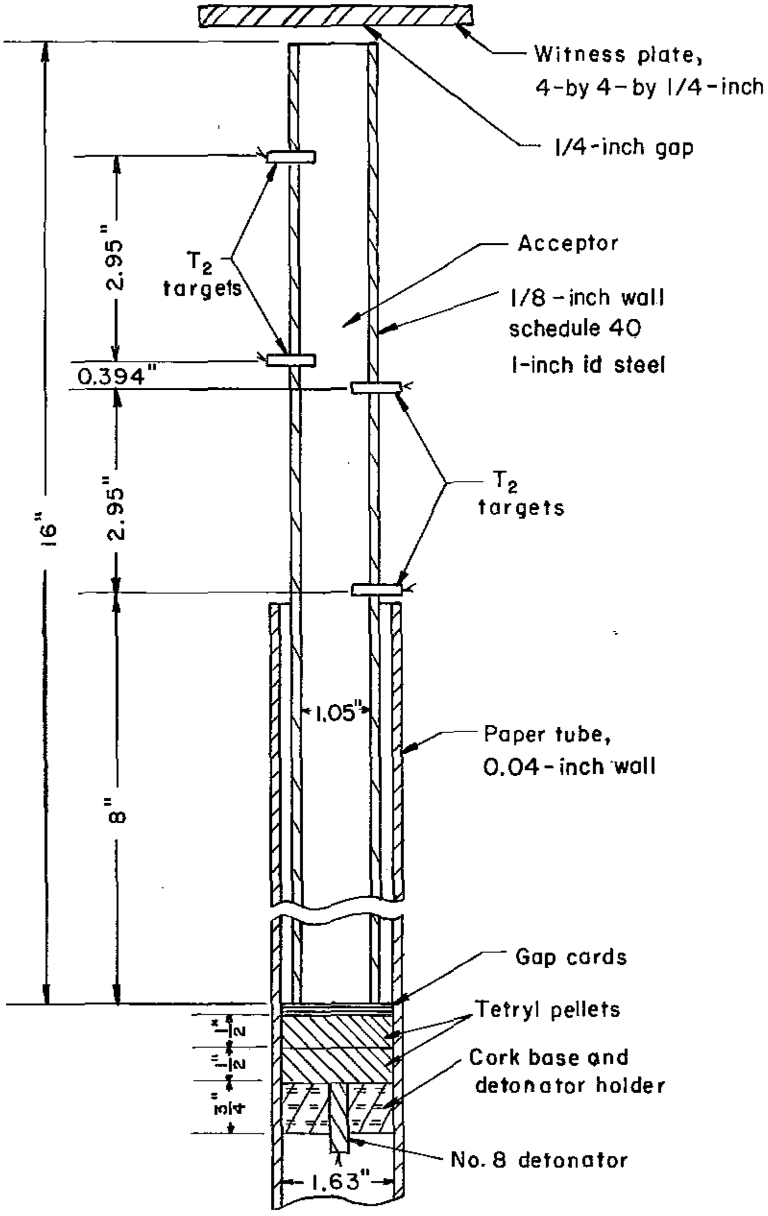

FIGURE 35. - Modified Card-Gap Arrangement A.

In the usual card gap test,[1] [2] the sample is contained in a 3-inch-long 1-inch schedule 40 iron pipe. Experience with this test at the Explosives Research Center has shown that this experimental technique does not enable an adequate evaluation of less sensitive materials. Modifications of this procedure have been found to be much more informative. The first modified arrangement is shown in figure 35.

In this arrangement the acceptor cup is lengthened from 3 to 16 inches and rates of propagation are measured between pressure probe stations placed along the length of the cup. Lengthening the acceptor cup eliminates the ambiguity often observed in the different types of target plate damage sustained with 3-inch length cups. In addition to target plate damage, the extent and type of damage to the cup is also taken into consideration when evaluating the results.

