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IDEAL DETONATION VELOCITY OF AMMONIUM PERCHLORATE AND ITS MIXTURES WITH H. E.

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IDEAL DETONATION VELOCITY OF AMMONIUM PERCHLORATE AND ITS MIXTURES WITH H.E.

By

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ABSTRACT: Work with finely ground AP led to the infinite diameter relationship

$$D_i(\text{mm}/\mu\text{sec}) = 1.146 + 2.576\ \rho_o$$

over the range $0.55 \le \rho_o \le 1.0$ g/cc. D and ρ_o are, respectively, detonation velocity and charge density. The quadratic mean error found was 0.040 mm/µsec. Several computations of D_i as a function of ρ_o are summarized and compared with the experimental data. Estimated limits on the detonation temperatures are proposed.

Detonation velocity measurements were made on AP/H.E. mixtures containing 20% of HMX, PETN, and TNETB. They indicated an oxidation-reduction reaction for AP/HMX only. The AP in the other two mixtures contributed to the detonation velocity, but the additivity rule does not seem applicable to mixtures of AP with organic H.E.

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This work was carried out under the tasks MAT 03L 000/R011 01 01 FR 59 and ORDTASK 033 102 F009 06 01. It is part of a continuing program on the systematic investigation of the explosive behavior of composite propellant models.

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Captain, USN
Commander

Albert Lightbody
ALBERT LIGHTBODY
By direction

TABLE OF CONTENTS

ILLUSTRATIONS

ILLUSTRATIONS (Cont'd)

TABLES

IDEAL DETONATION VELOCITY OF AMMONIUM PERCHLORATE AND ITS MIXTURES WITH H.E.

In earlier work[1-3], very few detonation velocity (D) measurements were made on ammonium perchlorate (AP) charges of loading density $\rho_o <$ 1.0 g/cc because such charges were of very poor quality. Moreover, extrapolation of the D vs reciprocal diameter (d^{-1}) data to the ideal or infinite diameter value D_i at $\rho_o >$ 1.0 g/cc was suspect because of the nature of the $D(\rho_o, d)$ function for AP[3]. The present work was therefore undertaken to obtain a D_i vs ρ_o curve for $\rho_o \leq$ 1.0 g/cc and to see if it could be extrapolated to higher densities.

A new lot of more finely ground AP was used to prepare charges of 0.55 and 0.70 g/cc. The results of extrapolating D vs d^{-1} data were then combined with previously reported D_i for 0.72 and 1.0 g/cc to obtain the desired D_i vs ρ_o curve for $\rho_o \leq$ 1.0 g/cc. The extrapolation of this latter curve to higher densities was then explored by studying the D_i values of AP/H.E. mixtures at a high percent of their theoretical density, i.e., in regions where pure AP cannot be detonated at $d \leq$ 7.62 cm.

EXPERIMENTAL

A new lot of AP, propellant grade, was ground to an average diameter of 11.6 μ by surface mean (determined microscopically). This material, supplied by N.O.S., Indian Head, Md., is designated N-128. According to Heywood[4], the microscopic measurement corresponds to a Micromerograph particle size measurement of 0.67 x 11.6 or 7.8 μ. It is therefore somewhat finer than the 10-11 μ (Micromerograph values) size AP previously used. A second lot of AP, prepared by N.O.S. is designated N-133. It had an average diameter 11.3 μ by surface mean and a micromerograph value of 7.7 μ (0.67 x 11.3 = 7.6). A third lot of AP (N-136) was ground on the same schedule as that used for N-133. This lot had a micromerograph value of 8.4 μ. A fourth lot AP (N-138) again ground on the same schedule had a micromerograph value of 8.9 μ.

Charge preparation and handling were identical to those in previous work[3]. AP charges of $\rho_0 \le 1.0$ g/cc were hand packed and fired immediately after preparation. Charges were of various diameters, 20.32 cm long, and boosters were 50/50 pentolite ($\rho_0 = 1.56$ g/cc) of the same diameter and 5.08 cm long. The experimental assembly and instrumentation (70 mm smear camera with writing speed up to 4 mm/μsec) were also the same[3].

Record reduction was carried out as in the earlier work[3]. In addition, small corrections, not used in the previous work, have been made on the present data. They are shown in the tables and consist of the following:

1. Correction of measured D to that expected at $\rho_0 = 1.0$ g/cc. The charges used in the series of $\rho_0 \sim 1.0$ g/cc had a density range of 0.988 to 1.009 g/cc, and the small correction was made by use of the smoothed D vs ρ_0 curve at the appropriate diameter in the earlier work. The results in both D and ρ_0 were expressed in four figures throughout the series of corrections. Final results should be rounded off to three figures.

2. D was corrected for the effect of using a non-planar initiating shock[5], i.e., the measured velocity on the charge surface was corrected to the corresponding axial velocity. For this correction, the 5.08 cm long booster is treated as part of the charge length and as if the detonation velocity of the booster were the same as that of the charge. The correction was made for an axial point 3.8 cm from the free end of the charge; this location corresponds to the midpoint of that part of the smear camera trace read for the velocity determination.

3. This correction is made for the difference in booster and charge detonation velocities. It will be fully described in a subsequent report. Its derivation assumes one constant velocity in the booster and another constant velocity in the charge, in other words, no overboostering. (For pentolite, D = 7.2 mm/μsec and is always greater than D of AP.)

RESULTS AND DISCUSSION

AP

The fine material, AP N-128, had a pour-density of about 0.5 g/cc. Charges of 0.55 and 0.70 g/cc prepared from it were of better uniformity than the low density charges in previous work, but were still of lower quality than desired. Because we are now at about the limit of available grinding equipment, there seems little chance of making any further improvement in the charge quality without using a new technique such as recrystallization of the AP.

The data, D as a function of d at various ρ_0 (0.55 to 1.0 g/cc) are shown in Table 1. Two sets of data were previously reported[1]; two are new. Each measured value of D was corrected as shown in the table. Correction 2 (for non-planar initiation) reduces the measured value whereas correction 3 (for booster detonation velocity) increases it. These two corrections are therefore somewhat compensating and the corrected results will probably bracket the true velocity. Thus Table 1 shows the minimum (D_{min}, correction 2 only) and the maximum (D_{max}, corrections 2 and 3). Each corrected D vs d series was then fit by least squares to a linear D vs d^{-1} which could be extrapolated to the infinite diameter value D_i. The values so obtained and the quadratic mean error (q.m.e.) for each fit are also given in Table 1. The average relative deviation for each of the linear fits lies between 1.0 and 1.2%.

Figure 1 displays the results graphically. The straight lines are the least square results D vs d^{-1}, the data points are the D_{max} values. (Graphs based on D_{min} look much the same and are so close to the D_{max} values that they cannot be shown on the same plot.) The low density charges gave reasonable linear D vs d^{-1} curves despite the fact that the charges were not as uniform as desired. The two curves for N-128 confirmed a previous observation on XP-17, that the slope of the D vs d^{-1} curve steepens as ρ_0 increases. In two of the curves (XP-11 and, to a lesser extent, N-128 at ρ_0 = 0.701 g/cc), the value at d = 6.35 cm (d^{-1} = 0.157 cm^{-1}) seems to be most out-of-line. This is discussed later in Appendix A.

TABLE 1 ORIGINAL AND CORRECTED DATA FOR SEVERAL APs.

Shot No.	ρ_o g/cc	d cm	D mm/µsec	$D(\rho_o=1)$	D Min[a] mm/µsec	D Max[b] mm/µsec	Negative of Slope of D vs d^{-1} curve, cm mm/µsec: Min		Max	
	XF - 17[1]									
49	1.006	2.54	2.872	2.870	2.865	2.867				
55	1.005	2.54	2.852	2.850	2.845	2.847				
66	1.005	2.54	2.754	2.752	2.747	2.750				
60	1.009	3.495	3.027	3.009	2.999	3.004				
61	1.009	3.495	3.073	3.055	3.045	3.050				
54	0.988	5.08	3.258	3.288	3.265	3.274				
53	0.988	5.08	3.299	3.329	3.305	3.315				
63	1.001	7.62	3.427	3.424	3.373	3.393				
64	1.001	7.62	3.426	3.423	3.370	3.392				
					3.677(0.047)[c]	3.702(0.046)[c]	2.193	(7.0%)[d]	2.254	(6.6%)[d]
	XP - 11[1]									
369	0.723	3.495	1.889		1.883	1.887				
370	0.723	5.08	2.245		2.229	2.239				
371	0.721	6.35	2.462		2.436	2.451				
376	0.722	7.62	2.486		2.448	2.469				
					2.993(0.045)[c]	3.026(0.044)[c]	3.858	(10.0%)	3.960	(9.4%)
	N - 128									
413	0.701	3.495	2.223		2.216	2.220				
414	0.701	5.08	2.497		2.479	2.489				
415	0.701	6.35	2.623		2.595	2.610				
416	0.701	7.62	2.618		2.578	2.599				
					2.954(0.046)	2.986(0.044)[c]	2.523	(15.5%)	2.626	(14.2%)
404	0.551	3.495	1.942		1.936	1.940				
405	0.551	3.495	2.009		2.002	2.007				
406	0.551	5.08	2.123		2.108	2.117				
407	0.550	6.35	2.247		2.223	2.238				
408	0.550	7.62	2.288		2.253	2.274				
					2.499(0.032)[c]	2.529(0.033)[c]	1.863	(12.0%)	1.958	(11.8%)

