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ALUMINIZED ORGANIC EXPLOSIVES

By
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ABSTRACT: Available detonation velocity (D) and pressure data for aluminized organic explosives have been reviewed. The observed decrease in D caused by addition of aluminum can be explained theoretically on the basis of entrainment and a small amount of compression of the Al. But the large particle size effect and the porosity effect cannot be so explained. It has been suggested that an endothermic reaction could explain the enhanced effect on D with decreased particle size of the Al. Consideration of recent studies, however, leads to the conclusion that Al is chemically inert during detonation. Hence, the particle size effect and also the porosity effect seem better explained by heat transfer to the Al.

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8 June 1972

ALUMINIZED ORGANIC EXPLOSIVES

This work was carried out under tasks MAT 03L 000/R011 01 01 FR 59 and ORDTASK 033 102 F009 06 01 which has now been terminated. It was done to provide a comparison between aluminized organic explosives and aluminized ammonium perchlorate, the subject of a special study described in a parallel report. The present results and conclusions on aluminized H.E. should be of general interest in the area of explosive effects.

ROBERT WILLIAMSON II
Captain, USN
Commander

ALBERT LIGHTBODY
By direction

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INTRODUCTION

About 13 years ago the writer reviewed the literature and available data for aluminized organic H.E. At that time the various investigators agreed on one point, namely, that aluminum lowers the detonation velocity (D) of H.E. On the question of how it caused the lowering, there was violent disagreement. It is the purpose of the present report to review more recent data and to reassess our knowledge of aluminized explosives with particular emphasis on the effect on D of adding Al to organic H.E.

A most helpful current publication[1] presents data on the effect of adding 0 to 15% by volume of 5μ Al to HMX/Viton, 85/15. The motion of the metal walls in the cylinder test was used to compute the energy release of the test explosive relative to that of HMX. The most important contribution of reference (1) to this review is that the reaction of aluminum with the detonation products did contribute to the energy release but not until 4 μsec <u>after</u> the detonation. Its maximum contribution was reached at about 13 μsec at an energy indicating complete reaction (by relative Ruby code results) of half the Al present in a one-inch dia cylinder test. This seems strong evidence that finely divided Al does not react chemically with the detonation products of organic explosives in time to affect D, i.e., in times of 0.1 μsec and less. It is not conclusive because there is the possibility of a rapid endothermic reaction. However, equilibrium computations have not, as yet, revealed such an endothermic reaction that is thermodynamically possible.

It was, and is, generally agreed that admixed aluminum in sufficiently fine form will react exothermally in time to contribute to some effects. Inasmuch as the time available for contribution in the NOL fragmentation test is about 15 μsec[2], 5μ Al should have a significant effect on the fragmenting ability of charges in that particular test configuration. For blast and underwater damage, the available time for reaction is one to two orders of magnitude greater for one-pound charges, and even larger for larger charges. It is common knowledge that even coarse Al can increase the damage in such cases.

EFFECT OF ALUMINUM ON DETONATION VELOCITY

On the evidence given above, it seems likely that the Al in an organic H.E. is an inert diluent as far as its effect on D is concerned. Since it does lower D, it must do so by decreasing the energy available for propagating the front by one or more of the following mechanisms:

a. entrainment in the gas products,

b. absorption of heat,

c. compression.

In an earlier study of solid diluents in H.E.[3], we found that air (or voids) was the most efficient diluent available for lowering D. To take care of this very large effect in porous charges, valid comparison of solid diluents must be made at equal volume fractions of air (y_a). Comparisons at the same absolute density, although still popular, are invalid.

Thus, examination of NOL data for aluminized TNT, RDX, and TNETB[4] revealed that the void content of the charge was of comparable importance with the Al content in determining the extent to which D is lowered. Hence, all curves here are given in the form

$$D(\Delta,u) = a(u) + b(u)\Delta \qquad (1)$$

where Δ is the ratio ρ_o/ρ_v (actual density to voidless density) and $u = d^{-1}$ is the reciprocal diameter. Comparisons are then carried out at the same Δ value.

The best measure of the effect of Al on D would be given by the infinite diameter results:

$$D_i(\Delta) = a_o + b_o\Delta \qquad (2)$$

where a_o and b_o are constants and specific to the chemistry of the explosive tested. Unfortunately, the few diameter studies* available produce data far too sparse to measure the effect of Al. Consequently we have used the NOL data[4], obtained at a constant dia of 50.8 mm, and have rejected all data for solid diluent contents above about 32 weight %. There are two reasons for this. First, any diameter effect on the measured rate would be expected to increase with increasing amounts of an inert diluent. Second, several of the curves, b(u) vs % Al, show a sharp change of slope at this point.[4] It is hoped that the trends obtained at d = 50.8 mm will not be too distorted by the diameter effect and hence will not differ greatly from those that would be obtained at u = 0, provided % diluent ≤ 32%.

TNT Mixtures

Figure 1a shows the effect of Al on lowering the detonation velocity of TNT as D vs Δ curves for 0 to 32% Al. In this case, all charges had a diameter of 50.8 mm and the Al was Navy Spec. atomized material which passed through a No. 100 sieve (149μ opening).[4] Figure 1b shows analogous curves for the effect of NaCl as a diluent.

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*One on HBX-1 and one on a tritonal.[4]

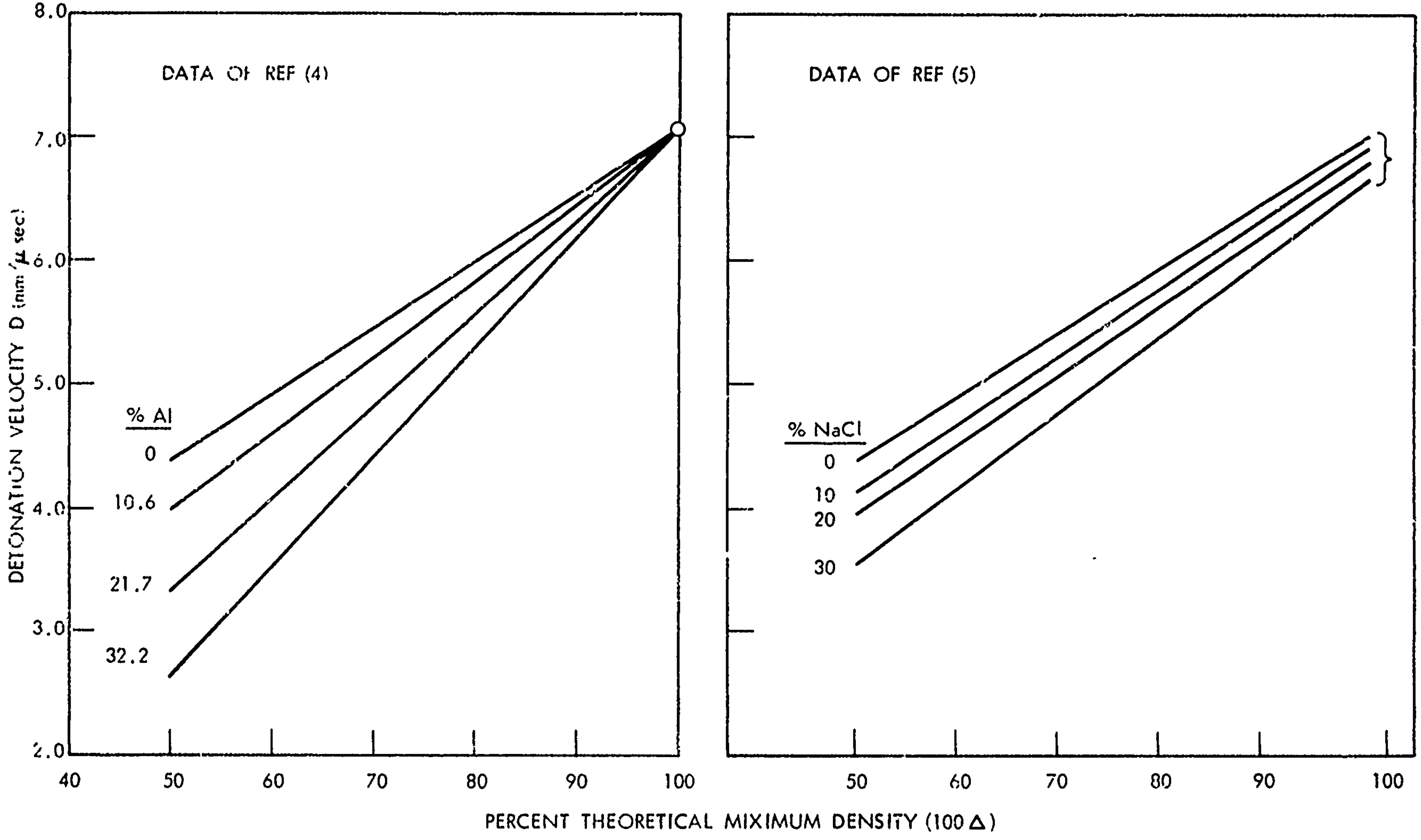

FIG. 1 EFFECT OF DILUENTS ON DETONATION VELOCITY OF TNT

In these charges, the NaCl was -20 + 28 mesh (840 - 590μ) and the charge diameter was unspecified although it was intended to be large enough to produce infinite diameter D values.[5] Figure 1 compares the effect of the two diluents at the same Δ and at various weight fractions of the diluent. A somewhat better comparison is on an equal volume basis; this assures that diluents will be compared at the same y_e (volume fraction) of the energy producing organic explosive. The diluent effect on D can be expressed by the ratio D/D_α where D_α is the velocity of the undiluted TNT at the same Δ value. Figure 2 shows curves of D/D_α vs y_d (volume fraction of diluent) at Δ values of 0.95 and 0.80. It is quite evident that at equal volume fractions, salt lowers the rate more than Al if the charge is near voidless density, whereas the roles of the diluents are reversed for more porous charges. Neglect of this large porosity effect accounts for much of the confusion in the older literature on the extent to which addition of Al affects D. Both Figures 1 and 2 show that the diluent effect, (the lowering of D) increases as the porosity increases; it is, therefore, easier to measure at low Δ.