The donor charge consists of two tetryl pellets, 1.63 inches in diameter by 0.96 inch in length, weighing a total of 50.5 grams. These pellets are formed in a Stokes pellet press to a density of 1.57 grams ± 0.01 gram per cubic centimeter. Initiation of the donor is accomplished by a commercial No. 8 detonator positioned at the axis of the donor charge.

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[1] Joint Army-Navy-Air Force Panel on Liquid Propellant Test Methods. Test No. 1, Card Gap Test for Shock Sensitivity of Liquid Monopropellants. The Liquid Propellant Information Agency, Applied Physics Laboratory, John Hopkins University, Silver Spring, Md., 1960, 24 pp.

[2] Maček, A. Sensitivity of Explosives. Chem. Rev., v. 62, 1962, pp. 41-63.

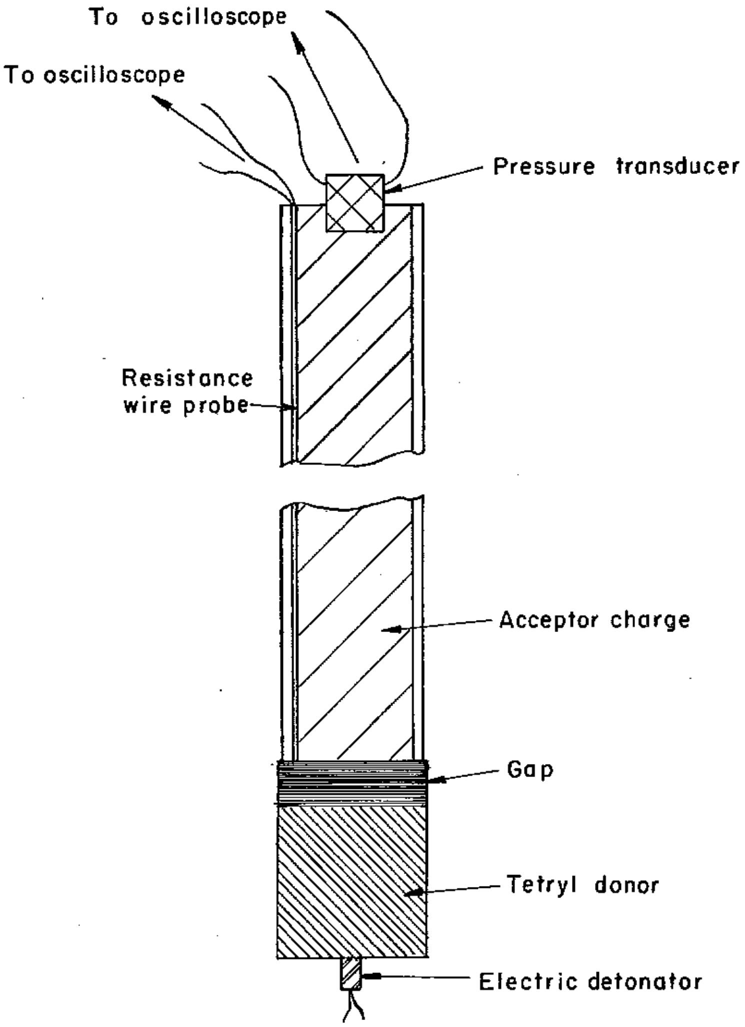

FIGURE 36. - Modified Card-Gap Arrangement B.

The gap is built up using die-cut cellulose acetate cards, each about 10 mils in thickness by 1.63 inches in diameter, or polymethyl methacrylate disks ½ to 1 inch thick of the same diameter. This substitution has been shown to have negligible effects on the results.

The rate of detonation is obtained by measuring with a Beckman-Berkeley 10-megacycle counter chronograph, the transit time for the detonation wave to pass between T-2 targets[3] spaced 7½ centimeters apart in the column of explosive. Usually, two sets of T-2 targets are placed in each charge arranged at different distances from the initiated end of the charge.

The entire test assembly is aligned by means of a 1.68-inch id by 25-inch-long paper tube and appropriate rings are cut from cork. The desired firing temperature is controlled to within ± 1° C by preheating separately both the acceptor cup and the charge prior to pouring the latter into the cup.