TABLE 1 ORIGINAL AND CORRECTED DATA FOR SEVERAL APs. (Cont'd)

Minimum: $D_i = 1.104(8.0\%) + 2.591(4.5\%)\ \rho_o$ (0.038)

Maximum: $D_i = 1.146(8.3\%) + 2.576(4.8\%)\ \rho_o$ (0.040)

a. Corrected for curvature of initiating shock, Reference (5).

b. D min value corrected for difference in detonation velocity of booster and of AP charge.

c. Infinite diameter value from least squares extrapolation of above D vs d^{-1} data. Value in parenthesis is quadratic mean error defined as

$$\sigma = \sqrt{\frac{\Sigma\,(y_i - \hat{y}_i)^2}{n-k}}$$

where $y_i{}'$ = experimental values
$\hat{y}_i$ = calculated values
n = number of data points
$k = 2$ = number of coefficients to be determined in D vs d^{-1} or D_i vs ρ_o relation

d. Values in parentheses shown as percentage of either of the two coefficients determined in the least squares fit to a linear function are the estimated standard deviation for that coefficient.

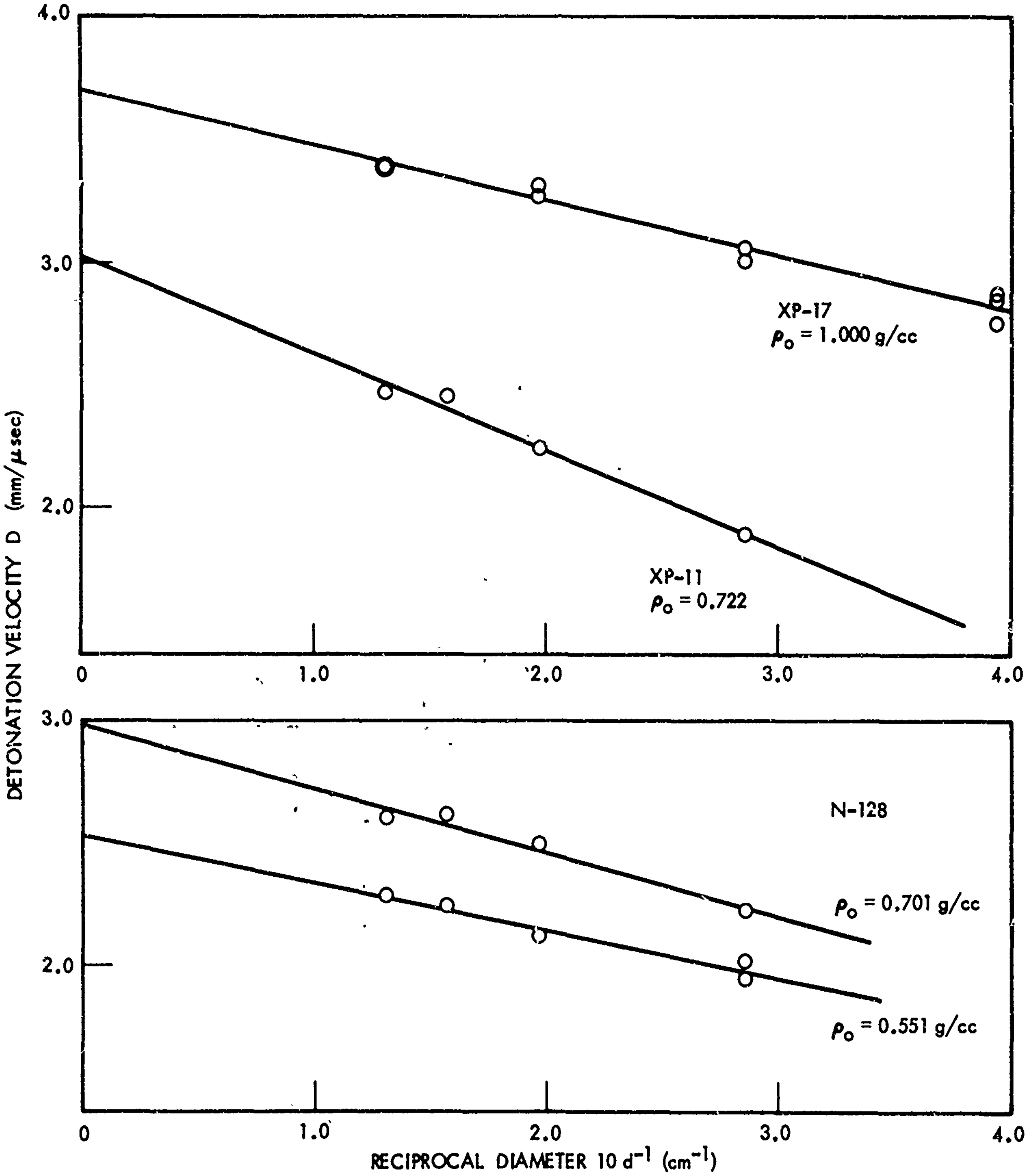

FIG. 1 DETONATION VELOCITY VS RECIPROCAL DIAMETER CURVES FOR AP (D_{max} FROM TABLE 1)

The D_1 vs ρ_o data were weighted according to the number of measurements made at each density and then fitted by least squares to a linear D_1 vs ρ_o. The results, given in Table 1, can be summarized as

$$D_1\ (\mathrm{mm}/\mu\mathrm{sec}) = \begin{cases} 1.104 + 2.591\ \rho_o & \text{min.} \quad (1a) \\ 1.146 + 2.576\ \rho_o & \text{max.} \quad (1b) \end{cases}$$

where ρ_o = 0.55 to 1.0 g/cc. The curve for the maximum D_1 is shown in Figure 2. Extrapolated results from three different lots of fine AP lie on the same linear D vs ρ_o curve in this experimental range.

The difference between the maximum and minimum values of Eqs. (1) is 0.033 and 0.027 mm/µsec at the respective densities of 0.55 and 1.0 g/cc. It amounts therefore to 1.3 to 0.7% in D_1. At crystal density (1.95 g/cc) the difference is 0.01 mm/µsec. Since the two equations are nearly the same, Eq. (1b) rather than both will be used for subsequent work.

Eqs. (1) are remarkably close to the curve given by Andersen and Pesante[6] shown in Eq. (2).

$$D_1\ (\mathrm{mm}/\mu\mathrm{sec}) = 1.012 + 2.688\ \rho_o \qquad (2)$$

They differ markedly from the equations reported in the earlier work[1,3]:

$$D_1 = -0.016 + 3.784\ \rho_o \qquad 0.6 \le \rho_o \le 1.26\ \mathrm{g/cc}$$

and

$$D_1 = -0.45 + 4.19\ \rho_o \qquad 1.0 \le \rho_o \le 1.26\ \mathrm{g/cc}$$

although all four equations agree at ρ_o = 1.0 g/cc. However, it was pointed out in our earlier work[1,3] that the derived value D_1 (ρ_o = 1.26 g/cc) might well be too high. In view of the slopes of Eqs. (1) (with the assumption that Eqs. (1) can be extrapolated above 1.0 g/cc) the first estimate of D_1 at 1.26 g/cc is too high by about 10%. It was also pointed out[1,3] that the low density charges were of unsatisfactory quality and hence only an estimate could be made for D_1 at $\rho_o \sim 0.6$ g/cc. Again by Eqs. (1), the original estimates seem about 12% too low.

