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PERFORMANCE PARAMETERS OF LOW-DENSITY AMMONIUM NITRATE BASE EXPLOSIVES; EXPERIMENTAL RESULTS AND J. TAYLOR'S METHOD

BY

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A

THESIS

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Approved by George B. Clark
Professor of Mining Engineering

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INTRODUCTION

Ammonium nitrate has been known to the explosive industry for a long time. Compelled by the ever increasing mining costs, in 1954 "Akremite" was introduced to the market. It is a simple carbonaceous ammonium nitrate mixture and is the cheapest explosive available to the open-pit operators.

During the following years considerable amount of research was done, resulting among others with the introduction of ammonium nitrate-hydrocarbon mixtures as an explosive. During the Second World War research was done toward the refinement of the hydrodynamic theory. Several methods of calculating the detonation velocities of the explosives were introduced: Brown (1942), Kistiakowski and Wilson (1942), and Brinkley and Wilson (1943). During the post-war period two more methods were introduced, namely by Cook (1947-8) and by Taylor and Patterson (1949).

This thesis concerns mainly with the behavior of ammonium nitrate and fuel oil No. 2 mixture. The Taylor's method has been chosen to check the experimental data.

Experiments were performed during the period July - November 1957.

REVIEW OF LITERATURE

Ammonium nitrate (NH_4NO_3) has both military and civilian uses. It serves as an oxidizer when mixed with TNT in the manufacture of explosives and is one of the best known sources of nitrogen for agricultural purposes. Chemically pure ammonium nitrate is pure white and contains 35% nitrogen. Ammonium nitrate fertilizer, however, contains only 33.2 to 33.8% nitrogen and as such contains 95 to 96% ammonium nitrate. The remainder is mainly the wax coating (no longer employed) on the grains of ammonium nitrate and kaolin-type clay, both of which are added to prevent the material from absorbing water and caking, and gives the material a dark-cream or light-straw color.

The finished fertilizer is required to meet the following specifications[1]:

Moisture	0.25% max.
Esther-soluble material (a saturated white paraffin wax)	0.75±0.35%
Water-insoluble material (Kieselguhr)	3.50±1.00%
Total nitrogen	32.50% min.

Specifications for granulation are:

Through U. S. Standard No. 8 Sieve	100% min.
On U. S. Standard No. 35 Sieve	55% min.
Through U. S. Standard No. 100 Sieve	8% max.

Ammonium nitrate has been reported[2] to have rates of detonation

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[1] Scott, G. S., and Grant, R. L., Ammonium Nitrate: Its Properties and Fire and Explosion Hazards. U. S. Bureau of Mines Information Circular 7463, 1948, p. 9.

[2] Ibid, p. 18

ranging from as low as 1,000 to as high as 2,700 m./sec. depending upon the conditions. The most important of the contributing factors are:

- Confinement
- Pressure
- Charge diameter
- Strength of initiating impulse
- Packing density
- Particle size
- Heat
- Impurities

1. The Effect of Confinement.

W. G. Hiscock[3] investigated the effect of changes in the nature of the confinement on the detonation velocities of Roburite No. 4, an intimate mixture of ammonium nitrate, TNT, and salt in the proportion:

TNT	16%
Ammonium nitrate	60%
Sodium chloride	24%

Using 1¼ in. diameter cartridges of a rather similar explosive, Hiscock found that the detonation velocity when fired under 2 ft. of sand was 2,890 m./sec. If the same explosive was filled into a steel tube and buried under 3 ft. of sand the velocity was 3,760 m./sec.

2. The Effect of Pressure.

Numerous tests have been carried out[4] by several investigators to study the sensitivity of ammonium nitrate to friction and impact.

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[3] Taylor, J., Detonation in Condensed Explosives. London, Oxford University Press, 1952, pp. 139-140.

[4] Scott, and Grant, op. cit., pp. 19-20.

In 190 tests, Munroe (1922 and 1945) was unable to obtain an explosion of ammonium nitrate by friction. Dropping a 20-kilogram weight 1 meter onto ammonium nitrate, Munroe obtained no explosion in 10 tests. Jones (1924) dropped a 200-kilogram weight 7.5 meters on ammonium nitrate at 140°C. without explosion.

However, explosions were obtained by these investigators (at least one explosion in 10 trials) where a 2-kilogram weight was dropped from a height of 31 inches onto a piston which transmitted the impact to 0.001 gram samples of ammonium nitrate or ammonium nitrate fertilizer contained in concave steel cups at 25°C. At 175°C., explosions were obtained when the weight was dropped from a height of 12 inches.

After the disaster at Texas City, Texas, in 1947 the U. S. Bureau of Mines initiated an investigation[5] on the explosibility of ammonium nitrate. Explosions were obtained in bomb tests charged with chemically pure ammonium nitrate at temperatures between 277°C. and 344°C. and pressures between 2,600 and 3,000 psi. Explosions occurred in bomb tests on ammonium nitrate fertilizer at temperatures between 114°C. and 350°C. and pressures between 2,000 and 2,600 psi.

3. The Effect of Charge Diameter

Hiscock, again using Roburite No. 4, found[6] that its detonation velocity increased with cartridge diameter in the following way:

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[5] Burns, J. J., Scott, G. S., Jones, G. W., and Lewis, Bernard, Investigations on the Explosibility of Ammonium Nitrate. U. S. Bureau of Mines, Report of Investigations, 4994, 1953, 19 p.

[6] Taylor, Op. Cit., pp. 139-140

Diameter (in.)	7/8	1¼	1½	2
Velocity (m./sec.)Z	2,890	3,680	3,830	3,880

Firing cartridges of a wider range of diameters buried under 2 ft. of sand, the following results were obtained:

Diameter (in.)	Velocity (m./sec.
7/8	3,620
1	3,660
1 1/8	3,880
1¼	4,080
1½	4,160
1 3/4	4,380
2	4,610

4. The Effect of the Strength of Initiating Impulse

Grant[7] demonstrated the relative insensitivity to detonation by firing 5-gram charges of chemically pure ammonium nitrate, density 0.84 with No. 6 to No. 10 fulminate-chlorate (80-20) detonators, using small paper cartridges in the sand bomb, similar to the miniature-cartridge test.

Detonation of Ammonium Nitrate and TNT

Cap	Weight of Fulminate-Chlorate in Detonator, grams	Sand Crushed by 5 Grams of AN, gram	Sand Crushed by 5 Grams of TNT, gram
6	1.0	21	253
8	2.0	43	254
10	3.0	58	261

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[7] Grant, K. L. and Tiffany, J. E., Detonators: Initiating Efficiency by the Miniature=Cartridge Test. U. S. Bureau of Mines, Technical Paper 677, 1945, 34 p.

It is apparent that only a small fraction of the 5 grams of ammonium nitrate was brought to detonation, whereas the TNT detonated almost completely under similar conditions.

5. The Effect of Packing Density

The effect of packing density of ammonium nitrate has never been studied seriously. E. Jones[8] made a study on the rate of detonation of pressed TNT over a range of carefully measured densities.

Density of Pressed TNT gram/cc.	Detonation Velocities m./sec. in 1-inch diameter
1.53	6,920
1.40	6,450
1.34	6,180

It is expected that ammonium nitrate will behave similarly.

6. The Effect of Particle Size

Under the supervision of Dr. Messerly,[9] the Explosive Research Laboratory in Bruceton, Pa., conducted a series of tests to investigate the effect of particle size on the detonation velocities of ammonium picrate.

It has been found that the particle size distribution rather than the average particle size is the most important factor in determining the rate. The finest material studied (all particles smaller than 44 microns) had a detonation rate approximately equal to the theoretical one. The admixture of a small percentage of coarse material, which makes only a

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[8] Taylor,op. cit., p. 140.

[9] Messerly, G. H. and Martin, F. J., The Effect of Particle Size on the Detonation Velocity of Ammonium Picrate. OSRD Report 1755. 1943,p.7

slight change in the average particle size, produces a marked lowering of the velocity of detonation. If the fine particles are completely replaced by coarse particles, the rate decrease is greater, and is more pronounced the greater is the size of the particles of the explosive.

7. The Effect of Heat

Rapid heating, suitable confinement, and perhaps good insulation are likely to lead to explosion.[10] Of nine cases of fire in large quantities of ammonium nitrate, explosions followed in four cases, namely:

Brest, France, July 28, 1947
Texas City, Texas, April 16-17, 1947
Tessenderloo, Belgium, April 29, 1942
Oppau, Germany, September 21, 1921

Heat and quantity of ammonium nitrate alone are obviously not always sufficient to cause detonation.

8. The Effect of Impurities.

In 1944 the Explosives Research Group in Bruceton, Pennsylvania, made another study[11] on explosive mixtures containing ammonium nitrate. It was thought possible to increase the reaction rate of ammonium nitrate by utilizing the catalytic effect of some admixed material. Potassium nitrate is found to be effective in lowering the reaction rate. Several organic substances were incorporated with ammonium nitrate in the hope that the increased decomposition temperature would materially increase the rate of decomposition. These trials were also unsuccessful in raising

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[10] Scott and Grant, op. cit., pp. 21-22.

[11] Messerly, G. H., and Martin, F. J., The Detonation Velocities of Explosive Mixtures Containing Ammonium Nitrate. OSRD Report 3411.1944,34p.

the detonation velocity. To prevent ammonium nitrate explosives from caking, a solution has been found by Whetstone.[12] The ammonium nitrate is treated with a highly sulfonated compound, called Acid-Magenta, and a surface-active agent, called A.S. 2.

The small addition of 0.03% of Acid-Magenta and 0.003% A.S. 2 is insufficient to sensitize to thermal decomposition or to increase the explosive hazards of ammonium nitrate. It is found that Acid-Magenta and A.S. 2 do not react with ammonium nitrate, and thus do not appreciably affect the solubility or hygroscopicity of the salt. The thermal stability of the explosive is unaffected by the Acid-Magenta solution.

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[12] Whetstone, John, Solution to the Caking Problem of Ammonium Nitrate and Ammonium Nitrate Explosives. Industrial and Engineering Chemistry. Vol. 44, pp. 2663-2667. 1952.

PROPERTIES OF AMMONIUM NITRATE

A summary of the properties of ammonium nitrate, known up to 1947, has been given by Scott and Grant[13] in 1948.