A detonation or a failure is determined by the extent of damage to both the acceptor cup and ¼-inch-thick steel target plate. A stable detonation results in complete fragmentation of the cup and produces a clean cut hole in the target plate. In addition to cup and plate damage, the measured rates can also be used to distinguish between detonation and failure. The gap value is usually expressed in terms of the thickness of gap which would yield detonations 50 percent of the time. This value is readily determined if the up-and-down technique is used.[4] [5]

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[3] These are aluminum-cased pressure switches manufactured by the E. I. du Pont de Nemours and Company, Inc.

[4] Statistical Research Group, Princeton University. Statistical Analysis of a New Procedure in Sensitivity Experiments. Report to Applied Mathematics Panel. Nat. Defense Res. Committee, Rept. 101.1R, July 1944, 58 pp. Available on microfilm from U.S. Dept. of Commerce, Office of Tech. Service.

[5] Dixon, W. J., and F. J. Massey, Jr. Ch. 19 in Introduction to Statistical Analysis. McGraw-Hill, New York, 2d ed., 1957, pp. 318-327.

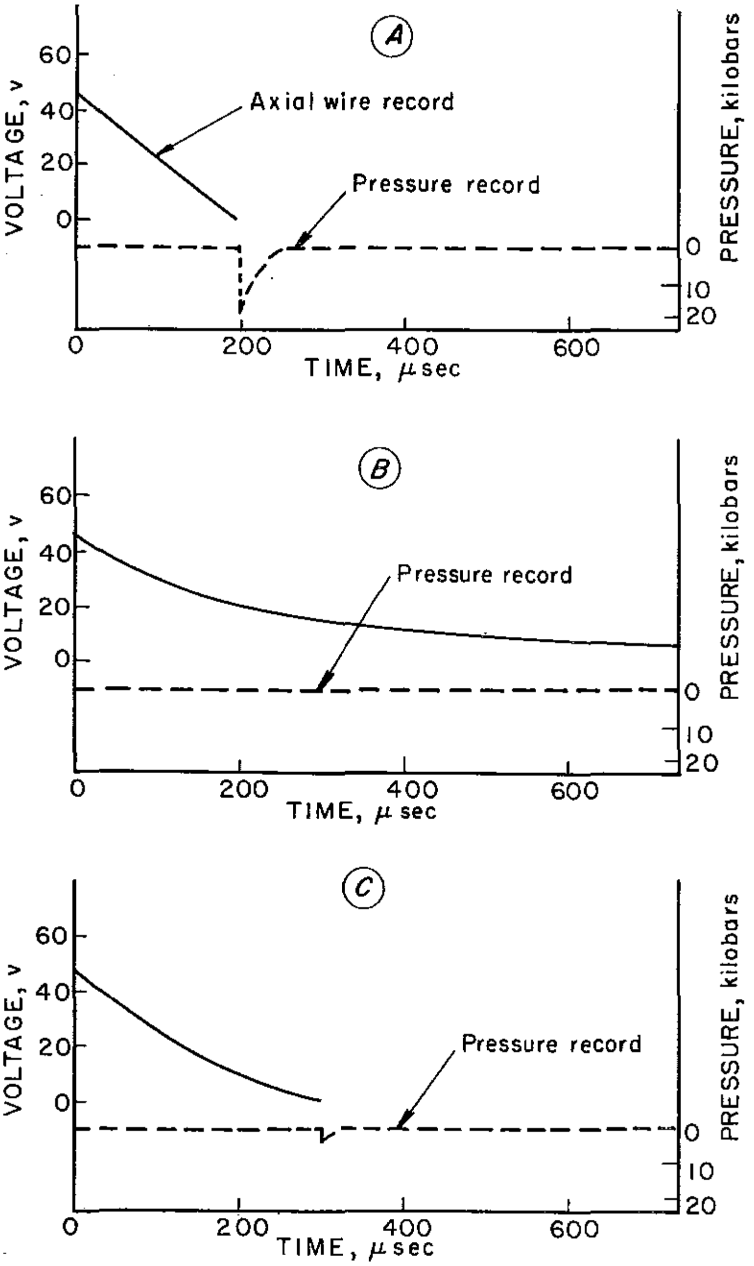

FIGURE 37. - Typical Axial Wire Trace and Pressure Trace for a Positive Shot A, a Negative Shot B, and a Decaying Shot C.