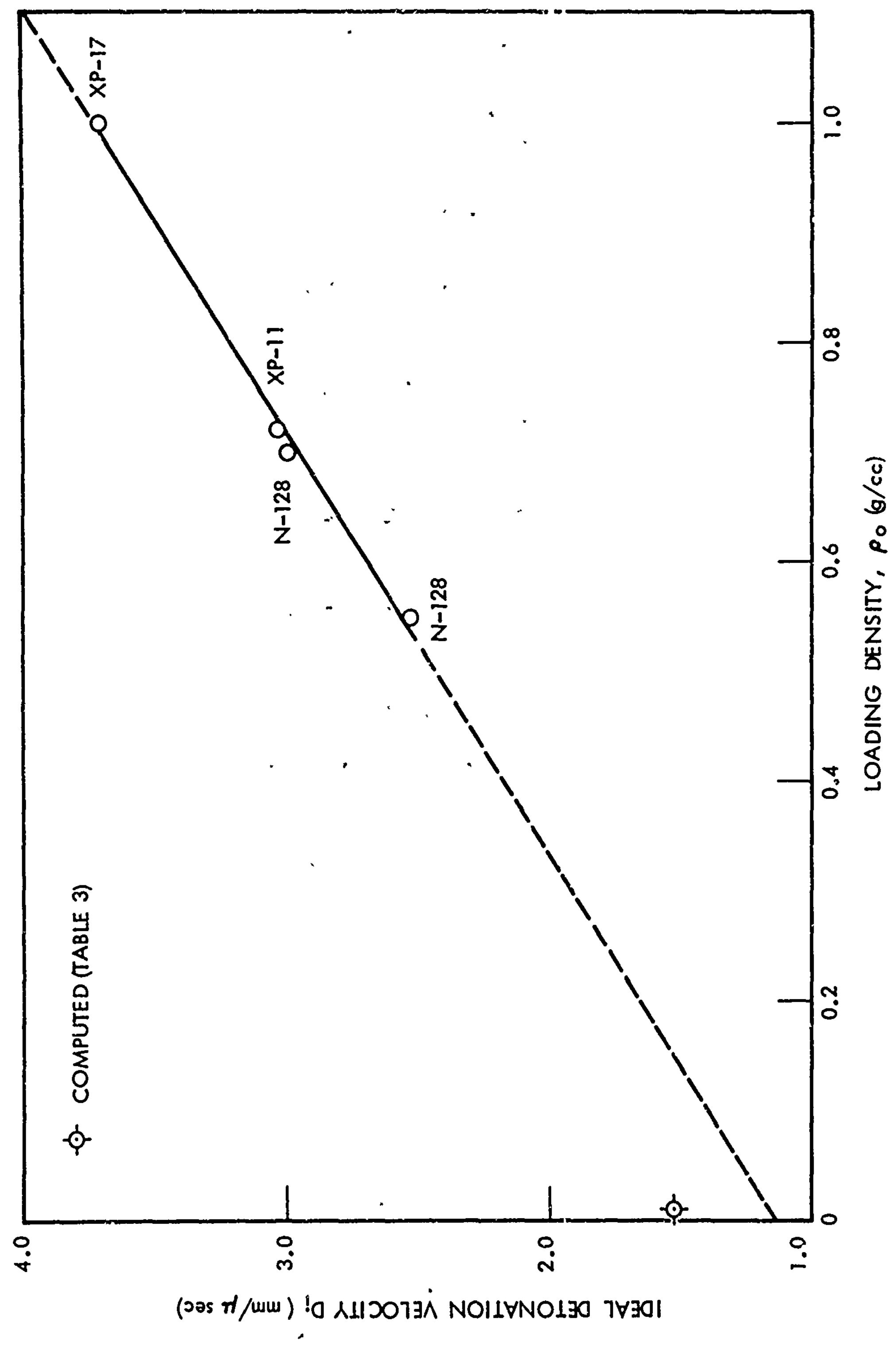

FIG. 2 IDEAL DETONATION VELOCITY VS LOADING DENSITY CURVE FOR AP

In reviewing the early as well as the present work at low densities we have found some evidence that a batch of AP will exhibit lower detonation velocities, for a given d and ρ_o, as it ages. (This evidence is described in Appendix B, and additional data on this topic are being obtained.) This trend with age could result from moisture pick-up by the AP* or from particle agglomeration or from both. Since shots at 0.6 g/cc were made about 3-6 months after the shots at 1.0 g/cc in the earlier work, an aging effect of the AP itself could have contributed to the low velocities found.

An effort was made to check the present D_i values (Eq. (1)) by electronic measurements of D in confined charges. For this purpose a steel tube was used to confine the charge. Results are shown in Table 2. Over the range 0.55 to 1.0 g/cc, the measured D is no more than 2% lower than D_i and at 1.355 g/cc, the difference is about 3% less than the D_i value from extrapolation of Eq. (1) to 1.355 g/cc. This seems encouraging, but at the bottom of Table 2, are given the D measurements from smear camera records of shots made with unconfined charges of 7.62 cm diameter. It is evident that the agreement in this case is just as good. Hence the confinement has made the effective diameter of the charge about 7.62 cm; it has not extended our effective experimental range in d or solved our problems of D vs d^{-1} extrapolation at $\rho_o > 1.0$ g/cc.

D for the shot at $\rho_o = 1.584$ (81.2% TMD) is 7% lower than the D_i obtained by extrapolating Eq. (1b). However, it is also the highest D value we have observed in pure AP, and the density is the highest at which we have found pure AP detonable. In this case, the first pin was located 1.27 cm from the pentolite booster. No overboostering was observed, and the q.m.e. for this shot was 0.213%. The same AP,

---

*Gor'kov and Kurbangolina[7] have shown that the critical diameter of AP is much more sensitive to its moisture content than is that of more common explosives. Presumably moisture would also affect the measured D.

TABLE 2

PIN MEASUREMENTS OF D ON CONFINED APs

ρ_o (g/cc)	AP Lot	D mm/µsec	D_i Eq. (1b)	Difference %
0.550	N133	2.530	2.563	-1.3
0.720	N133	2.934	3.001	-2.2
1.000	N133	3.680	3.722	-1.1
1.355	N133	4.487	4.636	-3.2
1.584	N138	4.862	5.226	-7.0
1.635	N138	F		

Charges in seemless steel tubes of 3.65 cm I.D., 4.76 cm O.D., 30.5 cm length.

Booster of 50/50 pentolite (1.56 g/cc), 5.08 cm diam x 5.08 cm length.

Pins spaced at 2.54 cm intervals; data for eight pins fit to straight line: x vs t, by least squares with a q.m.e. of about 0.5%

Optical Measurements on Unconfined AP (N136), d = 7.62 cm

	D_{max}			Shot No.
1.073	3.793	3.910	-3.0	603
1.290	4.405	4.469	-1.4	591

under the same confinement, fails at ρ_o = 1.635 g/cc (83.9% TMD). Nevertheless, shock from the booster induced some reaction which subsequently faded. Velocities over the successive intervals between pins were 4.58, 4.62, 4.40, 4.15, 3.50, 2.70, 1.83, and 1.37 mm/µsec; the 10th pin was not even shorted out by the attenuated front.

AP Computations

In Table 3 are the detonation parameters computed for a very low (0.01 g/cc) density; the computed velocity is shown on Figure 2. Like other computed values for very low density[8], this point falls above the extrapolated ideal curve of Eq. (1b). Of course, it has been established for some time that current Ruby code computations of the detonation velocity of AP do not reproduce the experimental value at 1.0 g/cc[9,10]. But the disagreement can be attributed to the improper equation of state or covolumes or both. Neither objection should be applicable to the present computation made at such a low density that ideal gas behavior can be assumed. Moreover, this calculation gives us some information about the detonation reaction of AP.

The low pressure burning of AP has been extensively studied and it is known that N_2O or NO (depending on the temperature) is a major product. However, in detonation at low pressure (low charge density) we know from the data of Table 3 that the decomposition reaction approximates.

$$NH_4ClO_4 \rightarrow 0.5\ N_2 + HCl + 1.5\ H_2O + 1.25\ O_2 \qquad (3)$$

and that only a small amount of Cl is formed at 0.1 kbar and 1937°K, which is probably near the maximum temperature to be expected at any pressure. Eq. (3) is, in fact, the limit equation for "high pressure, high temperature" reaction which Simchen[11] derived from thermal decomposition data. In the practical range of densities, say from 0.55 to 1.0 g/cc, the reaction pressures in detonation will be much higher, however. If we use the data of Table 1 and the approximation $P_j \approx 0.25\ \rho_o\ D_i^2$, the range is 9-34 kbar, i.e., a 100 fold or greater increase in pressure. Under these circumstances, a shift in the decomposition reaction toward

$$NH_4ClO_4 \longrightarrow 0.5\ N_2. + 0.5\ Cl_2 + 2\ H_2O + O_2 \qquad (4)$$

TABLE 3

COMPUTED* VALUES FOR AP AT $\rho_0 = 0.01$ g/cc

C-J Values

Velocity	1.525 mm/μsec
Pressure	104.6 bars
Temperature	1937°K (chemical energy 342 cal/g)
Density	0.0180 g/cc
Gamma	1.245
Total gas	36.02 moles/1000g AP

Detonation Products**	Moles/ 1000g AP
Cl	0.269
Cl_2	0.438
H_2O	13.338
HCl	7.366
N_2	4.201
NO	0.107
O_2	10.297

* Ruby code with ideal gas law as equation of state for the products.