The usual packing density of ammonium nitrate is between 0.8 and 0.9 grams per cubic centimeter, depending upon the particle size and pressure applied, while the density of the crystals is 1.72. Ammonium nitrate may either take up from or give off water to the atmosphere, depending upon the temperature and relative humidity. This property causes the caking of the salt.

Berthelot[14] stated: "When rapidly heated, the explosive decompositions, properly called, of ammonium nitrate take place. One of them produces nitrogen and oxygen."

$$NH_4NO_3 = N_2 + \frac{1}{2}O_2 + 2H_2O$$

This is the basic equation to consider for ammonium nitrate, when it is mixed with other compounds to form an explosive mixture. According to the above equation, ammonium nitrate will have an oxygen balance of plus 20% (20% of the weight of the ammonium nitrate). The oxygen balance refers to the amount of oxygen in an explosive, greater than or less than that required for complete combustion of the combustible materials present.

There are also other equations[15] which may describe the course of the decomposition of ammonium nitrate:

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[13] Scott and Grant, op. cit., pp. 9-18

[14] Berthelot, M., Explosives and Their Power. London, John Murray, 1892, p. 6.

[15] Scott and Grant, op. cit., p. 12

$$NH_4NO_3 = NH_3 + HNO_3$$

$$NH_4NO_3 = N_2O + 2H_2O$$

$$NH_4NO_3 = \frac{1}{2}N_2 + NO + 2H_2O$$

$$3NH_4NO_3 = 2N_2 + N_2O_3 + 6H_2O$$

$$2NH_4NO_3 = 1\frac{1}{2}N_2 + NO_2 + 4H_2O$$

$$5NH_4NO_3 = 2HNO_3 + 4N_2 + 9H_2O$$

In the above equations, the nitrate is solid and all products are gaseous, and yet these equations cannot be taken into consideration since they all take place at much lower temperatures (200-340°C). Containing 20% of its weight as available oxygen when ammonium nitrate decomposed at higher temperatures, it is logical that organic or other oxidizable matter in contact with ammonium nitrate may produce violent combustion on ignition.

Hardesty and Davis[16] have shown that in the presence of carbonaceous material, the following reactions take place:

$$2HNO_3 + C = CO_2 + H_2O + NO_2 + NO$$

$$2NO_2 + 2NO + 3C = 3CO_2 + 2N_2$$

Various metals may also react with ammonium nitrate either at high temperatures or low temperatures.

During the Second World War the U. S. Bureau of Mines conducted an investigation on the explosibility of ammonium nitrate mixed with zinc and compressor oil. It was found[17] that ammonium nitrate and compressor

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[16] Hardesty, J. O., and Davis, R. O. E., Spontaneous Development of Heat in Mixed Feritlizers. Industrial and Engineering Chemistry. Vol. 38, pp. 1298-1303, 1946.

[17] Elliott, Martin E., Exothermal Decomposition of Mixtures Containing Ammonium Nitrate. U. S. Bureau of Mines Report of Investigations 4244, p. 10, 1948.

oil react exothermically after a temperature of 250°C is reached. However, if zinc is present, the reaction occurs at temperatures ranging from 100-140°C, even in the absence of compressor oil, at concentrations of zinc as low as 1% by weight and as high as 50% by weight. The behavior of zinc in explosives has so far not been studied.

Cook, et al.,[18] studied the effect of aluminum on explosives. It was found that aluminum lowers the "detonation pressure" and velocity even more, sometimes quite considerably more, than an ideal diluent. This is especially true for high explosives, such as TNT. Certain precautions should be taken into consideration in the manufacture of aluminized explosives.

Hart and Tomlinson[19] reported that in a mixture of ammonium nitrate, TNT and aluminum (plus a little moisture) ammonia is released and it will react with TNT to form a loosely bound diammoniate which will ignite as low as 96°C. Such a reaction has led to explosions. Further the explosive has to be kept dry or else moisture will react with aluminum and produce hydrogen, which will reduce the oidizing power of the explosive and lead to excessive gassing.

One of the first reports on the ammonium nitrate-hydrocarbon mixtures was given by Cook and Talbot[20]. They stated that the explosive

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[18] Cook, Melvin A., Filler, Aaron S., Keyes, Robert T., Partridge, William S., and Ursenbach, Wayne O., Aluminized Explosives. The Jl. of Physical Chemistry, Vol. 61, p. 189, 1957.

[19] Hart, R. D., and Tomlinson, Jr., W. R., Use of Finely Divided Metals in Explosives. Metal Progress, Vol. 65, p. 790, 1951.

[20] Cook, Melvin A., and Talbot, Eugene L., Explosive Sensitivity of Ammonium Nitrate-Hydrocarbon Mixtures. Industrial & Engineering Chemistry, Vol. 43, p. 1101, 1951.

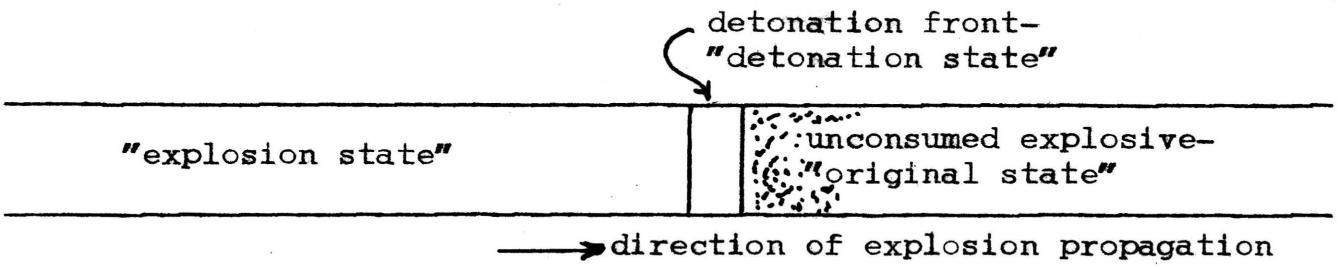
sensitivity of ammonium nitrate is almost invariably increased by incorporating in it small percentages of combustible materials. This is caused by the increased heat made available in the explosion of AN/fuel mixtures by the reaction of the excess oxygen of ammonium nitrate with the combustible.

CALCULATION BY TAYLOR'S METHOD

Taylor's method distinguishes three states in which the explosive may exist:

1. the original state
2. the explosion state, and
3. the detonation state.

In a cross-section of a tube, it is given as follows:



For one to be able to follow the discussion later, it is very important to know the outline of the calculation by Taylor's method. The method employs only 5 gaseous products, namely CO_2, CO, H_2O, H_2 and N_2. The rest are assumed to be negligible in amount compared to the main gases. The equation of state employed is:

$$P V = n R T \sigma$$

where P, V, n, R, and T have their usual meaning (pressure, volume, number of gaseous moles, gas constant and temperature), and

$$\sigma = 1 + x + 0.625 x^2 + 0.287 x^3 + 0.193 x^4$$

$$x = \frac{n_i b_i}{100/\Delta - \alpha}$$

n_i = number of moles of a gas

b_i = molar coefficient of the corresponding gas

Δ = loading density

α = volume occupied by non-gaseous products

If an explosion temperature or detonation temperature is assumed, a systematical method of determining the explosion products and the detonation state can be followed[21]. All tables necessary to carry out the calculations are also given by Taylor.

The only basic chemical equation required is the well known water-gas reaction:

$$CO_2 + H_2 \quad CO + H_2O$$

The equilibrium constant K for this reaction is defined as follows:

$$K = \frac{(CO)\ (H_2O)}{(CO_2)(H_2)}$$

where term in the parenthesis gives the concentration of each gas. The carbon dioxide dissociation-equilibrium exerts only a minor influence and as such can be neglected, because the equilibrium constant of the water-gas reaction is almost 10^5 greater than that of the carbon dioxide dissociation at a temperature of 3000°C.

For high temperatures it is necessary to correct for the effect of gas imperfection on the gases equilibria. The ideal equilibrium constant K thus requires multiplication by a factor G, where:

$$\log_e G = f(x) \sum n_i + (\sigma - 1) \sum n_i \left(\frac{nb_i}{b} - 1\right)$$

Wince for the water-gas reaction there will be no increase in molecules, and thus $\sum n_i = 0$, the equation becomes

$$\log_e G = (\sigma - 1) \sum (n_i b_i)\ \frac{n}{b} - (\sigma - 1) \sum n_i = \frac{n(\sigma - 1)}{b} \sum n_i b_i$$

in which: n = total number of moles

b = total of second virial virial coefficient (molar coefficient) of the gases

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[21] Taylor, op. cit., p. 64.

n_i = number of moles of a gas

b_i = molar coefficient of the corresponding gas

σ = a factor of x as has been given before

For the detonation state the calculation is more tedious. A detonation temperature is assumed to correct the composition of the gaseous detonation products. Then a similar procedure is followed as that used for the explosion state. After the composition of the detonation products is determined, Boltzmann's equation of state is employed and the procedure as given by Taylor followed to solve for the detonation pressure and detonation velocity.[22]

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[22] Taylor, op. cit., pp. 97-102

DISCUSSION

This thesis concerns mainly the behavior of 95/5 ammonium nitrate/ fuel oil mixture as an explosive. The fuel oil employed was a No. 2 fuel oil with the following analysis:

86.59% C

13.56% H

0.43% S Total: 100.58%

Corrected by the factor 100.00/100.58, the analysis becomes:

86.09% C

13.48% H

0.43% S

In the following calculations the small amount of sulphur present is neglected, since the effect upon the results is negligible. Thus the ratio of the atoms of C : H in the fuel oil is $\frac{86.09}{12.011} : \frac{13.48}{1.008}$ or 1 : 1.866 and not 1 : 2 as had been expected before. The specific gravity of the fuel oil is 0.8337 gr./cc. or 38.22532 API, with a heat of combustion of 10.93764 cal./gr. The equilibrium mixture of ammonium nitrate and fuel oil is then calculated and found to be: 5.47% fuel oil.

Sample Calculation of Explosion State

Take a 93/7 AN/fuel mixture, which is slightly oxygen-negative with a loading density $\Delta = 0.875$. Thus for each 100 grams of mixture, there are 93 grams of ammonium nitrate and 7 grams of fuel oil. This will be the basis of the following calculations.

93 grams of AN = 1.16180 moles, yielding the following gaseous products:

N_2 = 1.16180 moles

H_2O = 2.32360

O_2 = 0.58090

Heat of combustion of AN = 0.634 cal/gr.