In addition to the compaction and the diameter effect, one other factor that should be controlled for valid results is the particle size and shape. The effect of this last factor was not studied in the initial NOL work. Its importance is demonstrated, however, in data published by Dremin et al.[6] These workers were well aware of the importance of porosity, and made their measurements at 85.0 and 96.5% TMD. The D vs Δ lines, each constructed from the reported pairs of experimental points, are shown in Figure 3 in which the TNT/Al, 85/15, curves are very similar to those of Figure 1a. But Figure 3 supplies the additional information that 270μ Al has little or no effect on D whereas 0.2μ Al has a very large effect. (There was also one measurement made with 80μ Al at 85% TMD; that showed an intermediate effect.)

If the NOL data of Figure 1a are interpolated to TNT/Al, 85/15, they give a value of 6.10 mm/μsec at Δ = 0.85. Moreover, the data of reference (6), when plotted D vs δ(average particle size) or, better, D vs log δ, as in Figure 4, give reasonably smooth curves. Entering them at the NOL value of D for this composition (crosses on Figure 4) shows corresponding δ values of 22 and 18μ respectively. On this basis, the Al used in the NOL work appears to have had an effective diameter of about 20μ on the scale of reference (6). In this case, the charge diameter is not given; hence, the particle size scale may be influenced by a charge diameter effect.

To return to Figure 3, the curve for 85/15, TNT/fine W, is also shown from the reference (6) data. In this case, extrapolation to Δ = 1 does not give the 100/0 value of D, as seems to be the case for TNT/Al, but falls somewhat below it (by less than 3%). It is similar to results of the same extrapolation for NaCl; in Figure 1b the curve for TNT/NaCl, 70/30, extrapolates to about 6% below the TNT value at Δ = 1.

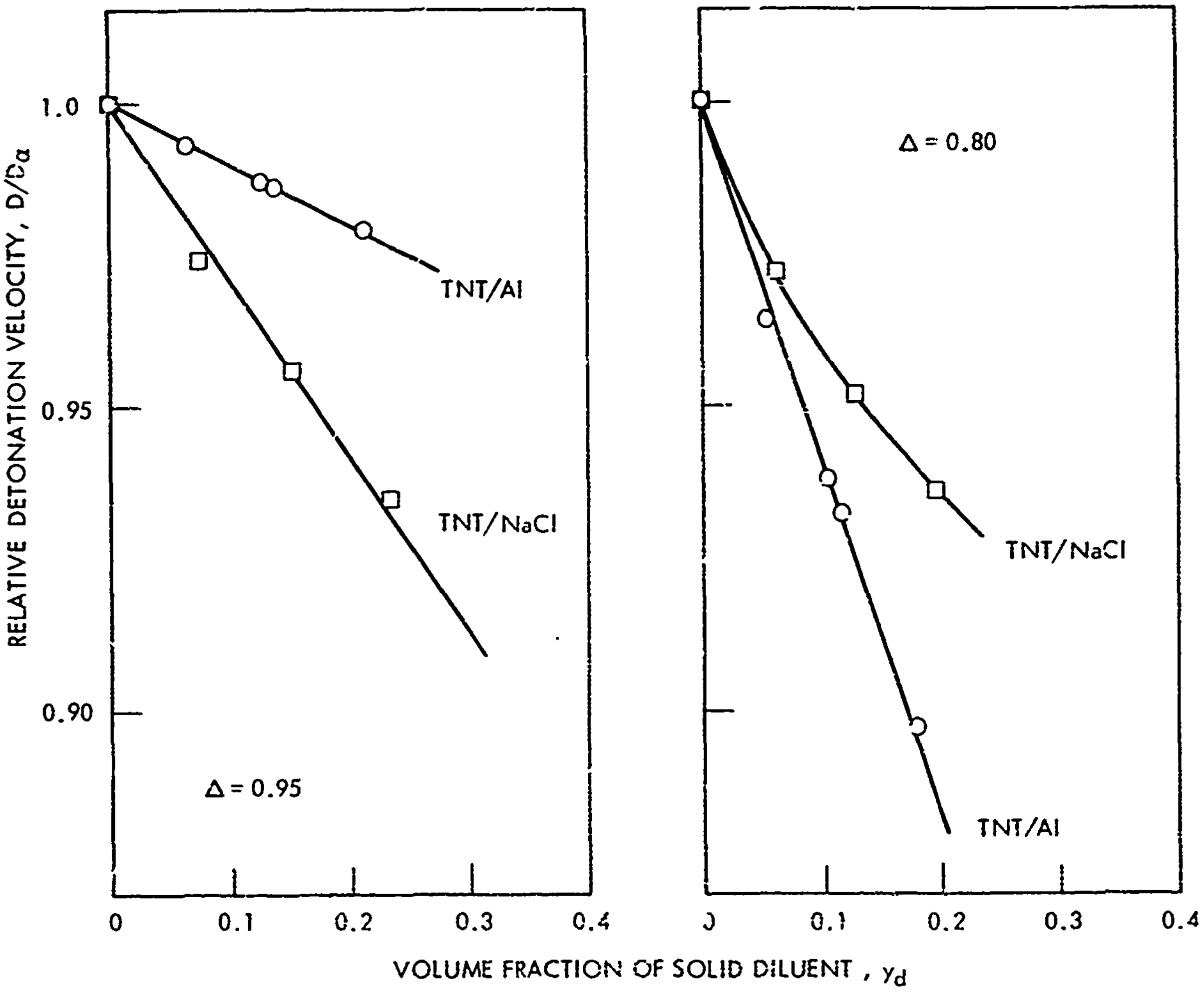

FIG. 2 COMPARISON OF DILUENT EFFECT OF Al AND Na Cl IN TNT CHARGES OF TWO COMPACTIONS.