** In decreasing amounts: NO_2, H_2, N_2O, and NH_3 with maximum concentration (NO_2) of 0.0022 moles/1000g AP.

would be favored. It will be shown a little later that equilibrium computations do indicate that Eq. (4) describes the detonation reaction. It is also worth noting that the first mechanism releases slightly less energy (346 vs 405 cal/g) and slightly more gas (36 vs 34 moles/kg) than the second.

It was remarked above that the current Ruby code does not produce the correct D_i value for AP. This is true, but it does not seem to be exclusively the fault of the equation of state used, and the current computations do seem to predict the correct relative trend of D_i vs ρ_o. Consequently, it seems worthwhile to review briefly those computations which have been made on AP and determine what information they give.

The Ruby code uses the BKW equation of state

$$PV_g/RT = 1 + xe^{\beta x} \quad \text{where}$$

$$x = \kappa \Sigma \nu_i k_i / V_g (T + \theta)^{\alpha}$$

and P, V_g, R, T, ν_i)k_i are pressure, molar volume of gas products, gas constant, absolute temperature, mole fraction of gas product i, and covolume of gas product i, respectively. The "constants" or equation of state parameters to be assigned values are the set (κ, α, β, θ) and the covolumes k_i. This code solves the hydrodynamic and the thermodynamic relationships simultaneously by an iterative method. Its computed ν_i are therefore correct amounts of equilibrium products for the conditions, P_j, T_j, it has computed from the hydrodynamic conditions; of course, P_j and T_j can be wrong to the extent that the equation of state is inadequate.

Table 4 contains the results of the computations for the parameters (11.85, 0.5, 0.09, 400)[9] and k_i set I[9] and (12.685, 0.50, 0.09585, 400)[12,13] and k_i set II[12,13]. Although the parameters have been changed slightly and the set of k_i, appreciably, the results of Table 4 show little difference between the values produced by these two calculations. In particular, both show ν_i closely approximating Eq. (4) over the range of P_j of 17 to 187 kbar and T_j of 780°-1722°K. Moreover, both overestimate D_i (and hence P_j) although they exhibit

TABLE 4

VARIOUS COMPUTATIONS FOR DETONATION OF AP

ρ_o g/cc	D_1 mm/μsec	P_1 kbar	T_1 °K	Chem. Energy cal/g	Total gas n moles/kg	Products, moles/mole AP N_2	Cl_2	H_2O	HCl	O_2	N_2O	NO	NO_2	Ref.
Arbitrary decomposition:				405	34	0.5	0.5	2.00	0	1.2	0	0	0	Eq.(4)
1.95	6.45	187	780	-	34	0.48	0.50	2.00	$\sim 10^{-14}$	0.96	$\sim 10^{-6}$	$\sim 10^{-6}$	0.042	9
1.56	5.82	127	945	401	34	0.496	0.499	2.00	$\sim 10^{-6}$	0.99	$\sim 10^{-5}$	$\sim 10^{-5}$	0.009	12
1.55	5.49	116	1039	..		0.491	0.501	2.00	$\sim 10^{-8}$	0.983	$\sim 10^{-5}$	$\sim 10^{-5}$	0.019	9
0.975	4.36	50	1403	400	34	0.497	0.493	1.994	0.0101	0.997	$\sim 10^{-5}$	0.0008	0.005	12
0.95	4.13	45	1464	..		0.497	0.501	1.998	0.0008	0.994	$\sim 10^{-5}$	0.0013	0.006	9
0.55	3.20	17	1722	400	34	0.50	0.48	1.99	0.046	0.994	$\sim 10^{-5}$	0.0049	0.003	9
0.01	1.53	0.11	1937	342	36	0.49	0.05	1.57	0.87	1.21	$\sim 10^{-6}$	0.0126	0.0003	Table 3
Arbitrary decomposition:				346	36	0.50	0	1.5	1.0	1.25	0	0	0	Eq.(3)

the expected trend of D_1 increasing with ρ_0. In particular, our Ruby computations[12] produce about the same slope as that found for the experimental curve (See Figure 3) although the absolute value of D_1 is about 0.7 mm/μsec too high. In view of the correct slope, it is possible that the relative trend is fairly good.

A much earlier computation was made with the BKW equation, the set of parameters (1.0, 0.25, 0.30, 0)[14,15] and the k_1 set III.[14,15] In this case, the equilibrium was not calculated; instead Eq. (4) was assumed. (Our current computations seem to justify this assumption completely; hence any difference in results must be attributed to the combination: different parameters and different k_1.) Table 5 and Figure 3 show the results of this earlier computation, which approximate the experimental values much better than the current calculations, despite the fact that the BKW equation is still used.

Finally, another of the earlier computations, which used the arbitrary decomposition mechanism* of Eq. (4) was carried out with an Abel equation of state[6]. This too is shown in Figure 3 and is, in fact, the closest to the experimental curve. However, we attribute this closest approach not to a superior equation of state, but to the fact that these computations were adjusted to agree with the experimental point at 1.0 g/cc[10]. A similar adjustment to the Reference 14 calculation might well have yielded just as good agreement with the experimental

It is not surprising that parameters of almost any real gas equation of state can be adjusted to give agreement for any particular explosive, but it is quite interesting that the parameters of Reference 14 were not so adjusted. They were the same parameters which had up to that time given acceptable agreement for conventional organic explosives. This raises the suggestion that the refinement of the computation in the present Ruby codes might even be a step backwards.

Although with the proper choice of parameters and covolumes either the BKW or the Abel equation can be used to predict D_1 (and presumably P_1) in agreement with those obtained experimentally,

---

*The equilibrium between Cl and Cl_2 was considered, but as we have already seen, this has little effect on the results.

TABLE 5

COMPUTED* DETONATION PARAMETERS FOR AP

Reference (14)

ρ_o g/cc	D mm/μsec	P kbar	T_1 °K
0.8	3.35	25	1940
1.0	3.82	39	1880
1.2	4.31	57	1800
1.4	4.80	79	1710
1.6	5.32	106	1620
1.95	6.29	118**	1400

* Covolumes used were those of Reference 13 and 514, 277 for Cl_2, O_2.