7 grams of fuel oil = 0.5150 mole, yielding the following gaseous products:

CO_2 = 0.5150 mole

H_2O = 0.4805

O_2 = -0.7562

The explosion products will then be:

CO_2 = 0.5150 moles

H_2O = 2.8041

N_2 = 1.1618

O_2 = -0.17530

Gaseous moles = 4.4809 = n

Heat of complete combustion of AN = 58.96

Fuel = 76.56

Heat of complete combustion =135.52 cal

Substract 135 . (O_2) = 23.66

Approximate heat of explosion =111.86 cal

Material balance: $C = (CO_2) = 0.5150$

$H = 2(H_2O) = 5.6082$

$O = 2(CO_2) + (H_2O) + 2(O_2) = 2.4835$

Estimation of the second virial coefficient:

$n_{CO_2}\, b_{CO_2} = 19.055$

$n_{H_2O}\, b_{H_2O} = 22.152$

$n_{N_2}\, b_{N_2} = 39.501$ Total: 80.708

Take $b_i = 80.77$ as a trial value

$$X = \frac{b_i}{100/} = \frac{b_i}{100} = 0.7067$$

$$6 - 1 = X + 0.625\, X^2 + 0.287\, X^3 + 0.193\, X^4 = 1.1682$$

$$\alpha = 0$$

$$\log_{10} G = \frac{4.38\ n}{b_i} (\sigma - 1)(1 - \frac{\alpha\Delta}{100}) = 0.2839$$

$K_{est.}$ for 2300°C = 6.30

$K' = K\ G = 6.30(10)^{0.2839} = 12.112$

$a = K' - 1 = 11.112$

$b = K'(\frac{1}{2}H + C - O) + O = 1.47095$

$c = C(C - O) = - 1.530$

$$(CO_2) = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = 0.31073 \text{ mole}$$

$(CO) = 0.51500 - 0.31073 = 0.20427$

$(H_2) = (\frac{1}{2}H + C - O) + (CO_2) = 0.14441$

$(H_2O) = O - (CO_2) - C = 2.65969$

$(N_2) = 1.16180$

Checking the value of b_i:

$n_{CO_2}\ b_{CO_2} = 11.497$

$n_{CO}\ b_{CO} = 6.741$

$n_{H_2}\ b_{H_2} = 2.022$

$n_{H_2O}\ b_{H_2O} = 21.012$

$n_{N_2}\ b_{N_2} = 39.501$ Total: 80.773

The assumed value of b_i is thus correct.

Heat of complete combustion of mixture = 135.52

Substract 67.33(CO) = 13.75

67.70(H_2) = 9.77

Available heat of explosion = 112.00 cal

The temperature of explosion can be calculated by tabulating the internal energies of each of the gases at the assumed temperature. (Table from Taylor).

	Number of moles	Internal Energies At 2300°C	 2400°C
CO_2	0.3107	8.07	8.47
CO	0.2042	2.89	3.03
H_2	0.1444	1.88	1.98
H_2O	2.6596	80.29	83.14
N_2	1.1618	16.27	17.06
		109.40	113.68

Since the available heat of explosion is only 112.00 cal, the temperature of explosion is found by interpolating to be 2,360°C or 2,633°K.

The explosion pressure can be calculated by using the

$$p_3 = \frac{0.8216\,\Delta\, nT}{1 - \frac{\alpha\Delta}{100}} \text{ atm.} \qquad \text{(T in° Kelvin)}$$

It is found to be 18,380 atm.

Sample Calculation of Detonation State

In the first place the gaseous products in the explosion state must be corrected, since the detonation temperature is much higher than the explosion temperature.

To do this, another value of K has to be assumed.

In this case, assume K = 8.04 (for 3400°C or 3670°K)

Then the same procedure as in the explosion state is followed by assuming another value of b_i.

The result is determined as follows:

Correct value of b_i = 80.62 per 100 gr. mixture

The detonation i products are: $(CO_2) = 0.295$ moles
$(CO) = 0.2197$
$(H_2O) = 2.6751$
$(H_2) = 0.1289$
$(N_2) = 1.1618$

The total of gaseous moles is thus 4.48090, while the corrected Q is 112.00116 cal. The detonation temperature is calculated by using appropriate formula.

Now that the gaseous products have been corrected, assume $v_2 = 0.840$ (for nomenclature refer to preceding pages) per gram explosive.

$$X = \frac{b_i}{v_2} = \frac{0.8062}{0.8400} = 0.9598$$

$$\sigma = 1 + X + 0.625\ X^2 + 0.287\ X^3 + 0.193\ X^4 = 2.9532$$

Thus: $\frac{d\sigma}{dX} = 3.6756$

$$\frac{d\alpha}{dV} = \left(1 - \frac{1}{\sigma} - \frac{X}{\sigma^2} \cdot \frac{d\sigma}{dX}\right) = 0.257$$

$$\alpha = V_2\left(1 - \frac{1}{\sigma}\right) \text{ or } \frac{\alpha}{b_i} = \frac{V_2}{b_i}\left(1 - \frac{1}{\sigma}\right) = \frac{1}{X}\left(1 - \frac{1}{\sigma}\right)$$

Hence: $\alpha = \frac{1}{X}\left(1 - \frac{1}{\sigma}\right)(b_i) = 0.556$

$$K = 1 + \frac{nR}{C_v} - \frac{d\alpha}{dV} = 0.941$$

$$V_2 = \frac{Kv_1 + \alpha}{K + 1} + 0.840$$

The assumed value is thus correct.

Assume a temperature of detonation = 3,680°K

$$\sum n_i\bar{C}_v = 38.39167$$

$$T_2 = \frac{(Q + 300\sum n_i\bar{C}_v)K}{K\sum n_i\bar{C}_v - \frac{1}{2}nR} = 3{,}670°K$$

The temperature of detonation is thus 3,670°K.

The velocity of detonation is found to be 4,552.71 m/sec. or 14,937 ft./sec. by using the formula:

$$D_2 = \frac{K + 1}{1 - \alpha\Delta}\sqrt{\frac{nRT}{K}}$$

The pressure of detonation is 34,890 atm., found by employing the same formula as in the explosion state.

On The Taylor's Method

In Figure 1 is given the effect of per cent fuel oil on the explosion temperature. It is logical to expect that the explosion temperature reaches its maximum at equilibrium mixture, since all available energy is liberated. The maximum temperature is 2,810°K.

The detonation temperature is affected in the same manner. The curve runs parallel to that of the explosion temperature, as can be seen in Figure 2.

The highest detonation temperature is 3,760°K or about 1,000°K higher than the explosion temperature. In short we can say that approximately:

$$T_d = T_e + 1{,}000^\circ$$

where:

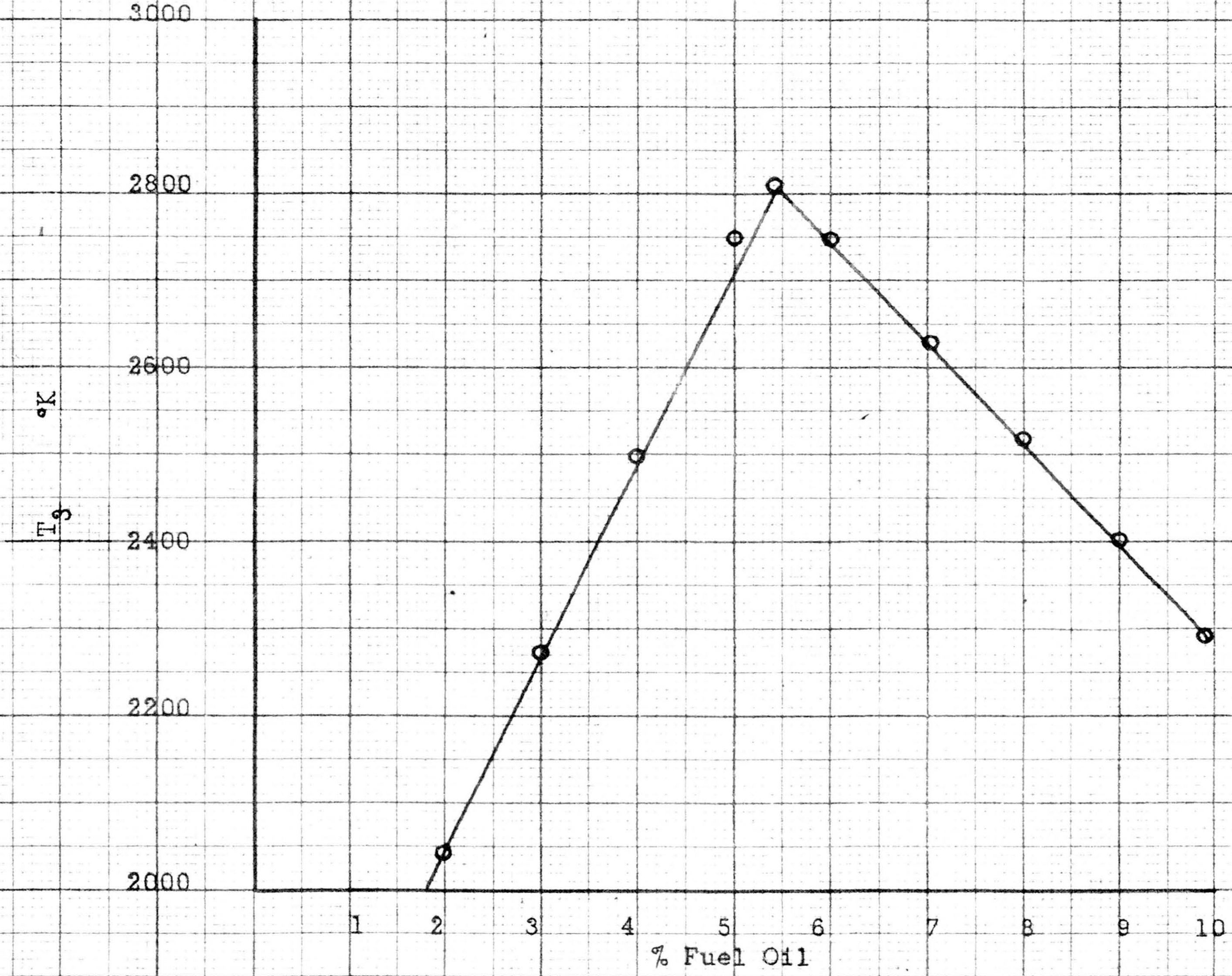

Figure 1. Explosion Temperature T_3 vs % Fuel Oil
Loading Density 0.875

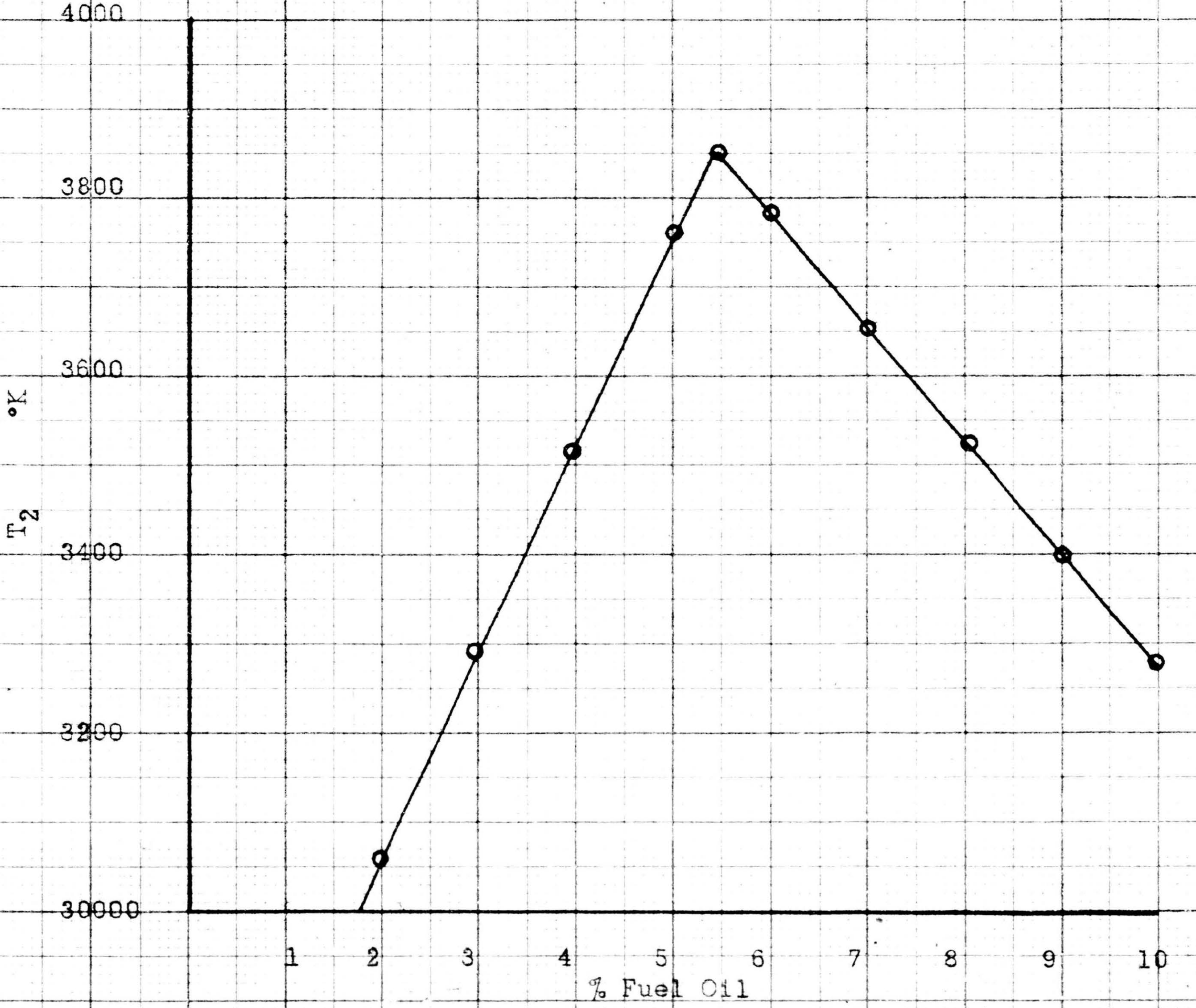

Figure 2. Detonation Temperature T_2 vs % Fuel Oil
Loading Density 0.875

T_d = temperature of detonation

T_e = temperature of explosion

No calculation has been made for mixtures containing more than 10% fuel, since it was found by earlier experiments that these mixtures did not explode at all. Since the relation between the temperature and the composition of the mixture is a straight line, explosion and detonation temperature at any composition can be read from the graph.

After calculating the temperatures, the corresponding explosion and detonation pressures can also be plotted. Figure 3 shows the effect of loading density on the explosion pressure for 95/5 AN/fuel mixture calculated by Taylor's method. It seems that the curve runs parabolically upward with a very small change of slope.

As can be seen from the formula:

$$p = 0.821 \frac{n\ T}{1 - \alpha\Delta/100}$$

in which:

n = number of gaseous moles

T = temperature of explosion in K°

Δ = loading density of mixture in gr/cc

$\sigma = 1 + x + 0.625x^2 + 0.287x^3 + 0.193x^4$

α = volume occupied by non-gaseous products per 100 grams of mixture

In our case n and T are constants and $\alpha = 0$. Thus in calculating p we have two variables, namely Δ and σ, which causes the parabolic appearance of the curve.

Hence, $\frac{dp}{d\Delta}$ will become steeper at higher density.

The effect of the percentage of fuel oil in the mixture on the explosion pressure at constant loading density is given in Figure 4.