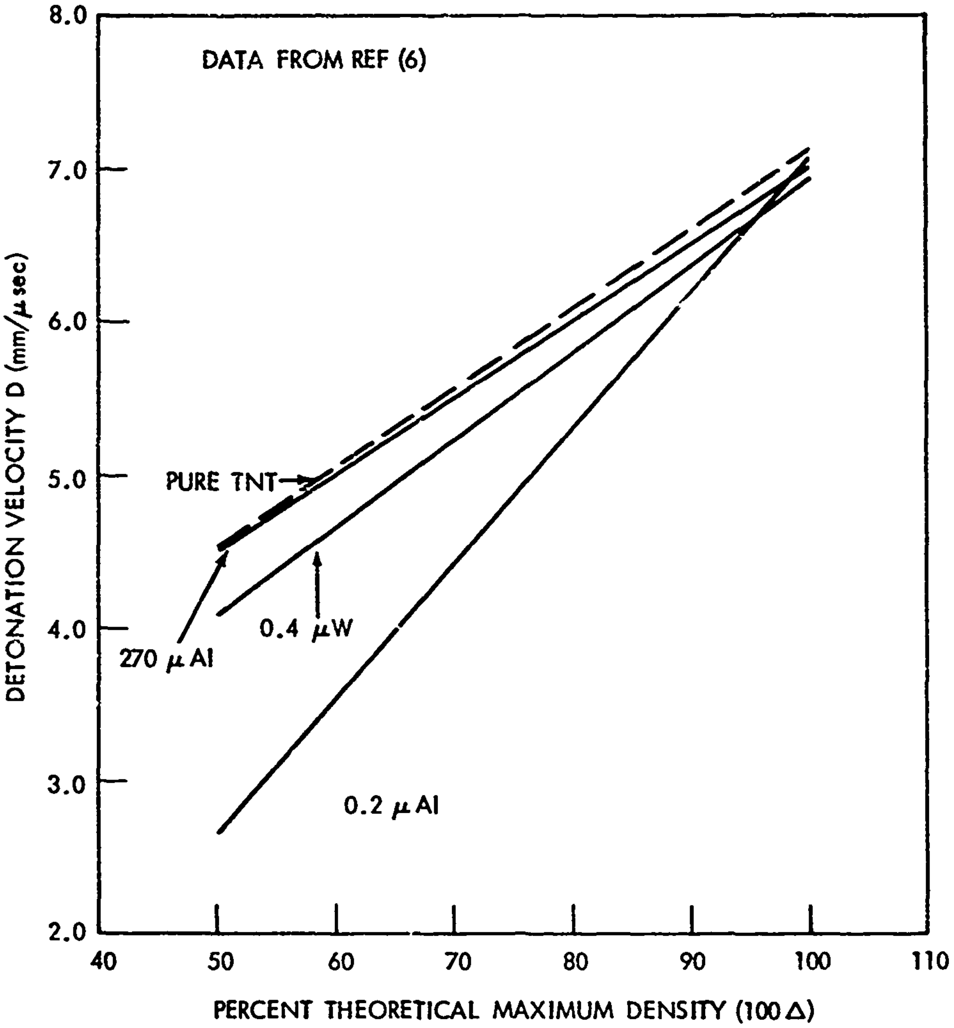

FIG. 3 EFFECT OF 15% DILUENT ON DETONATION VELOCITY OF TNT

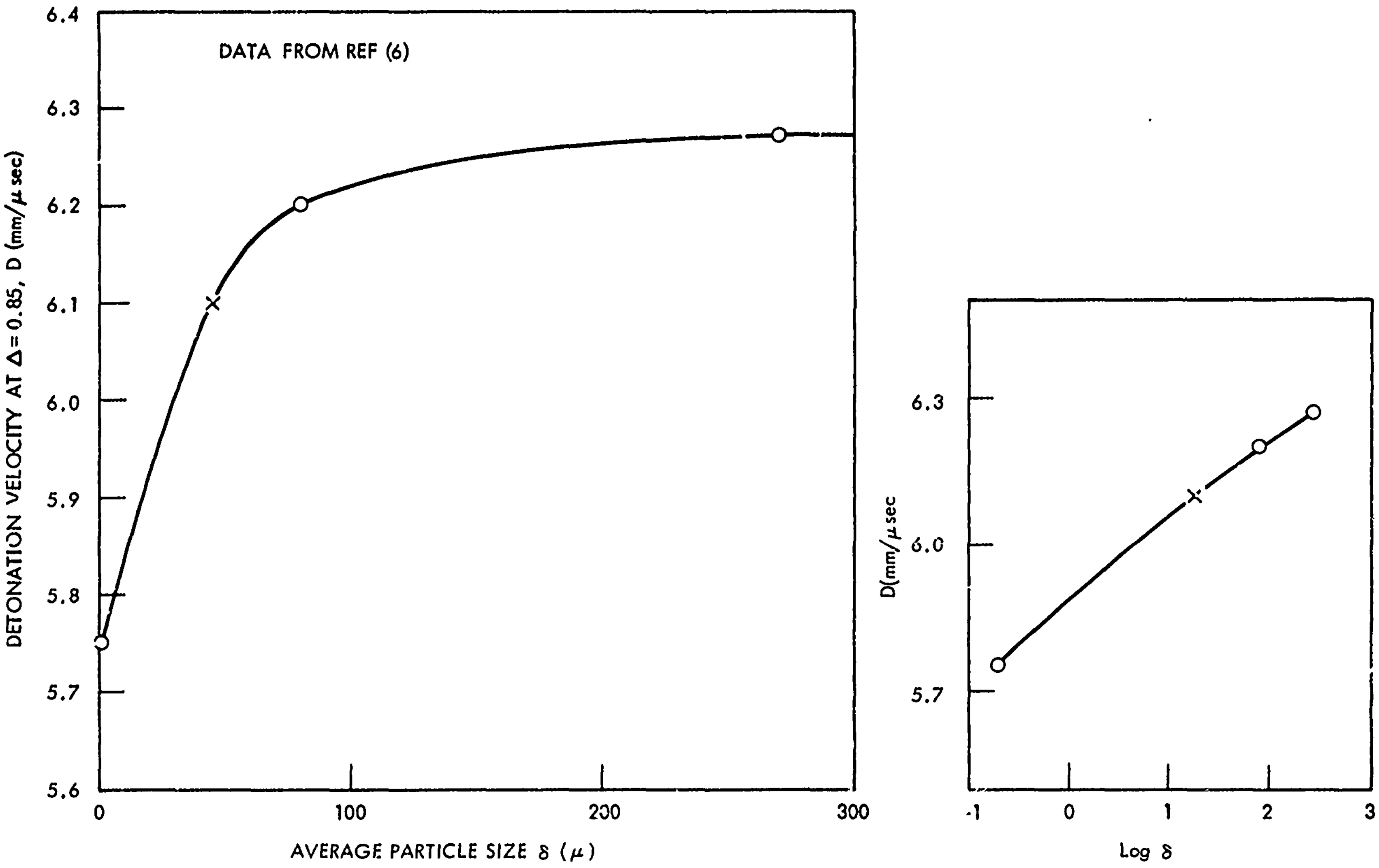

FIG. 4 VARIATION OF DETONATION VELOCITY OF TNT/Al, 85/15, WITH PARTICLE SIZE OF ALUMINUM (Δ = 0.85)

Dremin et al. also reported results from charges containing 15% of fine and of coarse SiO_2. At 85% TMD, these lie above the TNT/0.2μ Al curve; at 96.5% TMD, below it. The sharp change in the effect of this diluent was attributed to a phase change in the SiO_2.* Hence, this component is not comparable to the others (Al, W, NaCl) which show no such anomalous effect. Certainly the data cannot be used to construct a D-Δ curve if the diluent is in different phases at the two Δ values. Consequently, no curve for TNT/SiO_2, 85/15, is given in Figure 4.

Reference (3) reviewed the attempts to predict D of organic explosives to which inert solid diluents had been added. None of the models was completely successful and only one (that considering heat transfer) incorporated the effect of particle size. The work did, however, give guidance in the dependence of D/D_α on volume fraction of the diluent (y_d), density of diluent (ρ_d) and compressibility of diluent (α). Patterson[7] assumed the diluent chemically inert but entrained in the detonation reaction products. He then derived the relation

$$D/D_\alpha = \sqrt{\rho_e / y_e \rho_v} \tag{3}$$

where y_e is the volume fraction of the explosive, ρ_e the density of the explosive (1.654g/cc for TNT) and ρ_v the density of the voidless mixture, H.E./diluent. On the other hand, Copp & Ubbelohde[8] assumed that the inert diluent is not entrained but is heated both by compression and heat conduction from the hot detonation products. They felt that their experimental data (D measured on heavily cased charges of TNT mixtures including TNT/Al) were satisfactorily reproduced by their computations based on these assumptions. To compute D, they used Marshall's equation

$$D(\text{mm}/\mu\text{sec}) = 0.430\sqrt{nT} + 3.5(\rho_o - 1) \tag{4}$$

where n is the number of moles of gas produced per gram of explosive, ρ_o is the loading density, and T is the effective detonation temperature. Obviously a good many other assumptions had to be made to compute T; the final results gave the right order of magnitude for the diluent compressibilities, but sometimes inverted the rating between two materials.

The writer found that Equation (3) held fairly well for metals and simple inorganic compounds as diluents of TNT, but was quite inadequate for dilution with air or a plastic.[3] The available data on diluents were insufficient to test the Copp & Ubbelohde treatment. Instead, an expression for the effect of entrainment was derived. This was:

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*Occurrence of a phase change in SiO_2 in this pressure range has been verified. See, e.g., footnote aa of Table 1.

$$\begin{aligned} D/D_\alpha &\cong (1 + 0.5\, y_d)(1 - 0.5\beta\, y_d) \\ &\cong 1 + 0.5\, y_d\, (1 - \beta),\ y_d \text{ small} \end{aligned} \tag{5}$$

where $\beta = (\rho_d - \rho_e)/\rho_e$. Equation (5) is an approximate form of Equation (3) showing the dependence on y_d. When this equation was modified to include heating the diluent by compression, it became

$$D/D_\alpha \cong 1 + y_d(0.5 - 0.5\beta - a\alpha),\ y_d \text{ small} \tag{6}$$

where the diluent compressibility $\alpha = 1 - \rho_d/\rho_d'$, $a = \rho_j/(\rho_j - \rho_e)$*, ρ_d' is the density of the shocked diluent and ρ_j is the C-J density of the pure explosive. The approximate linearity of D/D_α with y_d for small y_d was substantiated with a number of solid diluents.[3] Figure 2 demonstrates it for Al and NaCl.

By Equation (6), the older data[3] indicate a compressibility of 12% for NaCl; the data of Figure 2 (for NaCl coarser than 500μ), 16%. Interestingly enough, Copp & Ubbelohde found 13 to 15% for NaCl of an average particle size of about 42μ. When so many variables are involved, the value indicated for α does not seem a very sensitive test of the initial assumptions.

With the same procedure at Δ = 0.95, the NOL data (Figure 1a) indicate α(20μ Al) = 0.073 whereas from Figure 3 data, α(0.2μ Al) = 0.154. In other words, α(Al) appears sensitive to a particle size effect whereas α(NaCl) does not.** The simplest explanation is that NaCl acts to lower D chiefly by its compressibility and, because of its poor thermal conductivity, is not much affected by particle size; whereas metals, which are good thermal conductors, can absorb heat from the hot detonation product gases. For this mechanism the total amount of metal surface exposed to the gases and hence the particle size would have a large effect. Thus for Al and other metals Equation (6), which omits the heat absorption mechanism, is probably incomplete and certainly inadequate.

If α is estimated from data of Figure 2b(Δ = 0.80 instead of 0.95) and Equation (6), the value found for Al is nearly triple that calculated for the less porous charge; the computed α value for NaCl, however, changes only about 10% with the same change in porosity. This again suggests the need to supplement Equation (6) with some consideration of heat absorption by the diluent. Such an effect will be small at any porosity for nonconductors such as NaCl; it evidently increases with porosity for metals, as is reasonable in view of the increasing accessibility of surfaces for thermal transfer and the increase in detonation reaction time, i.e., increased exposure time of diluent.

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*Derived for Δ = 1, a = k + 1 where k is the adiabatic exponent for the explosive at its crystal density. The value of a used for TNT in reference (3) was 4.32. The value used here is 3.85 in agreement with recent Ruby code results for TNT.