** This is obviously a typographical error and all of the values computed at this density have been discarded.

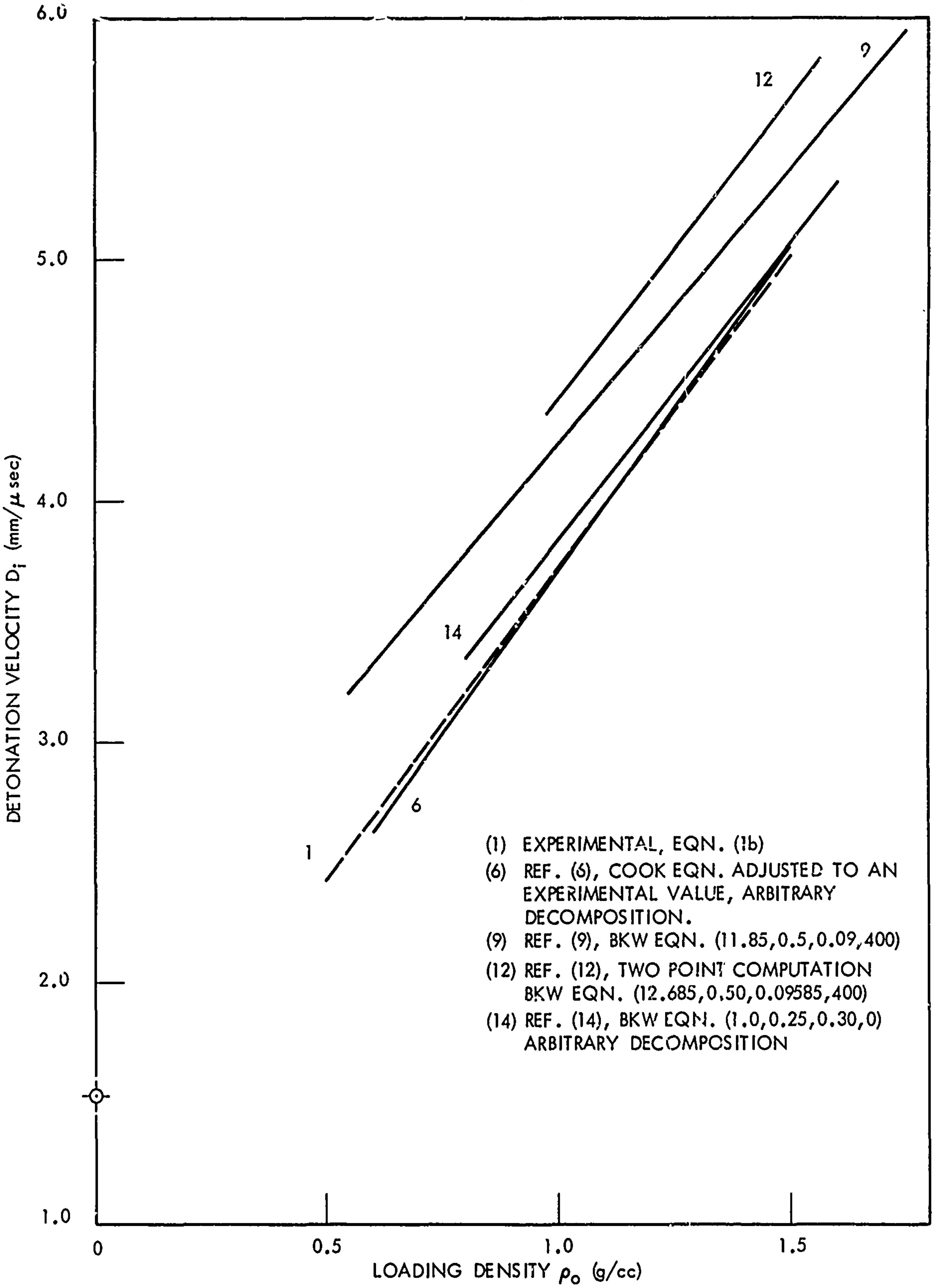

FIG. 3 COMPARISON OF EXPERIMENTAL D_i VS ρ_o CURVE FOR AP WITH SEVERAL COMPUTED CURVES

temperature is another matter. The fundamental objection to the Abel and the ideal gas equation in any practical range of detonation of solid H.E. is that they include no intermolecular forces; such forces must be operative in real, dense gases. Hence all the energy produced by the detonation appears as increased temperature of the gas products, and the calculated T_j will be too high. The fundamental objection to the BKW equation of state is that it assumes only repulsive intermolecular forces and hence much of the energy appears in a density dependent term of the internal energy of the products and does not contribute to raising their temperature. Hence this equation of state should predict T_j which are too low.

It seems reasonable to take about 2000°K as an upper limit of T_j for AP at any charge density. This is based on the computed T_j of 1932°K for low pressures where Eq. (3) is operative, allows for some increase as the decomposition shifts to Eq. (4) and its 15% increase in chemical energy, but also keeps the net temperature increase low because the repulsive forces also become more important with increasing pressure and density. The trend of decreasing T_j with increasing ρ_0 can be accepted as a reflection of increasing molecular repulsion.

The adiabatic flame temperature (T_f) at atmospheric pressure is chosen as a lower limit for possible T_j. From previous computations,[16] generally $T_f < T_j$ (95% TMD) $< T_j$ (% TMD < 95) when the T_j were computed with the BKW equation of state. From the arguments just given above, these T_j values are already too low. Hence T_f seems a very conservative lower limit for the true detonation temperature. For AP, T_f is 1375°K.[17] Moreover, 1375°K is only about 100°K above the minimum temperature required for the lower pressure limit of steady state burning of AP*. As the pressure is increased, T_f also increases.

It is perhaps a matter of interest that Belyaev and Lukashenya have reported[18] that explosives burning at one atm. exhibit flame

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*E. A. Arden, J. Powling, and W. A. W. Smith, "Observations on the Burning Rate of Ammonium Perchlorate", Combustion and Flame, 6, 21 (1962).

temperatures below the computed values. Their measurements were made with thermocouples and checked with computations based on the temperature coefficient of the burning rate. However, Pokhil and Mal'tsev[19] used an optical method to measure flame temperatures in the range 20-100 atm. Their results at 20 atm. on tetryl, PETN, and RDX were very close to our computed flame temperatures[16] ($p = 1$ atm.).

Figure 4 shows these two limits for the detonation temperature and the variation T_j vs ρ_o from the various computations already compared for D_i in Figure 3. Only one of the four curves, that of Reference (14) stays within the two limits and that would have to exhibit a small reversal to extrapolate to the low pressure value. Reference (9) and Reference (12) values are much too low, and Reference (6) values seem too high although that curve too might, with a small reversal, extrapolate to the low pressure value.

AP/HE

Investigation of the model AP/HE is a portion of our planned systematic study of propellant models. The high density, high %TMD, part of the experimental range was investigated at this time with the hope that AP/HE charges, $d \leq 7.6$ cm and % TMD $\geq 95\%$, could be initiated to detonation, and that the validity of extrapolating Eq. (1b) to $\rho_o > 1$ g/cc might be tested by use of the additivity rule. The first hope, i.e., detonation at high % TMD, was realized, but the second was not, as the data below will show.

A number of preliminary shots were made and these data are reported in Appendix C. We found that the 90/10 mixtures seemed less uniform than the 80/20; the finer the AP, the higher the measured D; the finer the H.E., the more detonable the charge. As a result of this exploratory work, we decided to work with 80/20 mixtures of as fine AP and as fine H.E. as were available. For all of the AP/H.E. work, charges were 22.9 cm long and the 1.56 g/cc pentolite boosters (of the same diameter as the charges) were 2.5 cm long.

To assess the extent of the effect on the detonation velocity of the reaction of the component AP in AP/H.E. mixtures, it is desirable to have data on analogous Inert/H.E. mixes. However, there are very few

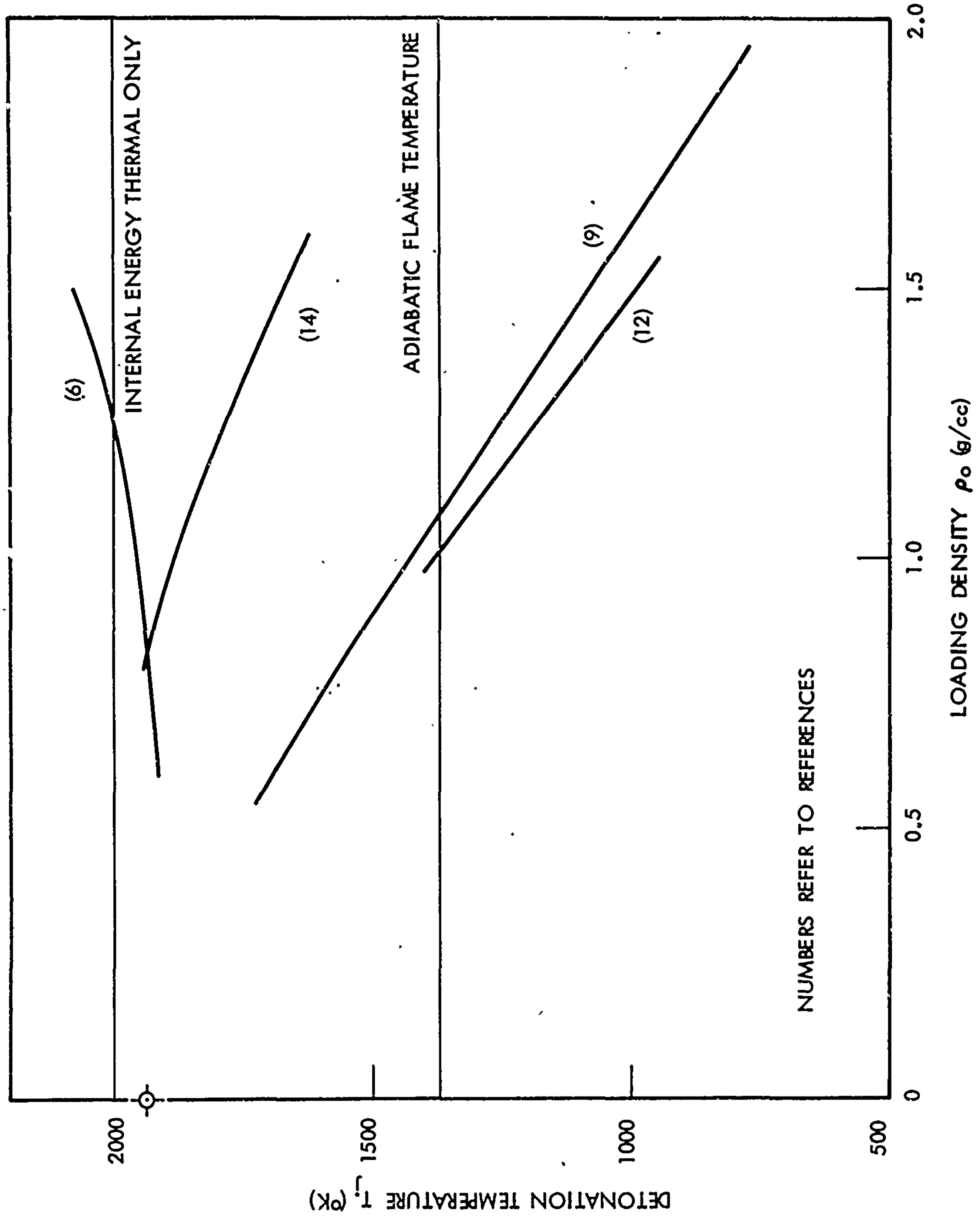

FIG. 4 COMPARISON OF SEVERAL COMPUTED T_j VS ρ_o CURVES FOR AP

data for mixtures containing 80% inert. Reference (20) contains data for PETN/Selectron*, 20/80; and reference (21), data for 15 μ-PETN/polynitrourethane**. At the common diameter of 41.3mm, both references give $D \approx 5.5$ mm/μsec. Hence we know that these 20/80 mixtures made with fine PETN can detonate. Moreover, reference (20) shows that inert diluents lower the detonation velocity according to their density and the volume fraction that can be incorporated into the mixture; the higher the density or the volume fraction, the greater the amount by which D is reduced. Finally, reference (21) shows that the diameter effect on D for 20/80, PETN/Inert is relatively large.