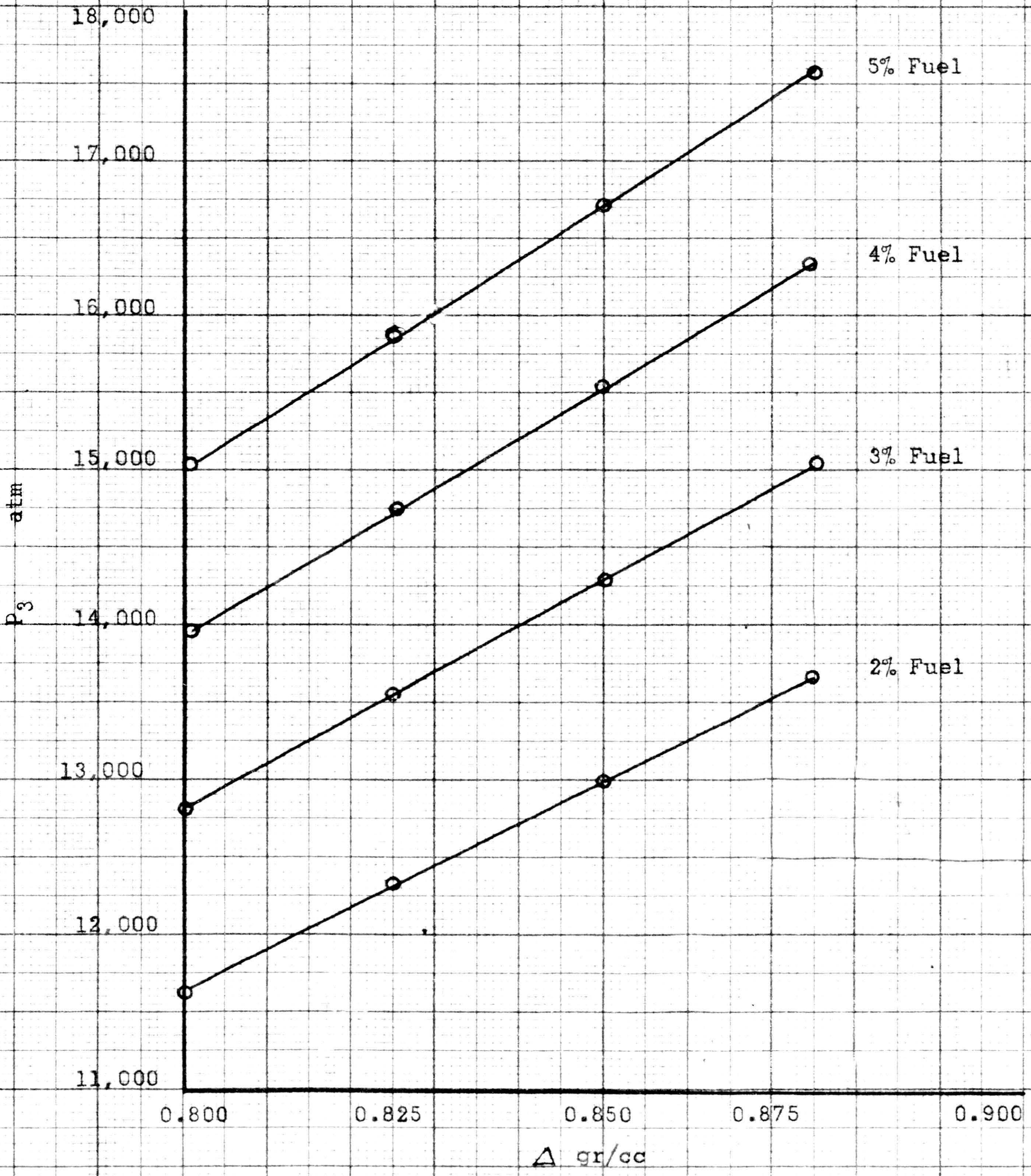

Figure 3. Explosion Pressure vs Loading Density
95/5 AN/Fuel Oil

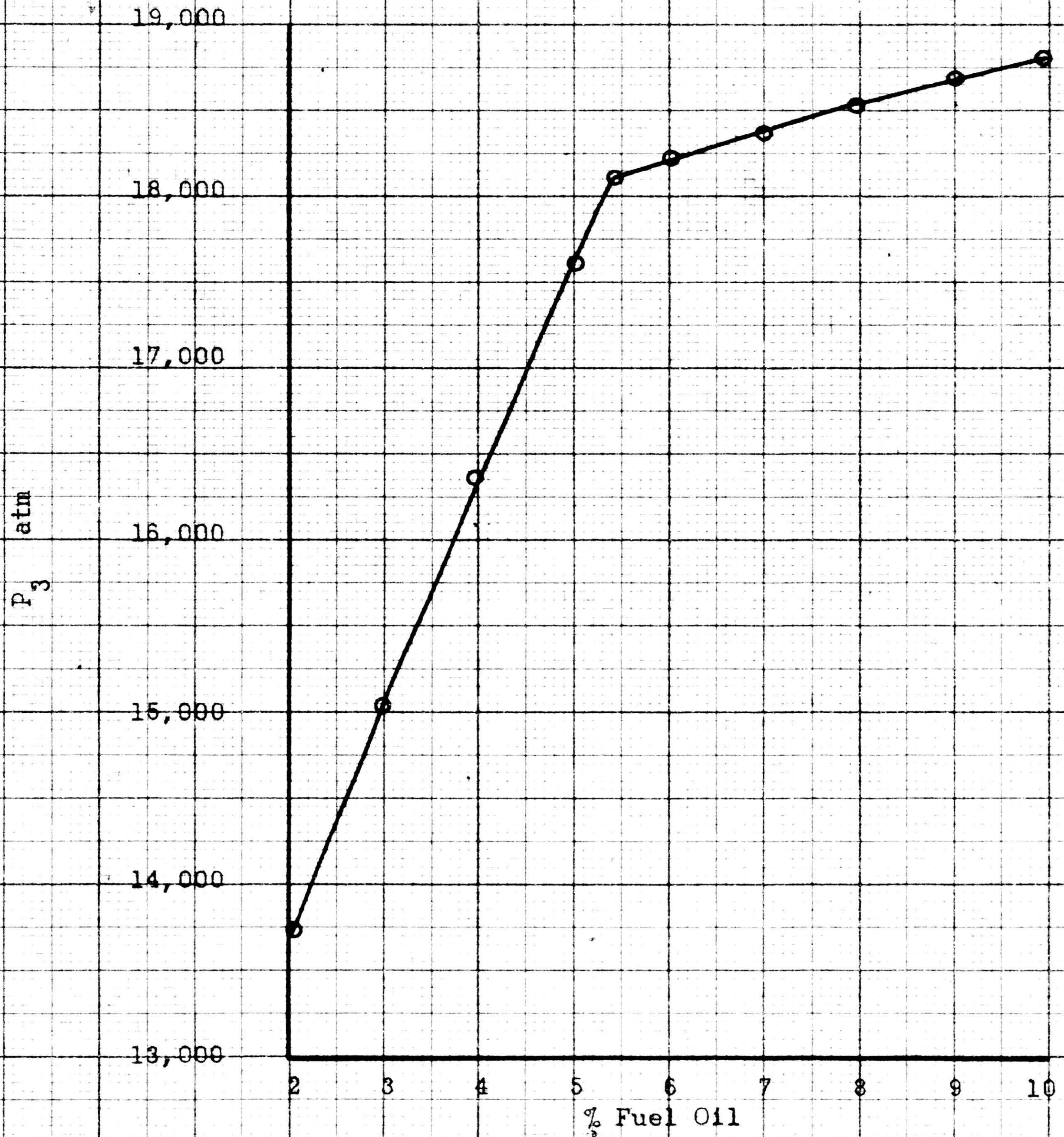

Figure 4. Explosion Pressure vs % Fuel Oil
Loading Density 0.875

Up to the equilibrium mixture the pressure rises very quickly. For oxygen-negative mixtures the pressure still increases with reduced slope, although according to Figure 1 the explosion temperature has already declined. This is caused by the increase of σ and n. The increase of σ with the change of loading density of the 95/5 AN/Fuel mixture is given in Figure 5.

How far the pressure will go up cannot be determined readily since theoretically n increases with the increase of fuel oil in the mixture. This has, however, a limited use, because a mixture with 10% fuel oil at ordinary conditions cannot explode at all.

Again, it is necessary to mention that the value of σ for the explosion state differs from that of the detonation state (see Figure 5). It is strongly influenced by the change in loading density and composition of the mixtures, especially for the oxygen-negative mixtures. The exact relationship between these three factors cannot be determined accurately and will have no direct use in the calculation if it was plotted in the graph, because it cannot be accurately determined.

The theoretical $D(\Delta)$ curve is drawn in Figure 6. The value of the detonation velocity D is calculated by using the formula

$$D = \frac{K_1 + 1}{1 - \alpha\Delta} \sqrt{\frac{n\ R\ T}{K_1}}$$

The terms α, Δ, n, R, and T have their usual meaning as given before, but:

$$K_1 = 1 + \frac{n\ R}{C_v} - \left(\frac{d\alpha}{dv}\right)_{v=v_2}$$

c_v = total ideal molal heat capacities of the gases

$$\frac{d}{dv} = 1 - \frac{1}{\sigma} - \frac{x}{\sigma^2}\frac{d\sigma}{dx}$$

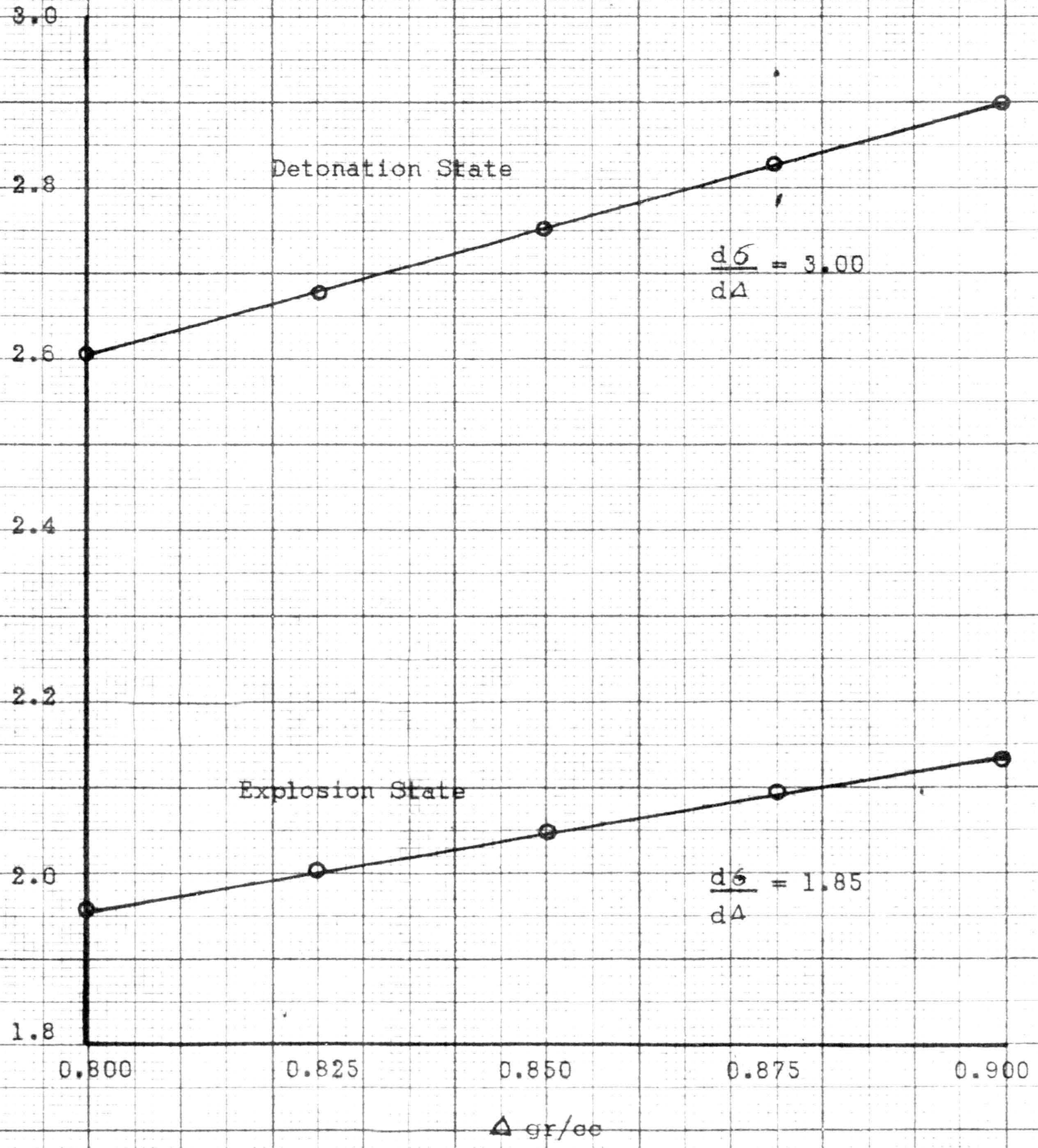

Figure 5. Value of δ for
95/5 AN/Fuel Oil

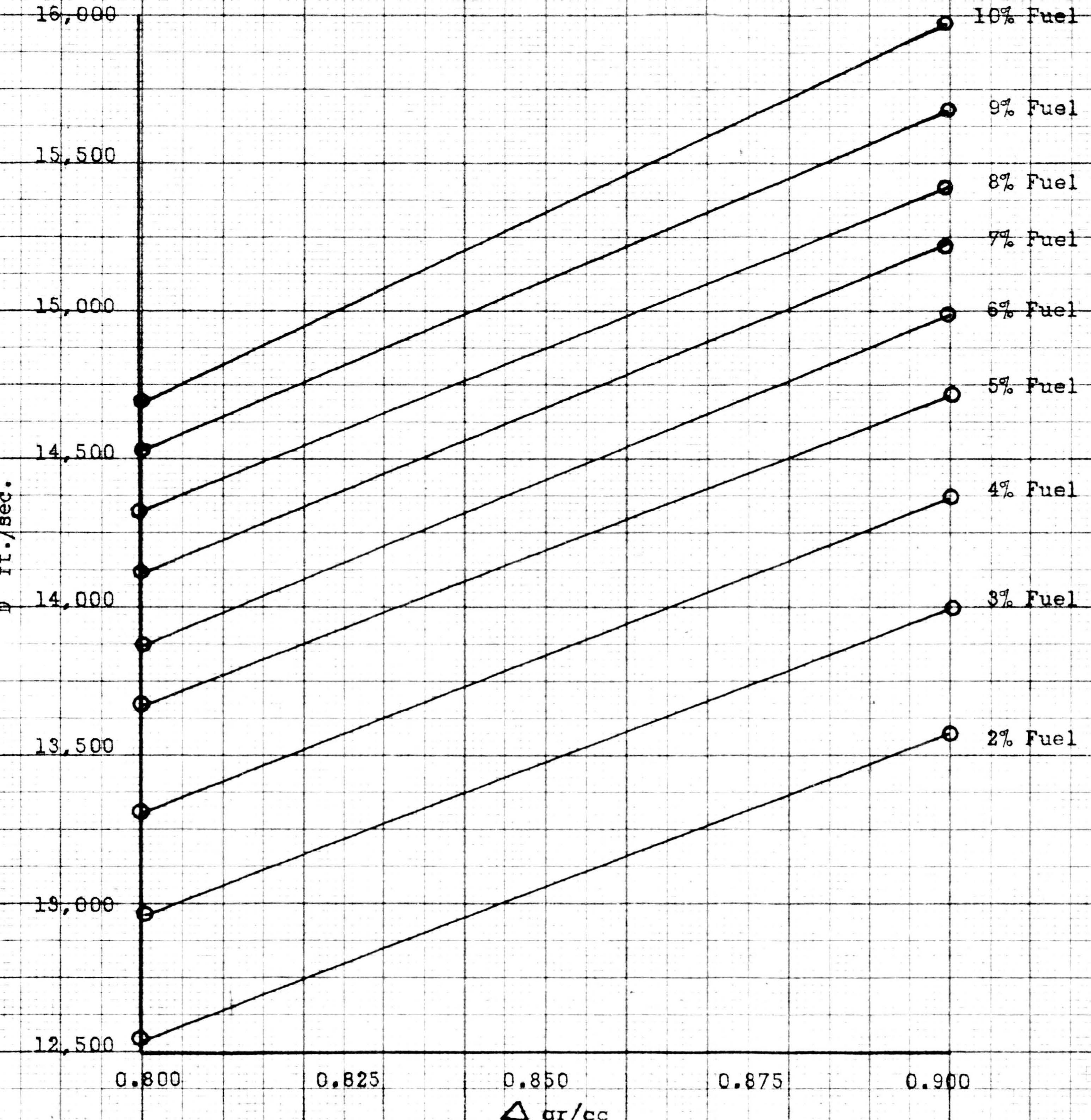

Figure 6. Theoretical
D-(Δ) curve

Although explosive mixtures containing more than approximately 5.5% fuel oil have lower explosion and detonation temperatures, the value of D still increases. It seems that the smaller value of T is counterbalanced by the larger value of n and α. Judging from the numerical value of each factor, the determining factor is α.

How the value of α is affected by the specific volume v_2 and the composition of the mixture is given in Figure 7. The experimental values of Cook are also plotted to give a better comparison. Cook's co-volume is a function of volume, while the one used in the Taylor's method is the Jones' co-volume, which is a function of the pressure of the gases only.

On The Experimental Results

The results of the experiments are tabulated in Appendix A.

Taylor[23] notes that a moderately coarse granular sample of ammonium nitrate cartridged at a density of 1.0 gr/cc. in 9 in. diameter cardboard cartridges could be detonated if it was primed with a large cartridge of blasting gelatine. Its detonation velocity was 1,250 m/sec. The same substance in a 12½ in. diameter cartridge detonated at 1,370 m/sec.

Hence the diameter at which the ideal (maximum) detonation velocity will be obtained, should be much larger than 12½ in. diameter, since the theoretical value is 3,460 m/sec. However, we are not so much interested in the ideal diameter. More important is the critical diameter or the minimum diameter at which ammonium nitrate or ammonium nitrate mixtures can detonate, although not completely. Taylor further mentioned that in some circumstances the critical diameter for ammonium nitrate is greater than 9 in.

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[23] Taylor, op.cit., p. 143.

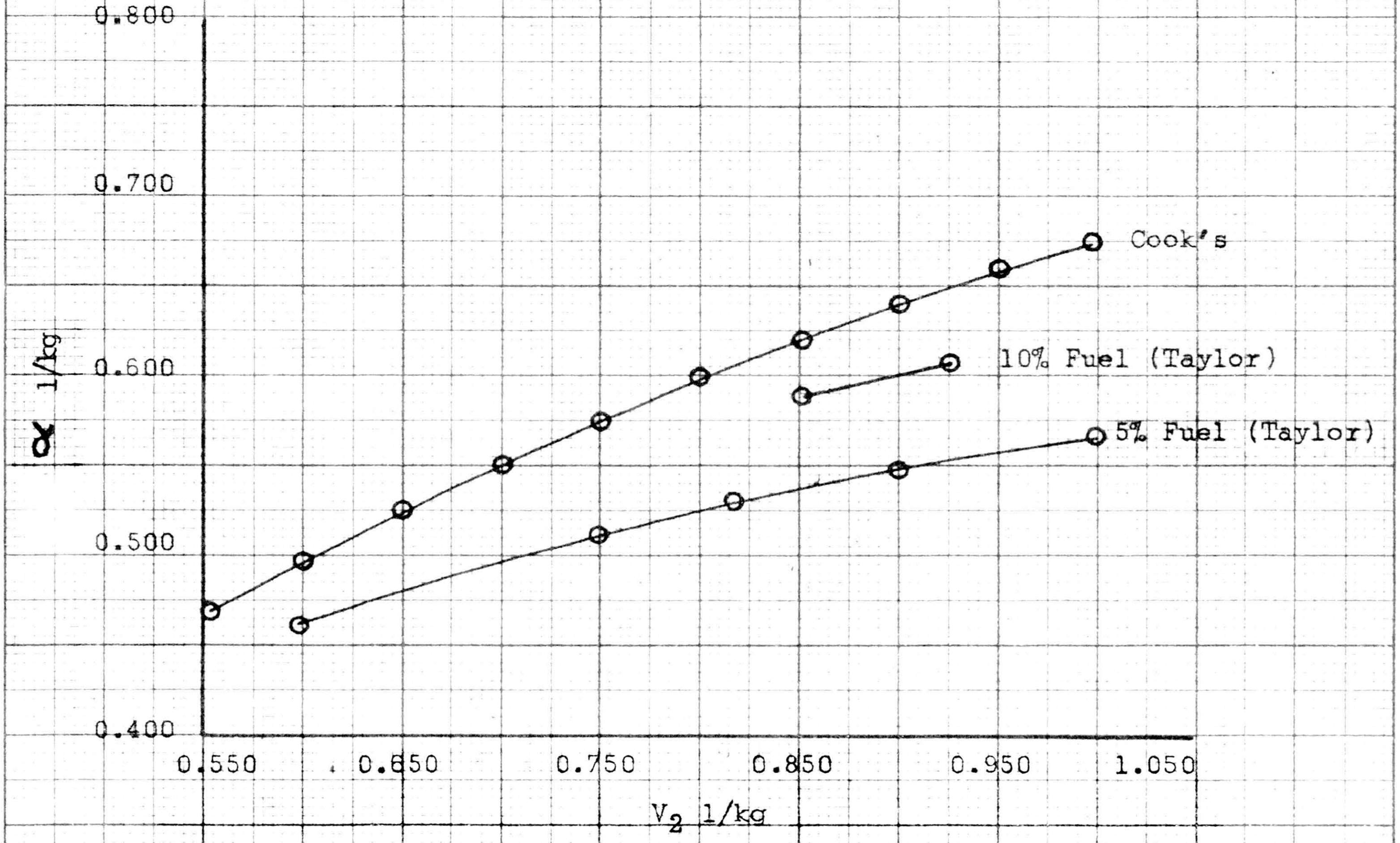

Figure 7. Comparison Between Taylor's Co-volume and Cook's

The effect of pipe diameter on the detonation velocity of 95/5 AN/Fuel mixture at a loading density of 0.890 is plotted in Figure 8. If we extrapolate the value of the experimental detonation velocity for the upper value, it can be seen that the ideal pipe diameter should be at least 9 in. This cannot be done, because the relation between the increase in detonation velocity with the increase in pipe diameter is not a straight line, but is more or less hyperbolic. Thus the ideal pipe diameter should be much larger than 9 in.

Cook[24] reported that for a 94/6 AN/Fuel Oil mixture which is slightly oxygen-negative, the ideal detonation diameter is 56 in.

In earlier stages of the experiments some qualitative tests were run successfully by using $1\frac{1}{2}$ in. diameter pipes and 95/5 AN/Fuel Oil mixture. It can be concluded that the critical diameter of this mixture should be approximately $1\frac{1}{2}$ in., depending on the initiator and the loading density as will be discussed later. The composition of the mixture is certainly a determining factor also as further stated by Cook.

In Figure 9 **is** plotted the actual $D(\Delta)$ curve for a 95/5 AN/Fuel Oil mixture (3 in. pipe diameter) initiated with a 60% dynamite. It was found that with 60% dynamite as the initiator a detonation is not obtained at a loading density greater than 0.900 for prilled AN tested. The critical loading density is defined as follows: "the maximum loading density at which an explosion/detonation still occurs." Again, this depends on the initiator and possibly the pipe diameter.

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[24] Cook, Melvin A., Large Diameter Blasting With High AN, Non-NG Explosives. Third Annual Symposium on Mining Research at University of Missouri School of Mines and Metallurgy, Tech. Bulletin #95, 1958, pp. 135-149.