**See also reference (8).

In summary, TNT/Al, like the TNT/inert mixtures of reference (3), shows a linear variation of D/D_α with y_d, the volume fraction of the diluent. There is evidence from both particle size and porosity effects that Equation (6) is adequate only when the diluent is in a coarse form, e.g., average particle size greater than 250µ, or is a thermal insulator or both. Otherwise, it requires a modification to account for heat transfer to the diluent particles; this transfer is particularly important for metals (good heat conductors).

Equation (6) serves to emphasize the necessity of making comparisons at equal volume instead of at equal weight fraction of the diluents. It also shows how two diluents of the same density (same β value) can have different effects on D by virtue of different compressibilities. The present discussion has also pointed out the possibility of different thermal properties effecting different amounts of lowering of the detonation velocity.

Table 1 shows what are considered the important properties of the diluent in determining its effect on D. It includes the diluents Al, NaCl, W, and SiO_2. As would be expected, the thermal conductivity of the metals is two orders of magnitude greater than that of the non-metals. Al is a better conductor than W when both are solids; with liquid Al (m.p. 660°C), the relationship is reversed. It takes very nearly the same amount of heat to raise equal volumes of solid Al and W to the same temperature, and that amount is about 30% greater than the thermal energy required to heat the same volume of NaCl or SiO_2 to the same temperature. The major difference in energy absorbed in the short (detonation reaction) times will therefore be determined by the rate at which heat can flow in, i.e., by the thermal conductivity of the material. Thus, the effect of equal volumes of Al and W at (nearly) the same particle size distribution* should be about the same as compared to the very different effects of diluents such as NaCl and SiO_2.

No attempt will be made here to develop a model accounting for the effects on D of diluent density, compressibility, thermal diffusivity, and charge porosity. Rather, I will present a method of treating the relatively few data available so that some conclusions can be drawn about the effect of different diluents.

To compute the extent of the lowering of D from the data measured over a range in Δ, Equations (1) or (2) might be used to give

$$D/D_\alpha = \frac{a + b\Delta}{a_e + b_e\Delta} \qquad (7)$$

Where the subscript e designates the explosive matrix of the diluted mixture. However, the form of Equation (7) is a bit awkward; it is more convenient to use the form

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*These two conditions cannot be exactly satisfied simultaneously unless the diluents have equal densities. This restriction will be considered later.

Table 1

PROPERTIES OF SOME OF DILUENTS FOR TNT

Diluent	Voidless Density ρ_v, g/cc	β	Shock Compressibility[a] 100-kbar	200-kbar	Thermal Conductivity[b] at 100°C, watts/cm°K	Specific Heat s[c] 300°K, cal/g deg	Volume basis $\rho_v s$ cal/cc deg
Aluminum	2.70	0.635	0.095	0.156	2.30	0.216	0.583
NaCl	2.165	0.312	0.211	0.300	5.4×10^{-2}	0.208	0.451
W	19.1[d]	10.6	0.030	0.056	1.60	0.032	0.610
SiO_2	2.66	0.612	0.123	(0.151)[aa]	1.6×10^{-2}	0.178	0.473

[a] $(V_o - V)/V = 1 - \rho_d/\rho_d' = \alpha$. From compilation by F. Birch in Handbook of Physical Constants, Geological Society of America Memoir 97 (1966).

[aa] This value is at 144 kbar where first break, indicating a phase change, occurs in P-V curve.

[b] American Institute of Physics Handbock (Second Edition) McGraw-Hill.

[c] K. K. Kelley, Bur. Mines Bulletin 584 (1960).

[d] Value from reference (6) used.

$$D = A\Delta^n \quad (8)$$

so that

$$D/D_\alpha = \bar{A}\Delta^{\Delta n} \quad (9)$$

where $\bar{A} = A/A_e \approx 1$ and $\Delta n = (n - n_e)$. Since A is the value of D at $\Delta = 1$, the approximation $\bar{A} \approx 1$ is best for TNT/Al mixtures and poorest for TNT/NaCl, 70/30, (See Figures 1 and 3). Thus, Δn is a single dominant index of the effect of the diluent at all Δ.

Figure 5 shows that Equation (8) fits the NOL D-Δ data for 0 to 32% Al to well within experimental error in D. In this work, the parameters A and n were evaluated for a range of ρ_o = 1 to 2 g/cc. Both Equation (1) and Equation (8) are valid only when restricted to a specific range in Δ. The range chosen for evaluation of the parameters is not necessarily the optimum; hence the equations obtained are not necessarily the best fits. Nevertheless, they serve the purpose of the illustration quite adequately.

Table 2 contains the parameters of Equations (1) and (8) for the various diluents. In Figure 6, the diluent effect on D is approximated by Δn as a function of y_d^*, the diluent volume fraction at voidless density. W with its high density of 19 g/cc has a very small volume fraction at 15% by weight. The NOL data for TNT/20μ Al are bracketed by reference (6) data for 0.2μ and 270μ Al. The NaCl data (reference (5)) show, despite the scatter of the data, the small effect of that diluent. The similarity of metal diluents is indicated by the fact that a reasonable extrapolation of the TNT/0.4μ W will pass very near the single point for TNT/0.2μ Al. This possibility can be explored further by computing comparable values of D/D_α.

Although Δn may be considered the dominant parameter, Equation (9) which includes $\bar{A}$, must be used to compute D/D_α if inversions in ratings such as that of Figure 2 are to be found. Table 3 compares the computed results with the ratio values of the experimental results at the higher porosity where the change in D is larger. It can be seen that for Δ = 0.78 - 0.85, the computed values agree with the experimental to better than 2%. (This is just a test of the adequacy of the parameters A, n of Table 2 in reproducing the experimental data from which they were derived.) The D/D_α values show that on an equal weight basis and at Δ = 0.815 ± 0.035, Al decreases D more than does W. However, if we make a reasonable interpolation for 0.2μ Al, as shown by the dashed curve of Figure 6, on an equal volume basis at Δ = 0.85, W decreases D more than does Al. To be sure, the difference is not of significant size, but the calculated D/D_α values tend to be too low for Al and too high for W. So the difference is probably real and small.

On an equal weight basis, with particle sizes of 0.2 and 0.4μ, respectively, for Al and W, the number of Al particles is 56.6 times the number of W particles and the total surface of Al is 14.1 times