To obtain a more quantitative estimate of the effect of an inert, a few 5.08 cm diameter charges of HMX/Wax and HMX/KCl, 20/80, were tested. The data, given in Table 6, show that HMX/Wax behaves as a group 1 explosive and has a relatively high critical value of the % TMD below which the charge cannot be detonated. They also show that KCl, the higher density inert, lowers the detonation velocity more than wax although the volume fractions are 0.86 (wax) and 0.77 (KCl). KCl (1.99 g/cc) is a better match for inert AP (1.95 g/cc) than wax (1.0 g/cc).

In order to obtain an estimate for comparable PETN/Inert mixes, we assume that, at any fixed charged diameter and fixed weight fraction*** of the same diluent, the ratio of the detonation velocities of the analogous PETN and HMX mixtures will be the same as the ratio of the D_1s of the undiluted H.E., i.e., $(8.456/9.140) = 0.925$.**** The estimates for 20/80 PETN/Inert at $d = 4.08$ cm are 4.74 and 4.37 mm/μsec for wax and KCl respectively. These values and those of Table 6 for the HMX mixtures can be compared directly to the measured Ds of 5.08 cm

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* A thermosetting resin of 1.20 g/cc density.

** Density of 1.21 g/cc.

*** For PETN and HMX, the same weight fraction of the same inert diluent results in nearly the same volume fraction. The small amount of porosity will also have some effect[20], but it has been ignored in these estimates.

**** Reference 22 curves used for PETN at $\rho_0 = 1.78$ g/cc and for RDX at $\rho_0 = 1.90$ g/cc.

TABLE 6

DATA FOR HMX/INERT, 20/80
(d = 5.08 cm)

Shot No.	ρ_0 g/cc	%TMD	D mm/μsec
	HMX/Wax[a]		
516	0.543h	49.1	F
517	0.557h	50.4	F
519	0.697h	63.1	F, $\delta \geq 8.8$ cm
520	0.901H	83.4	F, $\delta \geq 15.3$ cm
521	1.080i	97.7	5.12
	HMX/KCl[b]		
597	1.919i	97.5	4.716
598	1.920i	97.5	4.715

a. ρ_v = 1.105 g/cc. Voidless densities of HMX and Wax are 1.90 and 1.00 g/cc, respectively.

b. ρ_v = 1.971 g/cc. Voidless density of KCl is 1.99 g/cc.

HMX, X586, is Grade II, Class E with an average particle size of about 14μ.

diameter charges of H.E./AP, 20/80. However, if an estimate of D_i rather than $D(d = 5.1 \text{ cm})$ is desired, we can use the factor of $[D_i/D(d = 5.1)] = 1.06$ from reference (21). Estimates of D_i for the H.E./KCl, 20/80, mixes are then 5.0 and 4.6 mm/µsec for HMX and PETN, respectively.

HMX and PETN mixtures. Both the fine HMX and PETN are stored under water and must be dried before they are used to prepare charges. No method of vacuum drying was entirely successful in preventing agglomeration. Consequently the charges were less uniform than desired and, in some series, twice the usual number of shots were made to compensate somewhat for the variation in charge quality.

The data for AP/HMX, 80/20, at 95.4% TMD are given in Table 7 and plotted in the top curve of Figure 5. The similarity of this D vs d^{-1} curve to those of AP/Wax,[23] in which an oxidation-reduction reaction occurs, shows that the HMX is acting as a fuel as well as an explosive. HMX is $C_4H_8N_8O_8$ and has an oxygen balance of 0% to CO and of -22% to CO_2. The curve of Figure 5 indicates that the effect of the fuel-oxidant reaction on D is not evident until larger diameters (say above 5 cm) are reached. This was also evident in the waxed APs and suggests that the oxidation reduction reaction requires a longer time than decomposition of H.E. Inasmuch as this reaction rate must be, to some extent, diffusion controlled, the longer time and reaction zone are to be expected.

If the 2-point extrapolation of results for the two largest charges of Figure 5 is made, the resultant D_i value is 7.49 mm/µsec. For the assumptions of no oxidation-reduction reaction and simple additivity of the detonation rates of AP and HMX, the computed D_i of AP from the measured value for the mixture is 7.15 mm/µsec. The D_i value for AP at the same % TMD (95.4%) by extrapolation of Eq. (1b) is only 5.94 mm/µsec. This is additional evidence that an oxidation reaction <u>did</u> occur and contributed to the measured D of the larger charges of AP/HMX, 80/20. Finally, the three AP/HMX series, reported in Appendix C, also show excessively high D values. We conclude that the detonation products of HMX are oxidized by those of AP, and that

TABLE 7

DATA FOR AP/HMX, 80/20 AT 95.4% TMD

Shot No.	Charge Diam. d, cm	ρ_o g/cc	D mm/µsec	D_1	D_2
525	2.540	1.849	6.225	6.214	6.215
524	3.495	1.849	6.249	6.229	6.229
526	5.080	1.854	6.486	6.442	6.443
533	7.620	1.851	6.896	6.791	6.793
	Av.	1.851			

AP, N133 (7.7µ by micromerograph)

HMX, X586 (14µ)

Voidless density of AP/HMX, 80/20, is 1.940 g/cc this contribution to the detonation behavior will also occur in propellants containing HMX.

In contrast to HMX, PETN ($C_5H_8N_4O_{12}$) has an oxygen balance of -10% to CO_2 and should be a much poorer fuel. Data for AP/PETN, 80/20 appear in Table 8, and are plotted in the lower curve of Figure 5. Here there is no indication of oxidation-reduction reaction, and the least squares fit of the D vs d^{-1} data extrapolates to D_i = 6.09 mm/μsec as compared to the estimated D_i of 4.6 mm/μsec for the analogous AP/KCl mixture. Hence there seems no doubt that the AP is contributing to the detonation velocity of the AP/PETN mixture of 99.1% TMD although AP itself will not detonate at that low porosity. From the D_i of the PETN mixture, we can compute by simple additivity D_i for AP at 99.1% TMD (1.931 g/cc) as 5.51 mm/μsec. Eq. (1b), on the other hand, gives D_i (ρ_o = 1.931 g/cc) as 6.12 mm/μsec or 10% higher. There are two possibilities: (1) that the AP in a mixture with common organic H.E. cannot contribute fully to the detonation velocity of the mixture at the relatively small charge diameters ($d \leq 7.6$ cm) used in the present work and (2) that the D_i vs ρ_o curve, Eq. (1b), cannot be extrapolated to $\rho_o > 1$ g/cc because the ideal curve for AP falls below this straight line at the higher % TMD. No selection can be made between the alternate possibilities without working at larger charge diameters than our firing facilities permit. Our opinion is that the first possibility is the more probable, and that the additivity treatment is not applicable to AP/H.E. mixtures (at least in relatively small diameter charges) because the reaction time of the AP in detonation is very much larger than that of the organic H.E.

It is of interest, though possibly fortuitious, that a 2-point extrapolation of the lower and presumed non-reactive portion of the AP/HMX curve (Figure 5) gives a D_i value of the mixture (95.4% TMD) as 6.26 mm/μsec. By additivity, this leads to D_i (1.86 g/cc) of 5.51 mm/μsec for AP as compared to the extrapolated value of 5.94 mm/μsec from Eq. (1b). In other words, the AP in AP/HMX charges of $d < 4$ cm and in AP/PETN at $d \leq 7.6$ cm seems to be making the same contribution to the D of the mixture.