The second modified arrangement B is shown in figure 36. Samples contained in 1½-inch schedule 40 seamless steel pipe (1.61-inch id by 0.145-inch wall by 16-inch length) are shocked by 160-gram tetryl boosters (2-inch diameter by 2-inch length, density 1.59 grams per cubic centimeter). The shock intensity is varied by insertion of an attenuator (cellulose acetate wafers or polymethyl methacrylate disk) between the donor and acceptor charges in a method similar to the standard card gap test. A probe containing a resistance wire is placed in the sample. A constant current flows through the wire. The shorting out of the wire at the detonation front enables one to follow the propagation of this front.

Three general types of records are observed with the resistance wire: (1) The sample detonates at constant velocity as indicated by a straight line of fixed slope (fig. 37, A). These results are recorded as positive; (2) detonation fails to propagate the entire length of the sample as indicated by a line whose slope rapidly approaches zero (fig. 37, B) and incomplete destruction of the container. These results are recorded as negative; and (3) detonation propagates the entire length of the sample but with a decreasing rate of detonation, which is indicated by a trace line with decreasing slope, as shown in figure 37, C. These results are recorded as negative as the reaction is decaying and does not represent a self-sustaining detonation. This differs from the interpretation of results in modification A where complete fragmentation of the sample container, under similar conditions, was considered to be evidence of a positive result. The pressure traces obtained simultaneously are shown as broken lines in figure 37, indicating in each case the time of arrival of the front at the top of the charge. An expendable pressure transducer[6] is inserted in the top of the charge. This transducer serves to indicate that a detonation has initiated and records the pressure transmitted to it from the detonating explosive.

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[6] This instrumentation is under development at the Bureau of Mines Explosives Research Center.

APPENDIX C.--PROJECTILE IMPACT TEST

The penetration of shock waves by projectile impact has some advantages over explosives generated shock waves in that the amplitude can be more readily varied, particularly in the low range.

The Bureau has adopted a projectile test which evaluates the sensitivity to projectile impact on a quantitative basis. Right cylinders of "free-cutting" brass, ½-inch diameter by ½-inch length, are fired from a smoothbore gun based on a Mauser 13-millimeter antitank action and chambered to accept M-2, .50 caliber ammunition. Cartridges are prepared by reloading .50 caliber ammunition, adjusting the original propellant weight to give the desired velocity. The void space above the propellant is filled with a tissue paper wad. The brass cylinder is set into the case to a depth of one-quarter inch. The gun is aimed to hit the center of the test charge with the axis of the projectile coinciding with the longitudinal axis of the charge and is fired by remote control, using a solenoid-actuated trigger. The projectile velocity was found to give a straight line when plotted against the square root of the propellant weight (fig. 38). The "up-and-down" technique[1] [2] is used to obtain the velocity V_{50}, at which 50 percent of the results are positive. Projectile velocities are measured with a 10-megacycle Hewlett-Packard counter chronograph, the starting and stopping signals being provided by breaking conductive tapes 0.5 meter apart, positioned between the gun and explosive. The circuit diagram is given in figure 39.

Two techniques were used to determine if initiation had occurred: (1) The use of an 8-inch length of detonating cord butted up against the rear face of the sample container below the line of flight of the projectile; the other end of the detonating cord was taped across a witness plate; positive results were indicated by the initiation of the detonating cord; (2) a blast gage consisting of a 0.032-inch-thick aluminum strip or "flag" 2 by 10 inches and mounted on a steel post was used. It was positioned as shown in figure 40, its center about one foot from the center of the back face of sample tube, the "flag" making a 45° angle with the center line of the tube. Shock pressures in AN may be estimated by a graphical solution of the impedance mismatch,[3] using Hugoniot relations for brass and for an explosive of approximately the same density.