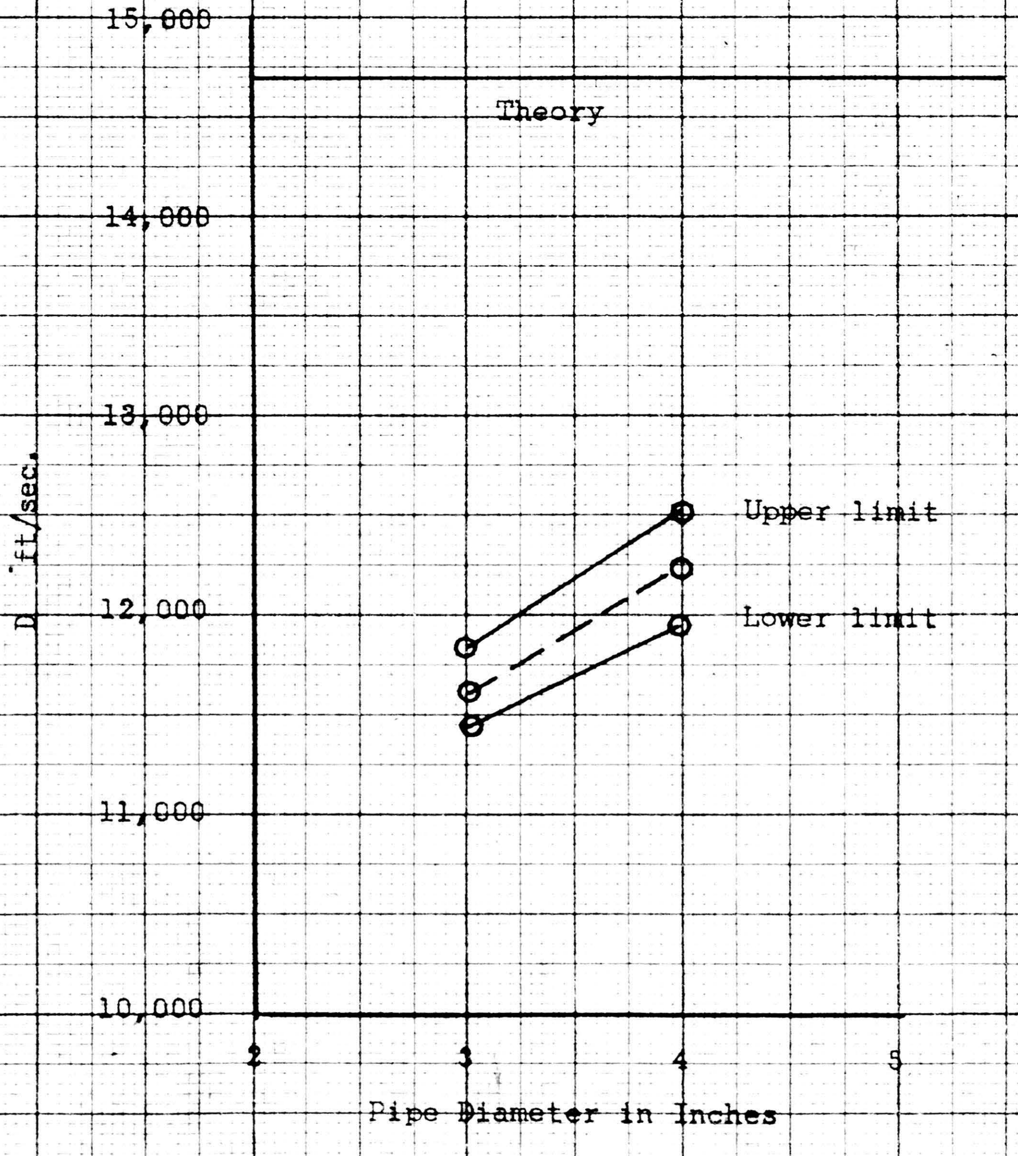

Figure 8. Detonation Velocity vs Pipe Diameter
95/5 AN/Fuel Oil
Loading Density 0.890
Initiated With 60% dynamite

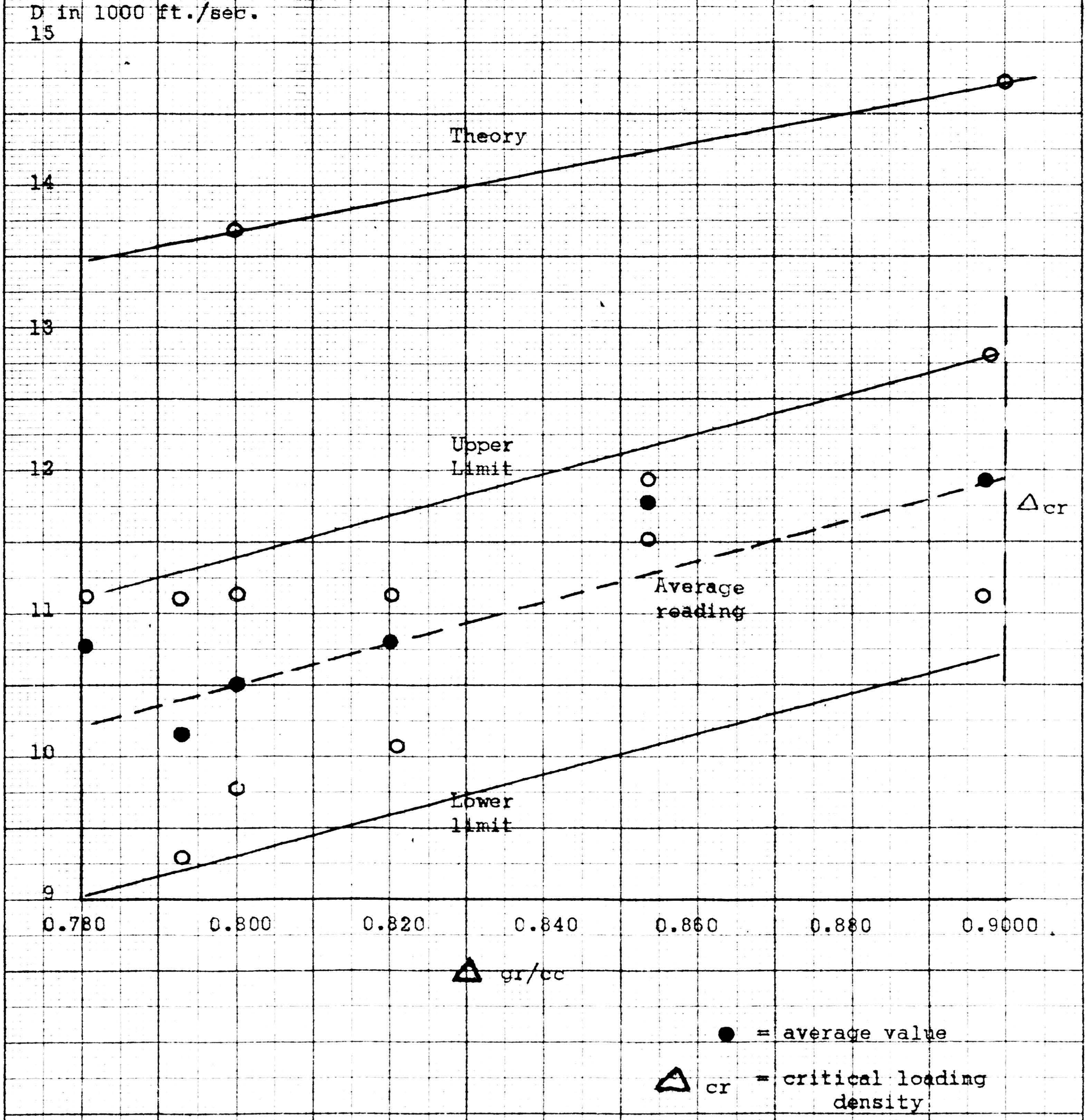

Figure 9. Theoretical and Experimental Results
95/5 An/Fuel Oil
Pipe Diameter 8 in.
Initiated with 60% dynamite

The influence of initiator on the critical diameter can be seen in Table I.

TABLE I

Influence of Initiator on the Critical Loading Density.
95/5 AN/Fuel, Initiated With One Foot of Different
Weight Primacord. Pipe Diameter - 3 inches.

Loading Density	D Observed (ft/sec)	Primacord
0.830	Failed	150# Grain
0.819	Not Available	300# Grain
0.841	Failed	300#
0.783	Failed	400# Grain
0.825	11,265	400#
0.831	11,420	400#
0.855	Failed	400#

By using different kinds of Primacord it is noted that there is an increase of critical loading density with the increase of the strength of the initiator. It increases from = 0.830 for 150# grain primacord to 0.855 for 400# grain. (Compare with 0.900 for 60% dynamite). From Figure 9 we can also see that the experimental D (Δ) curve approaches the theoretical D(Δ) curve at higher densities. However, as we have pointed out before, the critical loading density for this case is 0.900, which means that we will never reach the theoretical detonation velocity. In order to approach the problem, ammonium nitrate with smaller particle size has been used. The results are tabulated in Table II.

TABLE II

Influence of Particle Size on the Detonation Velocity.
95/5 AN/Fuel. Initiated with 60% Dynamite. Pipe
Diameter 3 inches.

Loading Density	Particle Size	D exp. (ft/sec)	D theor. (ft/sec)	Deviation
0.831	10/12 Mesh	11,940	14,000	2,060
0.827	14/16	12,450	13,955	1,505
0.900	30/35	13,870	14,715	845

It is obvious that the smaller the particle size of the ammonium nitrate the less the deviation of the experimental detonation velocity from the theoretical value will be. This agrees with the grain-burning theory[24] as has been checked by MacDougall (1943), Eyring, et.al. (1949) and Kistiakowski (1950), which states that chemical reaction once initiated on the surface of the explosive grains thereafter spreads inward at a rate determined by temperature and pressure. However, MacDougall[25] pointed out that attempts to prepare ammonium nitrate smaller than 10 microns were unsuccessful, principally because of the spontaneous growth of the small ammonium nitrate crystals due to their hygroscopicity.

During the experimentation no attempts have been made to check the effect of particle size distribution. MacDougall[26] also pointed out that the particle size distribution rather than the average particle size is the most important factor in determining the rate. No explanation has been advanced why the admixture of a small percentage of fine material to coarse material produces a marked lowering of the velocity of detonation.

The effect of the spacing of lengths of primacord on the stability of detonation can be seen in Table III, obtained from Tests 127, 131, and 137.

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[24] Taylor, op. cit., p. 174.

[25] Messerly, G. H., and Martin, F. J., The Detonation Velocities of Explosive Mixtures Containing Ammonium Nitrate. OSRD Report 3411. 1944. p. 2.

[26] Messerly, G. H., and Martin, F. J., The Effect of Particle Size on the Detonation Velocity of Ammonium Picrate. OSRD Report 1755. 1943. p. 1.

TABLE III

Influence of Spacing of Primacord on the Stability of Detonation. Pipe diameter 3 inches, 95/5 AN/Fuel

Primacord	Spacing	Loading Density	D Exp. high (ft./sec.)	D Exp. low	Average
400=+150=	Only 1′ used	0.801	11,850	10,350	11,042
400=+ 50=	Continuous	0.782	23,800	11,450	17,813
400=+ 50=	3′ in 21′ pipe	0.777	19,900	12,050	15,170

The most reliable result is the one using only one foot of primacord as initiator. A continuous spacing of primacord seems to give a doubtful result. The observed high detonation velocity is obviously caused by the detonation velocity of the primacord itself, which is around 20,000+ ft./sec. Judging from the ammonium nitrate particles spreading around the exploded pipe, we can say that it was an incomplete detonation. Due to the high speed of detonation of the primacord, the ammonium nitrate has no time to detonate itself completely. A 3-ft. spacing on a 21 ft. pipe still gives a doubtful result, although less than the continuous spacing.