TABLE 8

DATA FOR AP/PETN, 80/20
AT 99.1% TMD

Shot No.	d cm	ρ_o g/cc	D	D_1	D_2	D_2*
			mm/μsec			ρ_o=1.895
528	2.540	1.895	5.771	5.761	5.761	5.761
527	3.495	1.890	5.830	5.811	5.812	5.826
529	5.080	1.898	5.992	5.951	5.953	5.944
532	6.350	1.877	5.901	5.838	5.843	5.894
565	2.540	1.906	5.677	5.667	5.668	5.637
564	3.495	1.909	5.748	5.729	5.730	5.691
563	5.080	1.908	5.917	5.876	5.879	5.842
551	7.370	1.873	6.010	5.924	5.931	5.993

D_i $(\rho_o = 1.895) = 6.09\ (1.1\%) - 1.04\ (25\%)\ d^{-1}$ (0.068) q.m.e.

* Small corrections for density made with slope of 2.82 mm μsec^{-1} cc g^{-1}. This was derived from slopes of the D_i vs ρ_o curves for AP, Eq. (1b), and PETN[22]; the respective slopes used were 2.576 and 3.880. The derivation assumes simple additivity effect on the detonation velocity of the mixture.

AP, N133

PETN, X591, Primer grade, supplied by Hercules Powder Co.

Voidless density of AP/PETN, 80/20, is 1.913 g/cc

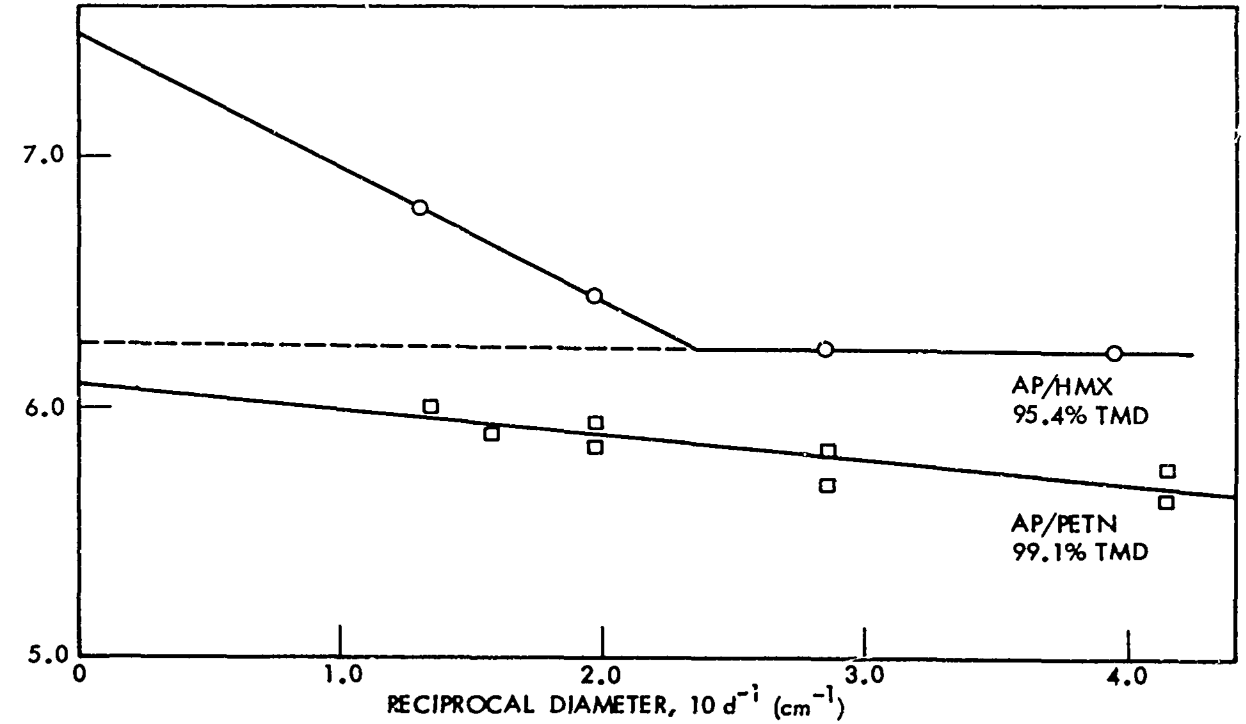

FIG. 5 EXTRAPOLATION TO INFINITE DIAMETER OF DATA FOR TWO AP/HE, 80/20, MIXTURES

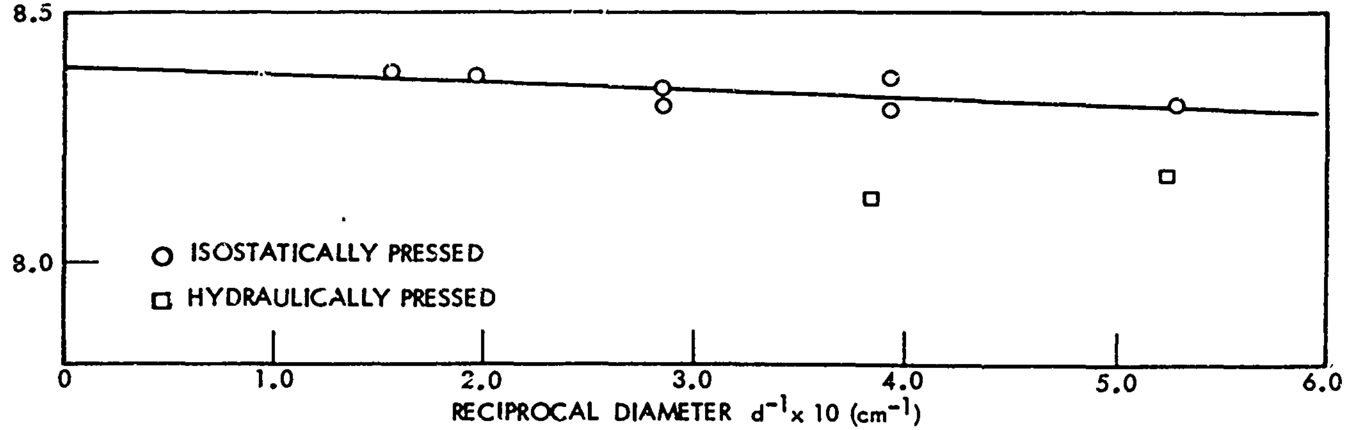

FIG. 6 EXTRAPOLATION TO INFINITE DIAMETER OF DATA FOR TNETB AT $\rho_o = 1.76$ g/cc

TNETB and AP/TNETB. Although no evidence of an oxidation-reduction reaction was found in the AP/PETN mixtures, we wanted to check that result with an H.E. containing more oxygen. The only such explosive available in sufficient amount was TNETB, $C_6H_6N_6O_{14}$, with an oxygen balance to CO_2 of -4%. Our supply of TNETB was stored dry in the magazine, and there was enough in moderately fine granular form to prepare H.E. charges. But for preparing AP/TNETB mixtures some of the explosive had to be recrystallized to obtain a fine material of about 10 μ particle size.

In order to interpret velocity data obtained on mixtures of AP/TNETB, it was necessary to establish the D_i vs ρ_0 relation for TNETB itself. The equation currently used is that reported in NOLTR 65-218 and is in error.* Fortunately, the error appears to be small.

Table 9 shows the shots fired in the present work and derivation of the value D_i (ρ_0 = 1.76 g/cc) = 8.389 mm/μsec for the isostatically pressed charges. The data and the extrapolation are illustrated in Figure 6 which emphasizes the very small diameter effect on D for this material at high density (e.g., the value at d = 2.5 cm is within 1% of D_i). This justifies the approximations of Table 10 where D measured at diameters of 5 and 4 cm for densities of 1.69 and 1.29 g/cc, respectively, are considered good approximations to the corresponding D_i. In fact, the subsequent treatment indicates that D measured at d = 1.28 cm and ρ_0 = 1.27 g/cc is also a good approximation to D_i.

Before leaving Figure 6, it should be noted that two D values from hydraulically pressed charges ($\rho_0 \sim 1.76$ g/cc) lie appreciably below the D vs d^{-1} curve derived for data obtained from isostatically pressed charges. The same difference, i.e., lower velocities measured on charges prepared in the hydraulic press than on those of the same density from the isostatic press, has also been noted and reported in recent work on AP and nitroguanidine. Not enough work has been done here or elsewhere to show whether the same extrapolated value (D_i) could be obtained with the two methods of preparation. Charges for D vs d^{-1} curves should all be prepared the same way.

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* N. L. Coleburn, private communication.