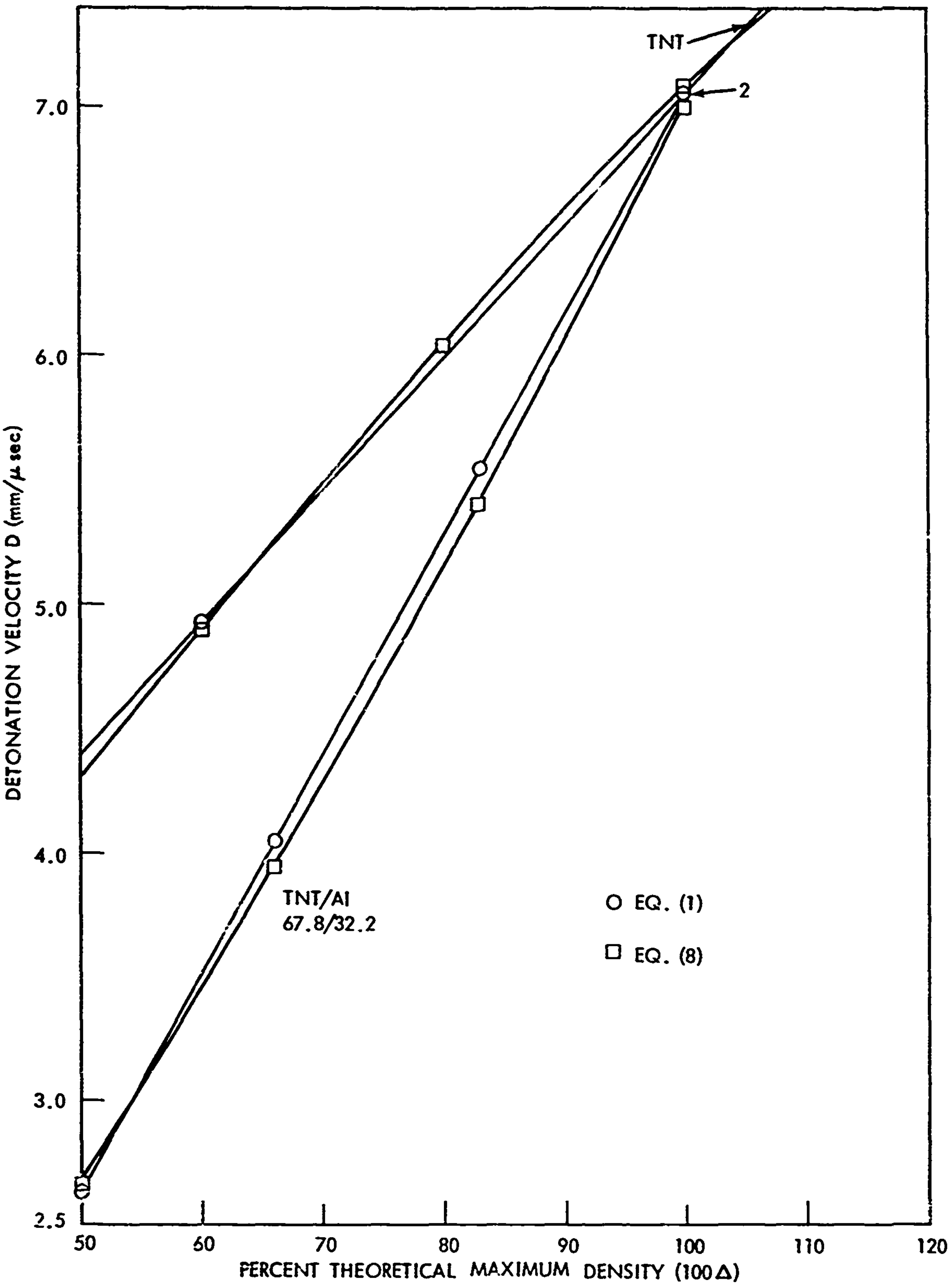

FIG. 5 EQUIVALENT ANALYTICAL EXPRESSIONS FOR DETONATION VELOCITY OF MIXTURES OF TNT AND TNT/Al

Table 2

SUMMARY DATA FOR BINARY MIXES WITH TNT

	Diluent Fractions				Equation (1)		Equation (8)		Diluent Effect	
Diluent	Weight x_d	Volume y_d^*	Al/O	Voidless Density ρ_v(g/cc)	a mm/μsec	b	A mm/μsec	n	$\overline{A}$	Δn
				Data from reference (4)						
None	0	0	0	1.65	1.73*	5.321*	7.10	0.722	1	0
Al (20μ)	0.106	0.0675	0.170	1.72	0.94	6.106	7.08	0.840	0.997	0.118
Al (20μ)	0.217	0.145	0.398	1.80	-0.35	7.398	7.03	1.064	0.990	0.342
Al (20μ)	0.322	0.225	0.680	1.89	-1.78	8.826	7.00	1.39	0.986	0.668
				Data from reference (6)						
None	0	0	0	1.65	1.94	5.186	7.19	0.694	1	0
0.2μ Al	0.15	0.0974	0.247	1.752	-1.77	8.85	6.98	1.345	0.971	0.651
270μ Al	0.15	0.0974	0.247	1.752	2.02	4.99	7.07	0.665	0.983	~0
0.4μ W	0.15	0.015	-	1.912	1.25	5.68	6.95	0.769	0.967	0.075
				Data from reference (5)						
None	0	0	0	1.65	1.73	5.33	7.13	0.724	1	0
NaCl	0.10	0.0781	-	1.691	1.27	5.69	7.01	0.786	0.983	0.062
NaCl	0.20	0.160	-	1.733	1.06	5.79	6.89	0.815	0.966	0.091
NaCl -20 +28 mesh	0.30	0.246	-	1.777	0.38	6.32	6.70	0.928	0.940	0.204

$y_d^* = x_d \rho_v / \rho_d$ = volume fraction of diluent in mixture at voidless density. At any given Δ, $y_d = \Delta y_d^*$.

*This is D-Δ equation used at time TNT/Al series were shot; the coefficients differ from extrapolated values of reference (4).

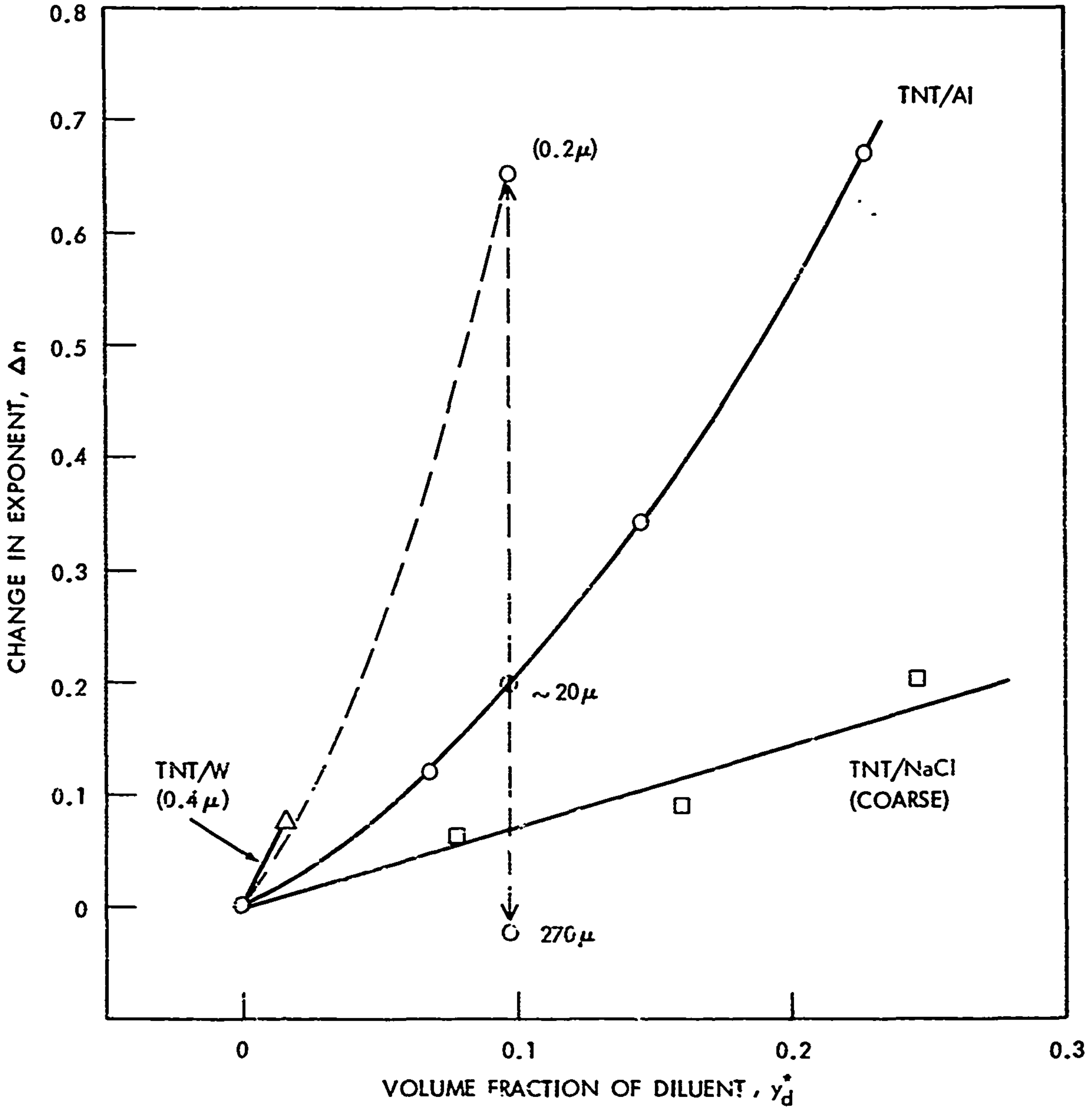

FIG. 6 CHANGE IN EXPONENT Δn EFFECTED BY VARIOUS TNT DILUENTS

Table 3

DATA FOR TNT/DILUENT FROM REFERENCE (6)

			Equal weight basis, $x_d=0.15$				Equal Volume basis, at $\Delta=0.85$	
	measured D mm/μsec		Exp. D/D_α		Calc. D/D_α from Equation (9)		D/D_α from Equation (9)	
Diluent	$\Delta=0.85$	$\Delta=0.779$	$\Delta=0.85$	$\Delta=0.779$	$\Delta=0.85$	$\Delta=0.779$	$y_d^*=0.097$	$y_d^*=0.015$
0.2μ Al	5.75		0.890		0.874		0.890	0.962
0.4μ W		5.68		0.948		0.949		0.955
Silica Powder*	5.98		0.942		-	-	0.942	
None	6.35**	5.98**	1.0	1.0	1.0	1.0		
270μ Al	6.27		0.986					
270μ SiO_2	6.27		0.986					
Coarse NaCl***					0.961		0.969	0.997

*Fine powder which appeared to be size of 0.2μ Al.

**Values from D-Δ curves.

***From interpolation A in Table 2 and Δn in Figure 6.

that of the W. In contrast, on an equal volume basis (say $y_d^* = 0.015$ and $x_{Al} = 0.0243$, $x_W = 0.15$), the number of Al particles is only 9.2 times the number of W and the surface area of Al only 2.3 times that of W. Insofar as heat absorption is important, there is good reason for 0.2μ Al to lower D more than 0.4μ W on an equal weight basis.

If the comparison could be made at equal y_d^* and equal particle size, the number of Al particles and total Al surface would still be 1.15 times the corresponding W values. This is because the ratio of the number of particles and of the surface area of two diluents varies inversely as the ratio of the voidless densities of the two mixtures. (For $y_d^* = 0.015$ that ratio for W and Al in TNT is 1.912/1.657 = 1.15.) Hence, only when the diluents have equal density is it possible to have equal y_d^* and an equal number of equal diameter particles at the same time.

Reference (6) did report on silica as a diluent and listed its density as 2.70 g/cc, in other words, equal that of Al. The authors then concluded that Al must react endothermally at $\Delta = 0.85$ because it lowered D more than did the inert SiO_2. On the other hand, they considered W inert because of its high m.p. (3370°C) and with that I agree. As was remarked above, Dremin et al. were aware of the necessity for comparisons at equal Δ, but they seemed unaware of the necessity for comparisons at equal volume of diluent. On this basis, Al seems no more effective in lowering D than the inert W when they are in comparable physical forms. Moreover, the lesser effect of the non-metals can be explained on the basis of their low thermal conductivity. Comparison of the results on an equal Δ, equal y_d, and comparable δ basis substantiates the conclusion of reference (1) that Al does not react in time to contribute to the detonation front of aluminized organic explosives.