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[1] Statistical Research Group, Princeton University. Statistical Analysis of a New Procedure in Sensitivity Experiments. Report to Applied Mathematics Panel. Nat. Defense Res. Committee, Rept. 101.1R, July 1944, 58 pp. Available on microfilm from U.S. Dept. of Commerce, Office of Tech. Service.

[2] Dixon, W. J., and F. J. Massey, Jr. Ch. 19 Introduction to Statistical Analysis. McGraw-Hill, New York, 2d ed., 1957, pp. 318-327.

[3] McQueen, R. G., and S. P. March. Equation of State for Nineteen Metallic Elements From Shock-Wave Measurements to Two Megabars. J. Appl. Phys., v. 31, July 1960, pp. 1253-1269.

APPENDIX D.--MATHEMATICAL DEVELOPMENT OF THE CONDITIONS FOR DEFLAGRATION TO DETONATION TRANSITION IN AMMONIUM NITRATE

Outline of Computations Involved in Theoretical Evaluation of DDT[1]

The equation of state of the products may be written in differential form as:

$$dP = \frac{n\ R\ T\ dM - P\ dV}{V}. \tag{1}$$

The usual mass burning rate expression is:

$$dM = \rho_p S\ d\xi = \rho_p S\ r_s\ dt = \rho_p S\ A\ P\ dt, \tag{2}$$

where S is given (see discussion) by:

$$S = s\ F_f\ V_b = \frac{2\pi}{3}\ s\ R_p^3\ \left(1 - \frac{3\ A\ R_p}{2\ \mu\ a} + \frac{3}{5}\left(\frac{A\ R_p}{\mu\ a}\right)^2\right) \tag{3}$$

where the appropriate form factor for spherical grains has been included. (Equation (3) is valid only for $AR_p/\mu a \le 1$, which will usually be the case for all solutions considered.)

The net volume available to the product gases is:

$$V = V_{int} + V_{displ}, \tag{4}$$

where:

$$V_{int} = f_v\ V_b, \tag{5}$$

$$V_{displ} = \frac{2\pi}{\rho L} \int_0^t R_p^2 \int_0^{t'} P\ dt''\ dt'. \tag{6}$$

The solution is facilitated by the transformation:

$$dt = r_b^{-1}\ dR_p. \tag{7}$$

Combining (1) through (7) above leads to:

$$dP = \frac{n\ R\ T\ \rho_p s\ \frac{A}{\mu}\ \left(1 - \frac{3}{2}\frac{A\ R_p}{\mu\ a} + \frac{3}{5}\left(\frac{A\ R_p}{\mu\ a}\right)^2\right) - 3\ \left(f_v\ \frac{P}{R_p}\ \frac{1}{\rho\ L\mu^2}\right)}{f_v + \frac{3}{\rho\ L\mu^2\ R_p^3} \int_0^{R_p} \frac{R_p'^3}{P}\ dR_p'}\ dR_p. \tag{8}$$

Equation (8) may be integrated in a straightforward manner, starting at an assumed initial pressure P_b to obtain the pressure P versus the position of

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[1] The various symbols used are defined in the glossary.

the burning front R_P. The transition distance R_T is considered to be the value of R_P at which the pressure attains a value of 5 times 10^9 dyn/cm^2. For values of R_P greater than $\mu a/A$ the form factor (in parentheses in equation (3)) must be modified. Moreover, since R_T must obviously be less than L, there will be a minimum L at which a transition is possible at all; in accordance with the comments made relevant to the velocity of propagation of the burning front, there will be a minimum and a maximum value of μ for transition at each value of L.

Values of R_T for various values of μ are given in table 15. The assumed values of the remaining parameters are listed in the glossary of this appendix.