It is possible that better theoretical results will be obtained by refining the Taylor's method. This can be done by taking not only one equilibrium (water-gas reaction) to determine the gaseous products, but three or four equilibria.

These equilibria are:

$$H_2O + CO \rightleftharpoons H_2 + CO_2$$

$$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2$$

$$\tfrac{1}{2}N_2 + 1\tfrac{1}{2}H_2 \rightleftharpoons NH_3$$

CONCLUSIONS

On Taylor's Method:

1. Maximum explosion temperature T_e and maximum detonation temperature T_d are obtained at oxygen-balanced mixture of AN/Fuel. The approximate relation between these two temperatures is

$$T_d = T_e + 1000°$$

The relation between temperature and percentage of fuel is a straight line.

2. The relation between pressure and loading density is not a straight line.

$$\frac{dP}{d\Delta} = \text{ is steeper at higher loading density.}$$

3. The value of σ in the explosion state differs considerably from that of the detonation state.

4. The increase in pressure between oxygen-positive mixtures is much higher than that of the oxygen-negative mixtures.

5. The detonation velocities increase with the loading density.

6. The D-Δ curve gives a questionable result. It is very doubtful that the detonation velocity still increases for oxygen-negative mixtures. Due to lack of experimental data, validity of the D-Δ curve for these mixtures cannot be checked.

7. The α-V curve is a function of the percentage of fuel in the mixtures and is generally lower than Cook's curve. The curve approaches Cook's curve at higher fuel percentages.

8. Taylor's method should give better results by taking NH_3 and CH_4 into consideration as gaseous products. This can be done by using more equilibria in the calculation.

On The Experimental Results:

9. The detonation velocity increases with the pipe diameter.

10. The experimental D-α curve approaches the theoretical D-α curve at high loading density.

11. Stability of detonation is limited by the critical loading density and the critical pipe diameter.

12. The strength of the initiator determines the critical loading density and the critical charge diameter.

13. Finer AN particles give higher detonation velocities and approach the theoretical results.

14. Stability of detonation is governed by the spacing of primacord.

15. The theoretical detonation velocity can only be obtained by increasing the charge diameter.

APPENDIX A

Experimental Detonation Velocities

No.	Pipe Diameter	Mixture	Filling Density	Primer	Detonation Velocity High	Detonation Velocity Low	Detonation Velocity Average	Remarks
102	3"	92.5% AN 7.5% fuel oil	0.852	60% dyn.	20800	11900	19500	Improvised Instrumentation
103	3"	92.5% AN 7.5% fuel oil	0.810	60% dyn.	—	—	—	Instrument Failure
104	3"	94% AN 5% fuel oil	0.820	60% dyn.	—	—	—	Instrument Failure
105	3"	95% AN 5% fuel oil	0.860	60% dyn.	—	—	—	Instrument Failure
106	3"	95% AN 5% fuel oil	0.898	60% dyn.	12800	11100	11925	
107	3"	96% AN 4% fuel oil	0.887	60% dyn.	11900	7580	11443	
108	3"	95% AN 5% fuel oil	0.854	60% dyn.	11900	11490	11763	

No.	Pipe Dia- meter	Mixture	Filling Density	Primer	Detonation Velocity			Remarks
					High	Low	Average	
109	3"	90% AN 10% fuel oil	0.871	60% dyn.	---	---	---	Failure
110	4"	85% AN 15% fuel oil	0.880	60% dyn.	---	---	---	Qualitative test only (failure)
111	3"	95% AN (10/12) 5% fuel oil	0.831	60% dyn.	13300	11100	11938	
112	3"	94% AN (14/16) 6% fuel oil	0.828	60% dyn.	13900	11700	12450	
113	3"	95% AN (fine size) 5% fuel oil	0.892	60% dyn.	15200	11900	13000	
114	3"	95% AN (fine size) 5% fuel oil	0.900	60% dyn.	15900	13300	13871	
115	3"	90% AN (fine size) 10% fuel oil	0.918	60% 1 dyn.	---	---	---	Instrument Failure
116	3"	85% AN (fine size) 15% fuel oil	0.973	60% dyn.	---	---	---	Failure
117	3"	95% AN 5% fuel oil	0.825	1' length 400 grain primacord + cap	11850	11110	11263	
118	3"	95% AN 5% fuel oil	0.819	1' length 300 grain primacord + cap	---	---	---	Instrument Failure

No.	Pipe Diameter	Mixture	Filling Density	Primer	Detonation Velocity			Remarks
					High	Low	Average	
119	3″	95% AN 5% fuel oil	0.830	150 grain primacord spaced cm. 3′4″ + cap	---	---	---	Failure
120	3″	95% AN 5% fuel oil	0.824	200 grain primacord, spaced 2½′on continuous strand of 50 gr. + cap	33330	18520	24090	
121	3″	95% AN 5% fuel oil	0.810	150 grain primacord, spaced 1″ on continuous string of 50 grain + cap	29880	13300	20232	
122	3″	95% AN 5% fuel oil	0.828	300 grain primacord spaced 1′ on continuous string of 50 grain + cap				Interpretation Difficulties
123	3″	97% AN 3% fuel oil	0.854	60% dyn.	10700	9770	10550	
124	3″	98% AN 2% fuel oil	0.874	60% dyn.	9760	9000	8430	
125	3″	95% AN 5% fuel oil	0.855	1′ length 400 grain primacord + cap	---	---	---	Failure

No.	Pipe Diameter	Mixture	Filling Density	Primer	Detonation Velocity High	Detonation Velocity Low	Detonation Velocity Average	Remarks
126	3"	95% AN 5% fuel oil	0.783	1′ length 400 grain primacord, + cap	---	----	---	Failure
127	3"	95% AN 5% fuel oil	0.801	1′ length 400 + 150 grain primacord + cap	11850	10350	11042	
128	3"	95% AN 5% fuel oil	0.797	1′ length 400 + a50 grain primacord + cap	---	---	---	Instrument Failure
129	3"	95% AN 5% fuel oil	0.803	400 grain spaced 3′ on continuous strand of 50 grain + cap	.	.	.	Interpretation difficulty
130	3"	95% AN 5% fuel oil	0.794	300 grain spaced 3′ on continuous strand of 50 grain + cap	---	---	---	Instrument failure
131	3" (21′ long)	95% AN 5% fuel oil	0.777	400 grain spaced 3′ on continuous strand of 50 grain + cap	19900	12050	15170	

No.	Pipe Dia- meter	Mixture	Filling Density	Primer	Detonation Velocity			Remarks
					High	Low	Average	
132	3"	95% AN 5% fuel oil	0.773	60% dyn.	---	---	---	Instrument failure
133	3"	95% AN 5% fuel oil	0.793	60% dyn.	11100	9250	10125	
134	3"	95% AN 5% fuel oil	0.821	60% dyn.	11100	10050	10768	
135	3"	95% AN 5% fuel oil	0.805	60% dyn.	---	---	---	Failure
136	3"	95% AN 5% fuel oil	0.800	60% dyn.	11100	9750	10534	
137	3"	95% AN 5% fuel oil	0.782	400 + 50 grain primacord, continuous strand	23800	11450	17813	
138	3"	94% AN 6% fuel oil	0.793	60% dyn.	---	---	---	Instrument failure
139	3"	93% AN 7% fuel oil	0.822	60% dyn.	11850	9750	10822	
140	3"	95% AN 5% fuel oil	0.780	60% dyn.	11100	9000	10725	
141	4"	95% AN 5% fuel oil	0.880	50% dyn.	12550	11950	12259	
142	5"	94% AN 6% fuel oil	0.792	60% dyn.	11100	9750	10680	

No.	Pipe Dia-meter	Mixture	Filling Density	Primer	Detonation Velocity High	Low	Average	Remarks
143	3"	92% AN 8% fuel oil	0.798	60% dyn.	11850	9750	10938	
144	3"	91% AN 9% fuel oil	0.861	60% dyn.	13850	10050	11325	
145	3"	95% AN 5% fuel oil	0.892	80% dyn.	11850	11450	11606	
148	3"	95% AN 5% fuel oil	0.831	1′ length 400 grain prima-cord + cap	20800	10350	11419	
149	3"	95% AN 5% fuel oil	0.841	1′ length 300 grain prima-cord + cap	---	---	---	Failure
150	3"	90% AN, fine size 10% fuel oil	0.878	60% dyn.	---	---	---	Failure
151	3"	92.5% AN, fine size 7.5% fuel oil	0.870	60% dyn.	13350	12050	12406	
156	3"	100%WP (10.5%)	0.839	60% dyn.	---	---	---	Failure
158	3"	100%WP (10.5%)	0.828	90% dyn.	12750	10350	11866	

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VITA

Mohammad Azhari Warga-Dalem, the son of Dr. Adnaan Warga-Dalem and and Mesayu Mazenah, was born on March 26, 1934 at Demak, Central, Java, Indonesia. He entered the 7-year European Elementary School in Padang, Central Sumatra, in 1940. After an interrupted study during the Japanese Occupation, he finished his elementary study in 1946. He entered the 3-year Junior High School in Payakumbuh, Central Sumatra, in the same year, where he graduated in 1948. A few months later the Republic of Indonesia was attacked by the invading Dutch forces, and again, he was compelled to leave his study behind. After the Round Table Conference in The Hague, Holland, at the end of 1949, he continued his study at Djakarta, the new capital of the Republic. He entered the 3 year Senior High School, where he finished in 1951.

In September 1951, he enrolled at the University of Indonesia, Faculty of Technical Sciences, in Bandung, West Java. In October, 1953 he was appointed Extraordinary Assistant for Mineralogy with teaching assignment.

He received his practical training, lasting one summer each, at the Petroleum Engineering Department of the Dutch Shell Group in Prabumulih, South Sumatra, the Banka Tin Mining Company in Tempilang, Banka, and the Umbilin Coal Mine in Sawah Lunto, Central Sumatra.

In December 1955, after passing his Kandidat Ingenieur examination, he was chosen by the Ministry of Education and the International Cooperation Administration of the United States Government to be sent to the United States, where he enrolled at the Missouri School of Mines in January 1956. He finished the requirements for the degree of Bachelor of Science in Mining Engineering in January 1957, and for the degree of Master of Science in Mining Engineering in January 1958.

Upon his arrival in his home country on January 3, 1958 he was appointed Assistant Academicus at the University of Indonesia, Faculty of Technical Sciences in Bandung. On April 1, 1958 he was appointed Assistant Lecturer.