Aluminized RDX and TNETB

The binary TNT mixtures were discussed at some length in the preceeding section because some systematic data were available for different diluents. This is not the case for other organic H.E. NOL data for the RDX/Al and for the TNETB/Al series[4] can be treated as were those for the TNT/Al series. The Al used was atomized, met Navy specifications and had been sieved through a No. 40 (420μ) screen. As for TNT, the velocities were measured at a constant charge diameter of 5.08 cm. Both aluminized series showed D-Δ patterns comparable to those of TNT/Al Figure 1a, i.e., increasing Al decreases D and increases the slope b. The D-Δ curves fan out from Δ ~ 1.0; hence the greater the porosity, the larger the decrease in D caused by a given amount of Al. Because of its small size, the decrease is therefore hard to measure near voidless density.

The data for these two series show more scatter than those for TNT/Al, but again D/D_α seems a linear function of y_d (at low contents of Al) and relative effects can be reversed at different porosities, as shown in Figure 2. At 5% porosity ($\Delta = 0.95$), a given volume of

Al decreases D(TNETB) more than D(RDX) whereas at 20% porosity the reverse is true.

Table 4 contains the parameters of Equations (1) and (8) for the RDX and TNETB series, and Figure 7 shows the plot of Δn vs y_d* for all three series. Two points from reference (6) have been included to show that the effect of Al particle size is much larger than any difference introduced by varying the matrix H.E. Therefore, we cannot tell how much the location of the curve is caused by particle size effect and how much should be attributed to the organic H.E. It is interesting, however, that a plot of Δn vs the ratio Al/O, shown in Figure 8, avoids any intersection of the curves. In Table 5, the approximate lowering of the detonation velocity $[D/D_\alpha \simeq \Delta^{\Delta n}]$ is shown at two porosities for each of the three aluminized explosives at the same values of Al/O. At these two porosities (10 and 50%), the amount of the lowering increases in the order: TNT, TNETB, and RDX series.

<u>Effect of Aluminum on Detonation Pressure</u>

Because addition of Al lowers the detonation velocity, it must also lower the detonation pressure (P). From the usual hydrodynamic relations,

$$P = \rho_o D^2/(k+1) = \Delta\rho_v D^2/(k+1) \qquad (10)$$

and also

$$P = \rho_o Du = \Delta\rho_v Du \qquad (11)$$

where ρ_o is charge density, k is the adiabatic exponent, and u is particle velocity. If we again let subscript α indicate the pure explosive at the same Δ as the diluted, then from Equation (10)

$$\frac{P}{P_\alpha} = \frac{\rho_v}{\rho_e}\,\frac{k_e+1}{k+1}\left(\frac{D}{D_\alpha}\right)^2 \qquad (12)$$

and from Equation (11)

$$\frac{P}{P_\alpha} = \frac{\rho_v uD}{\rho_e u_e D_\alpha} \qquad (13)$$

If the effect of the diluent is only a reduction of kinetic energy by entrainment, equation (3) can be used with Equations (12) and (13) to give

$$(P/P_\alpha)_{en} = y_e^{-1}(k_e+1)/(k+1) \qquad (14)$$

and

$$(P/P_\alpha)_{en} = \frac{u}{u_e}\left[\frac{\rho_v}{y_e\rho_e}\right]^{-\frac{1}{2}} = \frac{u}{u_e}\left[\Delta x_e\right]^{-\frac{1}{2}} \qquad (15)$$

Table 4

SUMMARY DATA FOR ALUMINIZED RDX AND TNETB

		Diluent Fractions		Equation (1)		Equation (8)		Diluent Effect	
Al/O	Voidless Density ρ_v, g/cc	x_d	y_d*	a mm/μsec	b mm/μsec	A mm/μsec	n	$\overline{A}$	Δn
				RDX[4]					
0	1.802	0	0	2.515	6.246	8.86	0.659	1.0	0
0.153	1.86	0.10	0.0689	0.100	8.742	8.65	0.985	0.976	0.326
0.343	1.93	0.20	0.143	-1.600	10.422	8.79	1.275	0.992	0.616
0.588	2.00	0.30	0.222	-3.100	12.000	8.90	1.618	1.004	0.959
0.915	2.08	0.40	0.308	-4.592	13.312	7.59	1.993	[0.857]	1.334
1.371	2.16	0.50	0.400	-6.078	14.688	9.75	3.384	[1.100]	2.725
				TNETB[4]					
0	1.78	0	0	1.947	6.515	8.52	0.726	1.0	0
0.114	1.84	0.10	0.0682	0.820	7.691	8.34	0.877	0.979	0.153
0.256	1.91	0.20	0.1414	-0.200	8.404	8.20	1.034	0.962	0.310
0.438	1.98	0.30	0.220	-1.200	9.504	8.49	1.222	0.996	0.498
1.022	2.15	0.50	0.398	-4.038	12.148	8.46	2.173	0.993	1.449