No solution for R_T exists for any value of μ for $L < 12.5$ meters. At this value of L a solution is possible at $\mu \approx 1.5 \times 10^{-5}$; at this value of μ the velocity of the burning front at 1,000 psi would be ~ 10 meters per second, the rate of regression of the prill surfaces would be ~0.14 centimeters per second. At the "transition pressure" of 74,000 psi the velocity of the burning front would be ~750 meters per second, and the prill regression rate ~10 centimeters per second. For larges L values, solutions are possible for a range of values of μ, the range increasing as L increases, as shown in table 15.

Impact Shock Pressures in AN due to Free Fall (One-Dimensional Sonic Approximation)

When two bodies collide one-dimensionally with a relative velocity u, the impact shock pressure can be found by solving the Hugoniot equation-of-state relations for the materials involved:

$$P_A = f_1 \ (u_A),$$

$$P_B = f_2 \ (u_B),$$

where P is the shock pressure,

u is the mass flow ("particle") velocity,

A and B refer to the two materials, respectively,

together with the conditions,

$$P_A = P_B, \qquad (3)$$

$$u_A + u_B = u. \qquad (4)$$

If u is not too great (1) and (2) may be rewritten (sonic approximation) as:

$$P_A = \rho_A c_A u_A, \qquad (5)$$

$$P_B = \rho_B c_B u_B, \qquad (6)$$

where ρ is the density,

c is the sonic velocity.

In particular, if $\rho_B c_B >> \rho_A c_A$ corresponding to the impact between a dense rigid body and a light pliable body, the approximate solution is:

$$P = \rho_A c_A u.$$

If the velocity at the instant of impact is due to free fall from a height h, then u is given by the equation:

$$u = \sqrt{2gh}, \qquad (8)$$

where g is the acceleration of gravity = 980 cm/sec^2 .

Combining (7) and (8) we have:

$$P = \rho c\sqrt{2gh},$$

where P is in dynes/cm^2,

c is in cm/sec,

h is in cm,

ρ is in gm/cm^3.

In the more familiar units of lb/in^2 for P, ft/sec for c, and ft for h, we have:

$$= 0.11\ \rho c\ \sqrt{h}.$$

Assuming $\rho = 1.0$,

$c = 3{,}300$ ft/sec,

$$P = 360\ \sqrt{h}.$$

Thus for a 1-inch drop, P = 104 psi.

Glossary of Symbols and Table of Assumed Values

a = radius of spherical grain (prill) = 0.1 cm.

A = constant of burning rate expression = 2 x 10^{-9} cm^3/dyn-sec.

f_v = volume fraction of void space in bed = 0.3.

F_f = form factor for grain burning.

L = radius of bed (assumed hemispherical).

M = mass of AN which has burned up to any given time.

n = number of moles of products per gram of AN = 0.04375.

P = pressure of products.

P_o = "starting" or ignition pressure = 7×10^6 dyn/cm^2 .

R_p = position of burning front.

R = gas constant = 8.315×10^7 erg/mole-degree.

s = total grain surface area per unit volume of bed = 21 cm^{-1}.

S = total grain surface area.

T = temperature of gaseous products = 1,500° K

V = volume occupies by gaseous products.

V_b = volume of burning zone.

V_{int} = interstitial volume, that is, void space in burning zone.

V_{displ} = volume made available by displacement of unburned bed (due to pressure exerted by products).

μ = "permeability" of bed to flame propagation.

ρ = bulk density of bed = 0.85 gm/cm^3.

ρ_p = density of individual prill = 1.2 gm/cm^3.

ξ = thickness of layer on prill surface burned.

c_A, c_B = acoustic velocities of materials A and B, respectively.

g = acceleration of gravity.

h = height from which a free falling body is dropped.

P_A, P_B = impact shock pressure produced in materials A and B, respectively.

u = relative velocity between bodies on impact.

u_A, u_B = mass flow (particle) velocities in materials A and B, respectively.

ρ_A, ρ_B = densities of materials A and B, respectively.