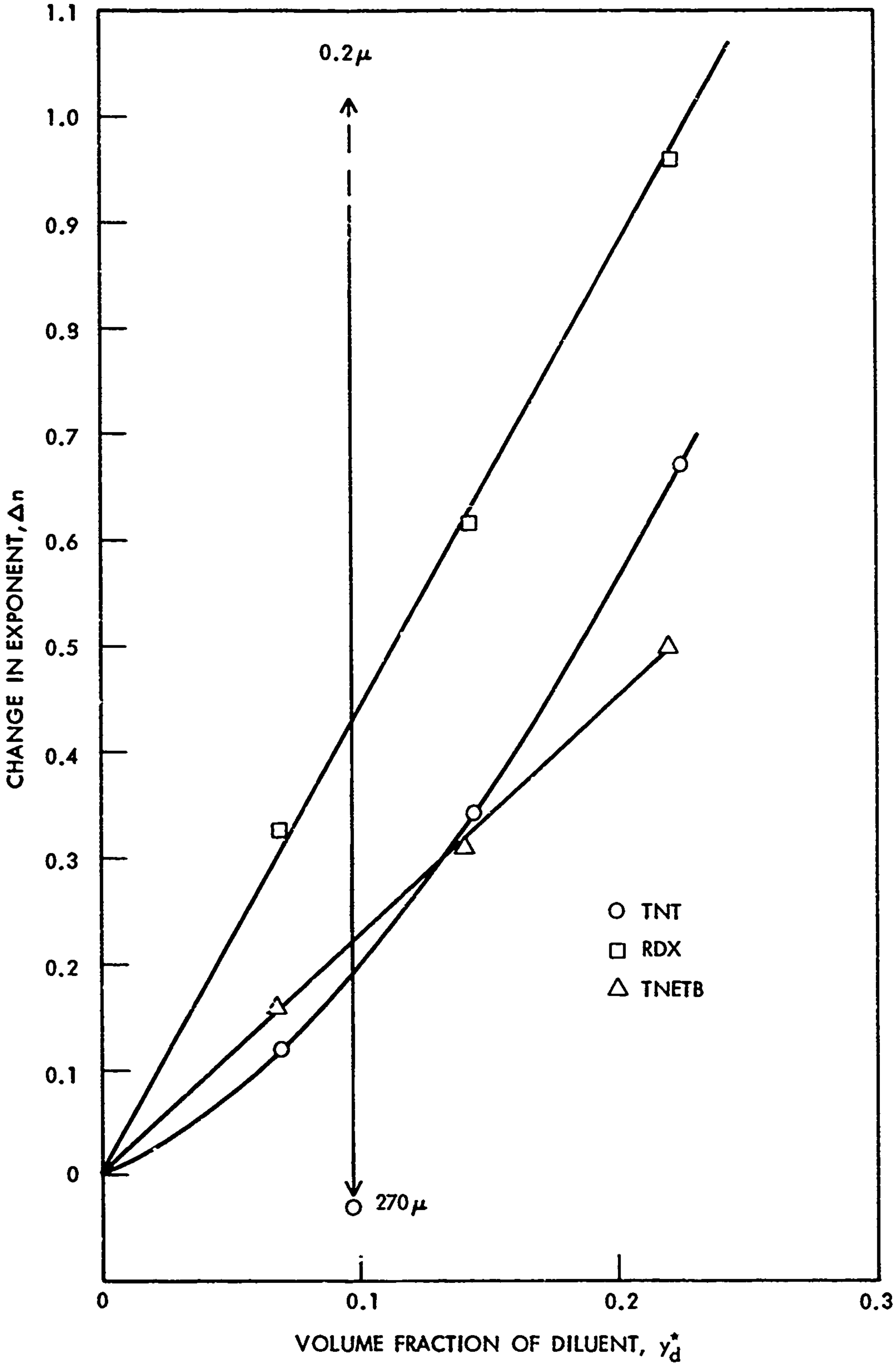

FIG. 7 CHANGE IN EXPONENT Δn EFFECTED BY DIFFERENT MATRICES IN HE/Al MIXTURES

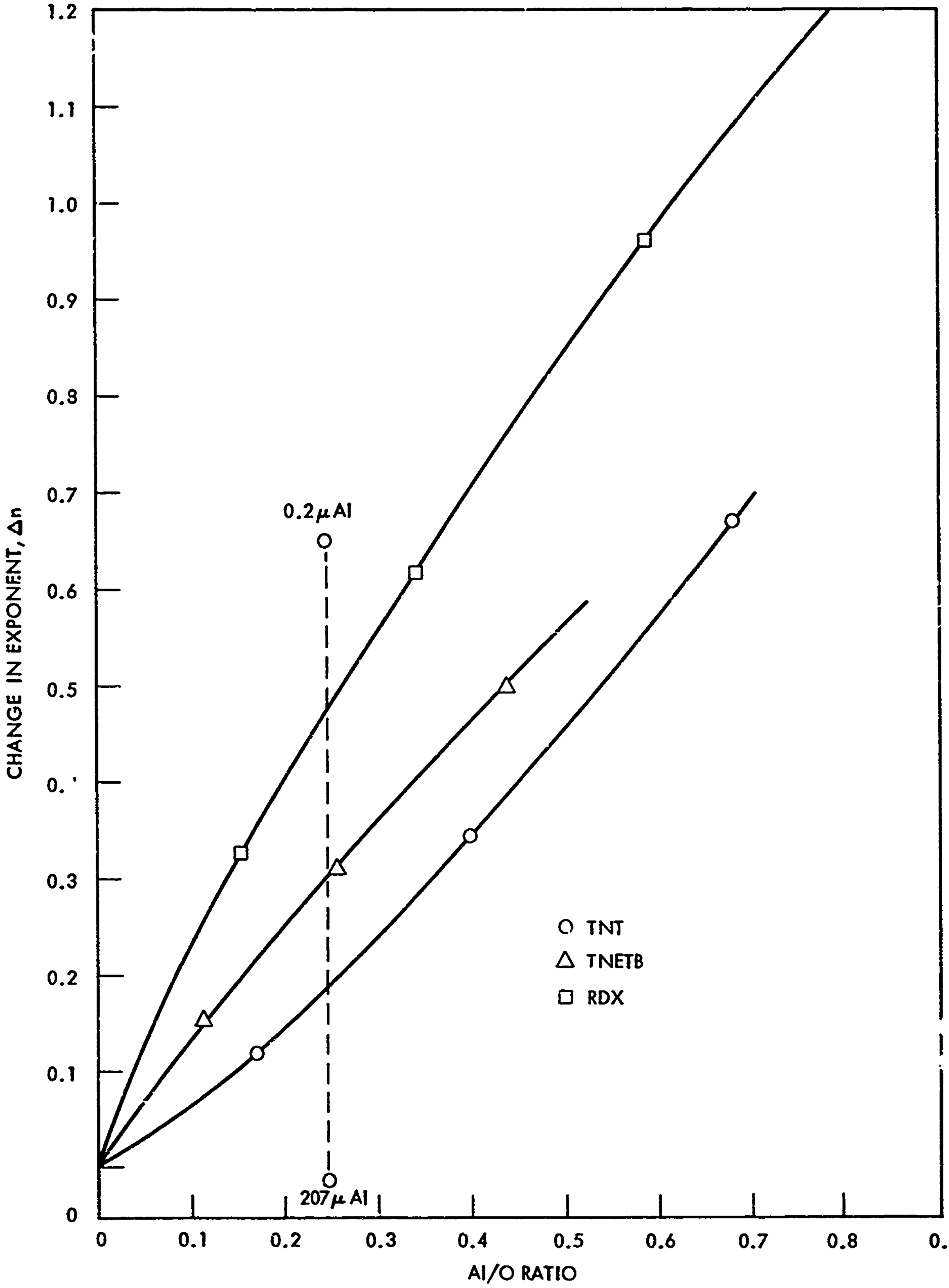

FIG. 8 CHANGE IN EXPONENT Δn AS FUNCTION OF Al/O RATIO OF VARIOUS HE/Al MIXTURES

Table 5

$D/D_{\alpha} \sim (\Delta)^{\Delta n}$ FOR THREE ALUMINIZED EXPLOSIVES

H.E. Matrix	$\Delta = 0.9$	$\Delta = 0.5$
	(Al/O) = 0.2	
RDX	0.96	0.76
TNETB	0.97	0.84
TNT	0.98	0.90
	(Al/O) = 0.4	
RDX	0.93	0.62
TNETB	0.95	0.73
TNT	0.96	0.79

Dremin et al.[6] measured u_{CJ} and D of TNT and 85/15, TNT/diluent at 96.5 and 85% TMD. They found that much of their data was well expressed by

$$\begin{aligned} u &= u_e \Delta\rho_e / \Delta\rho_v \\ &= u_e \rho_e / \rho_v \end{aligned} \tag{16}$$

where u and u_e are, respectively, the C-J particle velocities of the mixture and of the pure explosive. This expression in Equation (13) results in

$$(P/P_\alpha)_D = D/D_\alpha, \tag{17}$$

an unexpected result because it indicates that the aluminum lowers the pressure by the same percentage that it lowers D rather than D^2. The few pairs available (HBX-1 & HBX-3, and Comp B and H-6) do not validate Equation (17), although those data of reference (6) for which Equation (16) holds do conform to Equation (17).

Equation (16) holds for the aluminized charges (0.2 and 270μ Al) at 96.5% TMD and to within 6% for the charges (80 and 270μ Al) at 80% TMD. It is off by 21% for 0.2μ Al at the lower % TMD. The authors attribute the 6% discrepancy to heat absorption; they computed a decrease of up to 5% for this mechanism. For the very fine Al at the higher porosity they believe the large decrease is caused by endothermal reaction between the Al and explosive. From qualitative arguments above, heat loss by absorption, compression, and entrainment seem sufficient to explain the observed effects; semi-quantitative considerations are given in the Appendix. As I pointed out earlier, the possibility of endothermic reaction is still unresolved.

The fact that Equation (16) holds for aluminized TNT at high TMD suggests the possibility of better approximating pressure from measured D values in cast aluminized explosives. The usual approximation $P \approx 0.25\rho_0 D^2$ generally gives too high a value for aluminized H.E. because k is greater than 3 and $(k+1)^{-1} < 0.25$. On the other hand, the usual approximation fits the reference (6) data for high Δ, aluminized TNT to 1.5% or better than it fits the data for pure TNT (to 5.8%). The approximations

$$P \cong 0.25 \Delta\rho_e D^2 \tag{18a}$$

$$P \cong 0.25 \Delta\rho_{ew} D^2 \tag{18b*}$$

as well as the conventional one have been used for the comparisons of Table 6. In view of the uncertainty in the measured values of P and also of the D value for HBX-3, the results are inconclusive. Equation (18b) seems to be a slightly better approximation for the four explosives of Table 6 than Equation (18a); both seem better

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*ρ_{ew} is voidless density of the matrix including the wax.

Table 6

COMPARISON OF APPROXIMATED WITH MEASURED PRESSURES FOR ALUMINIZED H.E.

Material	% Al	% Wax	ρ_o g/cc	Δ	ρ_e*	ρ_{ew}**	D mm/μsec	$P_{meas.}$ kbar	$\frac{\Delta\rho_{ew}D^2}{4}$	$\frac{\Delta\rho_e D^2}{4}$	$\frac{\rho_o D^2}{4}$	Ref.
Alex 20	20.0	4.00	1.80	0.99[a]	1.74	1.68	7.53	230	235	244	255	9
HBX-1	17.1	4.80	1.71	0.972	1.72	1.66	7.31	222	215	224	228	10
H-6	21.0	4.76	1.75	0.972	1.74	1.67	7.50	245	227	237	241	11
HBX-3	35.0	5.00	1.85	0.979	1.72	1.64	7.16[b]	206	205	216	237	11

*Density of matrix with both Al and wax removed.

**Density of matrix with Al only removed.

[a] Assumed

[b] Value given in reference (11) was 7.53; that is much too large compared to 7.31 for HBX-1, an explosive with approximately the same matrix and only half the amount of Al. The value of 7.16 is estimated from unreported NCL data.

than the usual $\rho_0 D^2/4$. If this proves to be the case when better data are obtained, it might still be restricted to this particular type of explosive (aluminized Comp B) within a restricted range of aluminum content.

Lyutov et al.[12] have derived an expression for the detonation pressure of explosives containing an inert additive; they consider Al inert. In our notation, their relationship is

$$P = \frac{\rho_0 D^2}{k+1}\left(1 - x_d \frac{\rho_0}{\rho_d}\right)$$

$$\text{or} \qquad (19)$$

$$P = \rho_0 D^2 y_e/(k+1)$$

This is the usual hydrodynamic relation [Equation (10)] with a correction factor. The authors claim that detonation pressures calculated according to Equation (19) for mixtures of PETN with Al and Mg as well as of TNT with Al, SiO_2, and NaCl (data of reference (6)) containing up to 50% inert additive agree with the experimental values within 10%. Their tabulation shows that they used a constant value of k = 2.80 for the calculations regardless of matrix, diluent content, and charge porosity. Hence, Equation (19) can hardly be considered an established relationship.

In summary, addition of Al to organic explosives lowers the detonation pressure. There is no convenient approximation available with which to estimate the extent of the decrease.

SUMMARY

A review and examination of available data for aluminized organic explosives has shown that:

1. In all probability, the aluminum does not react in the detonation front but sometime later.

2. Al as a diluent lowers D. The lowering is a linear function of the volume fraction of Al present; it also depends on the density and compressibility of Al as well as on its particle size and shape -- probably on the total surface and heat conductivity.

3. The lowering of D by dilution with Al also depends on the particular H.E. used. The same amount and form of Al has a larger effect (expressed as %D) on explosives of initially higher D values. Thus the effect decreases in the order RDX, TNETB, TNT.

4. Aluminum as a diluent lowers P.

5. The decrease in D and P is most obvious at high porosity (low Δ) and high Al content; the former is the more important factor.

SYMBOLS AND DEFINITIONS USED

Subscripts

i	Component i of mixture (also ideal value of D)
e	Explosive component
d	Solid diluent
a	Air
v	Voidless
o	Initial value
α	Reference value D or P of pure explosive at corresponding porosity.

Others

x	Weight fraction
y	Volume fraction
v	Specific volume
ρ_o	Bulk density of charge

$\Delta = \rho_o/\rho_v = 1 - y_a$

$$\rho_v = \left(\sum_{i}^{\text{Solids}} x_i/\rho_i \right)^{-1}$$

$y_i = \Delta\rho_v x_i/\rho_i = \rho_o x_i/\rho_i$

α = Compressibility of diluent $= 1 - \rho_d/\rho_d' = (v_d - v_d')/v_d$ where prime indicates compression in detonation front.

$\beta = (\rho_d/\rho_e) - 1$

$a = 1/(1 - \rho_e/\rho_j) = k + 1$

k	Adiabatic exponent
$a(u)$, $b(u)$	Parameters of $D = a + b\Delta$
A, n	Parameters of $D = A\Delta^n$

Appendix A

ADDITIONAL CONSIDERATIONS OF ROLE OF ALUMINUM IN H.E./Al MIXTURES

Reference (6) does not give the calculations made for heat absorption by Al and the consequent effect on D. In view of our disagreement with the conclusions of reference (6), it seems worthwhile to present such estimates as we can carry out with our present knowledge of the characteristics of Al.

Lees[13] has studied the melting point of Al under pressure over the range 0 to 40 kbar. His data show the linear relation

$$T_m = 660 + 6.58P \qquad \text{(A1)}$$

where the units of T, and P are, respectively, °C and kbar. Krieger[14] has studied the thermodynamics of the aluminum/aluminum vapor system, and constructed the vapor pressure curve. From that curve, the boiling point of Al is 4300°K at 0.1 kbar, and greater than 6000°K at 1 kbar where it is still rising rapidly. Hence the Al may melt in the detonation zone, but it will not vaporize. Consequently, any diffusion reaction with the H.E. detonation products will be restricted to the surface of the Al melt, much as it is in the case of aluminized rocket propellants.

To consider the effect of heat absorption let us assume that the aluminum is exposed to the C-J temperature (T_j) at the C-J pressure P_j for an interval equal to the detonation reaction time τ. The detonation reaction zone, in the one dimensional case, is bounded by the leading von Neumann (vN) shock plane and the following C-J plane where the reaction for C-H-N-O explosives is essentially complete. From the vN plane to the C-J plane, the pressure decreases and the temperature increases. Hence T_j is higher and P_j is lower than the average values over the interval τ. However, there is no general agreement on the correct value of P_j (measured or computed) and even less on the value of T_j, which may vary by several thousand degrees according to the equation of state used for the gas products. Under these circumstances, there seems little point in trying to pick average values; Table A1 contains the P_j, T_j values for TNT (and their sources) chosen to estimate the order of magnitude of the heat effect. Also tabulated are measured values of the detonation reaction time τ. (This is not to be confused with a total reaction time; it merely indicates the interval beyond which reaction energy no longer contributes to propagation of the detonation front.) The values chosen for the measured P_j and the computed T_j are the lower of those available in the literature; the value of τ is an intermediate of those measured.

In addition to the above values, we need information about Al. Its melting point at the higher pressures is estimated by extrapolation of Equation (A1). The thermal conductivity, specific heat, and density of Al will all vary with temperature and pressure and so to will its thermal diffusivity. Because data are lacking, the value $\kappa = 0.94$ cm^2 sec^{-1} computed from the values of $k/s\rho_V$ of Table 1 is used for diffusivity. The necessary parameters $\kappa\tau/a^2$, where a is the average particle radius, are then those tabulated. Solution of the heat conduction equation for spheres with the surface temperature T_j for the time τ, shows that the entire particle of the 0.2μ Al is raised to a temperature above its melting point (in fact, it would be raised to T_j in time τ if its surface could be maintained at T_j) whereas only the outer layers of the larger (80 and 270μ) particles can be heated above the melting point. It follows that with sufficient time the 0.2μ particles could melt completely whereas the larger particles would show only a thin layer of melt on the surface. These data illustrate the particle size effect on heat absorption rather more strongly than the Δ effect, but that too is evident.

Although there have undoubtedly been many thermodynamic-hydrodynamic calculations of the detonation of aluminized organic explosives, very few have been published in accessible sources. Mader[16] used the LASL code for one aluminized H.E., the composite, RDX/TNT/Al/wax, 44/32.2/19.8/4 at Δ = 0.9945. Not only is this at a compaction where little or no effect of Al on D is expected, but he failed to run the computation on the non-aluminized matrix, RDX/TNT/wax, 54.86/40.15/4.99. With the assumption of complete reaction of Al to form $Al_2O_3(s)$, he computed D about 3% below the experimental value of 7.53 mm/μsec and P, 3% above the experimental value of 230 kbar. The Kamlet empirical method[18], which approximates very well the current RUBY code values for simple C-H-N-O explosives, can be used to estimate the parameters for the non-aluminized matrix. This was done and the wax was treated as a reacting component to obtain the values of 7.60 mm/μsec and 245 kbar respectively for D and P of the matrix. These values are, within the error of the method[18], the same as those measured on the aluminized charge at Δ = 0.9945. Hence they confirm the insignificant effect of Al at high compaction (relative to its matrix at the same Δ) but not the reason for this effect. Thus at Δ ~ 1 Mader computes the same result assuming reaction of the Al that Equation (6) would give for chemically inert Al that is compressed and entrained.

One other set of computations has been carried out by Chaiken[19] on the RUBY code for an RDX series at Δ = 1, again where the effect of Al should be insignificant. His results are shown in Table A-2, but they are very puzzling. The present LASL code is very similar to the RUBY code. There seems to be no reason for Chaikin's results for pure RDX to be so low; the LASL values agree with the experimental ones. If we assume an error in input for that explosive only, we can compare the RDX/Al results to the LASL RDX results. That comparison says that the Al has practically no effect on D and P at Δ = 1 when Al is assumed to react. The effect of melting the Al but not

Table A1

TNT AND TNT/Al, 85/15

TNT

	Reference	$\Delta=0.964$ $\rho_o=1.59$ g/cc	$\Delta=0.85$ $\rho_o=1.40$ g/cc
D(mm/μsec)	15	6.94	6.34
P_j(kbar)	15	175	130
T_j(°K)	16	2978	3100
τ(μsec)	17,15	0.14	0.29
Al,T_m(°C)	Eq. (Al)	1811	1515
T_m(°C)/ T_j(°C)		0.67	0.54

TNT/Al, 85/15

a(cm)	$\kappa\tau/a^2$ at $T \geq T_m$*		$\kappa\tau/a^2$ at $T \geq T_m$*	
0.01350	0.00073	~1μ outer layer	0.0015	2.7μ outer layer
0.00400	0.0082	2.5μ outer layer	0.017	5.2μ layer
0.00001	1330	whole sphere	2670	whole sphere

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*From Carslow & Jaeger, "Conduction of Heat in Solids" Oxford Press, Oxford (1959) pp 234 & 102

Table A2

RUBY CODE RESULTS FOR RDX SERIES[19]

Explosive	$\rho_o(\Delta)$ g/cc	D mm/μsec	P(kbar)	T(°K)	Comment
RDX	1.80(1)	8.03	287	1824	
RDX*	1.80(1)*	8.75*	347*	2,88*	*LASL code[16]
RDX/Al 80/20	1.94(1)	8.56	359	3882	Al reacts to form Al_2O_3(s)
RDX/Al 80/20	1.94(1)	9.11	332	2262	No reaction of Al but it melts

allowing it to react seems to be a 4% increase in D. This is hard to believe unless 4% is typical of the error in the program. In view of the reported result for RDX, it seems that results for the whole series must be considered unacceptable.

In earlier work[20] we have shown that Kamlet's method does not work well for aluminized explosives (Al assumed reacting), particularly as Δ decreases. If, however, we assume the Al inert and the relationship

$$D = n^{\frac{1}{2}} M^{\frac{1}{4}} Q^{\frac{1}{4}} (1.01 + 1.31\rho_V \Delta)^* \qquad \text{(A2)}$$

correct, we can use it to obtain an estimate of how much effect heat absorption could have at $\Delta = 0.85$. When the Al is 0.2μ diameter, data of Table 1 indicate that the particles can be melted and the melt heated to T_j in the interval τ. (This is an upper limit to the effect because the product gas environment could not maintain a temperature as high as T_j at the surface while it is losing heat to the Al.) Hence to apply Equation (A2) to TNT/Al, 85/15, the pure TNT values of n and Q must be reduced by the factor 0.85; M stays the same. In addition, Q must be further reduced by heating the Al to its melting point, melting it, and heating the melt to T_j. Thus for TNT, Q = 1282; for TNT/Al, 85/15, Q = 976. In Equation (A2) this gives D = 5.63 mm/μsec as compared to the value of 5.75 mm/μsec measured at $\Delta = 0.85$. Thus heat absorption alone could account for the lowering of D observed at this compaction. The example is very probably an over-estimate of this factor as entrainment and compression are also contributing.

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*n = moles of gas/gH.E., M = average molecule weight of gas and Q = chemical energy/gH.E.

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