TABLE 9

D vs d DATA FOR TNETB, X563, AT ρ_o = 1.76 g/cc

Shot No.	d (cm)	ρ_o g/cc	Velocities mm/µsec D	D_1	D_2	D_2 (ρ_o =1.76 g/cc)[a]	10 x d^{-1}
686	1.902	1.756i	8.309	8.301	8.301	8.315	5.258
601	2.540	1.756i	8.368	8.354	8.353	8.367	3.937
687	2.540	1.755i	8.297	8.283	8.282	8.300	3.937
647	3.493	1.761i	8.342	8.315	8.314	8.311	2.863
664	3.493	1.757i	8.362	8.335	8.334	8.344	2.863
648	5.080	1.762i	8.437	8.379	8.376	8.369	1.969
665	6.350	1.753i	8.448	8.358	8.353	8.377	1.575
669	1.905	1.760H	8.180	8.172	8.172	8.172	5.249
670	2.540	1.760H	8.136	8.122	8.121	8.121	3.837

Fit for isostatically pressed charges only:

D (mm/µsec) = 8.389 (0.4%) - 0.1530 (57%) d^{-1} q.m.e. = 0.0274
where d is in cm.

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a. Corrected with slope of 3.5 mm cm^3/µsec g for D vs ρ_o curve.

Table 10 shows the data which were assembled to derive the D_i vs ρ_o curve. They give

$$D_i \text{ (mm/}\mu\text{sec)} = 1.947 + 3.660\ \rho_o,\ \sigma = 0.015 \tag{5}$$

where ρ_o is in g/cc. This is remarkably close to the most recent curve reported for PETN* and not very different from the TNETB curve reported in NOLTR 65-218.** At high densities the latter curve and Eq. 5 produce essentially the same results.

The curve for Eq. 5 and the data points are shown in Figure 7 (solid line) together with three computations of D_i vs ρ_o (dashed lines) for TNETB. The Ruby code result with the RDX parameters gives a better approximation than the code with its original parameters, but the best approximation is that obtained with the parameters of Snay and Christian (See NAVORD 2611).

The AP/TNETB, 80/20, charges appeared more uniform than those prepared from either of the other two mixtures. (A barrel blender was used to prepare the entire batch of AP/TNETB in one operation. This may have improved the uniformity of this mixture over that attainable in the piece-wise mixing used for earlier batches.) Nevertheless the charge surfaces were speckled with agglomerates of up to 0.8 mm diameter. The data obtained on a diameter series for this mixture appear in Table 11. With the exception of the 5 cm diam shot, for which the value seems too high, all D's in this series fell within the range of 6.01 to 6.09 mm/μsec. Apparently the diameter effect on D is so small for this mixture (possibly as small as that for TNETB alone (Figure 6) that it is not detectable above the small random errors introduced by non-uniformity of charge, small errors in density, and the usual record reading errors. Consequently the values of Table 11 have been averaged to obtain a D_i of 6.07 mm/μsec for AP/TNETB, 80/20, at 97.6% TMD.

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* $D_i = 2.00 + 3.58\ \rho_o$, E. L. Lee and H. C. Hornig, "Equation of State of Detonation Product Gases." in Preprints of 12th Symposium (International) on Combustion, (1968).

** $D_i = 1.597 + 3.850\ \rho_o$

TABLE 10

DERIVATION OF IDEAL CURVE FOR TNETB AND SOURCE OF COMPUTED CURVES

d (cm)	ρ_o g/cc	D mm/µsec	Source	Comment
∞	1.760	8.389	Table 9	Corrected for non-planar initiation.
5.08	1.688	8.120	W. C. Holton, NavOrd 3968 (1954)	Initiated with PWB. Assumed good approximation to D_1.
4.140	1.290	6.690	*	Procedures of NavOrd 2611 (1952). Assumed good approximation to D_1.
4.140	1.295	6.670	*	
1.275	1.269	6.580	*	
1.275	1.274	6.610	*	

D_1 (mm/µsec) = $1.947 + 3.660\ \rho_o$ (0.015)

Computed Curves Shown in Figure 7

Curve No.	Source
1	N. L. Coleburn, method of NavOrd 2611.
2	Ruby code, original parameters, NOLTR 63-216.
3	H. Hurwitz, Ruby code, RDX parameters.

*N. L. Coleburn and T. P. Liddiard, unreported data.

Data have been used for unconfined, pressed charges only. Additional measurements were made* on cast charges and on very porous charges supported in glass or plastic tubes.

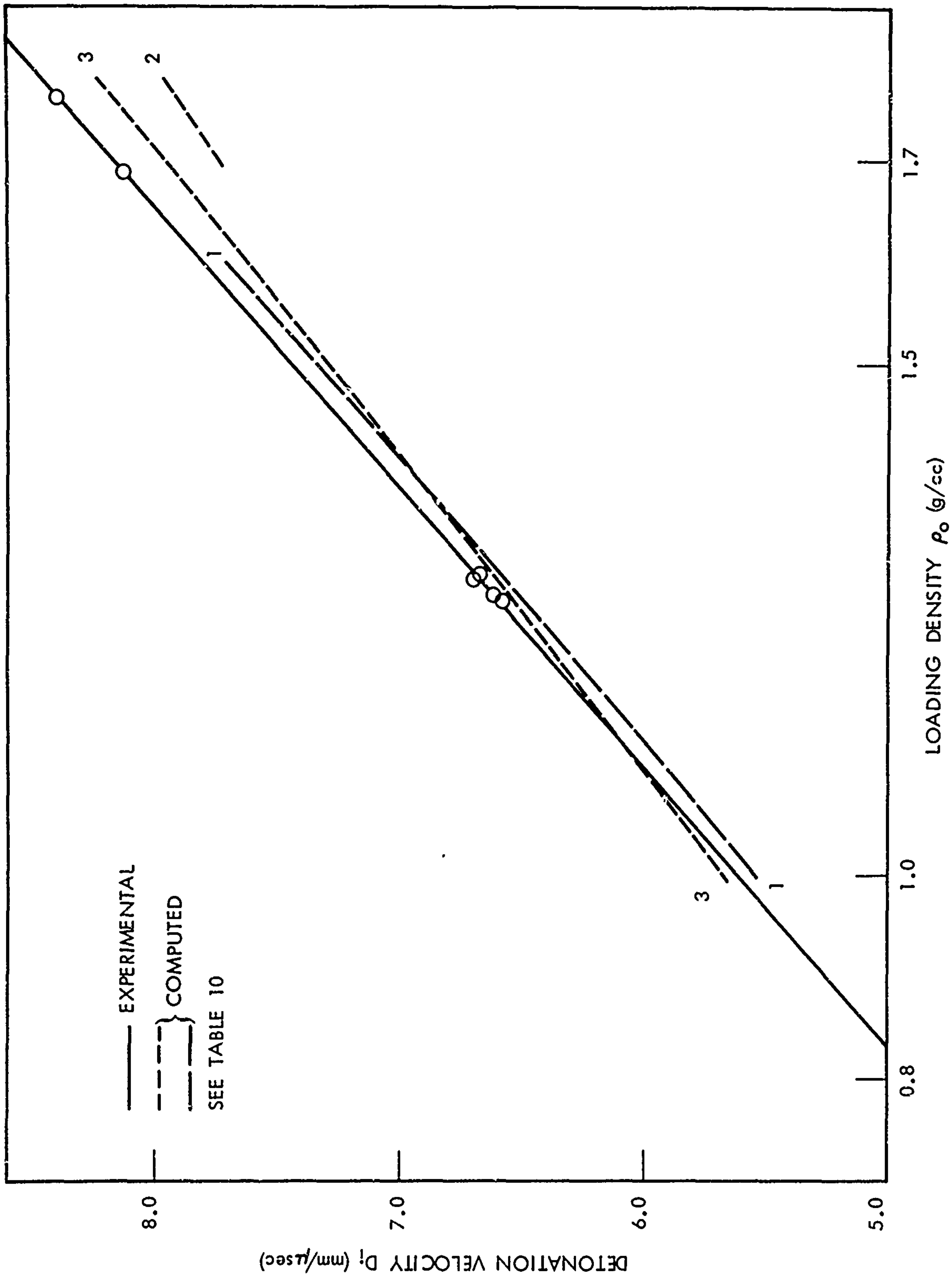

FIG. 7 D_i VS ρ_o FOR TNETB: EXPERIMENTAL AND COMPUTED CURVES

TABLE 11

D vs d DATA FOR AP/TNETB, 80/20, AT 97.6% TMD

Shot No.	d cm	ρ_o g/cc	D	D_1	D_2	$D_2(\rho_o = 1.868)$[a]
643	2.540	1.8671	6.074	6.064	6.064	6.064
644	3.495	1.8691	6.130	6.110	6.111	6.111
645[b]	5.080	1.8681	6.32	6.27	6.27	6.27[b]
646	6.850	1.8501	6.110	6.034	6.039	6.089
659	7.060	1.8871	6.134	6.053	6.059	6.007
			Average without No. 645:			6.07

[a] The small density correction was made with a slope of 2.75 derived from slopes of 3.50 and 2.576 for TNETB and AP, respectively.

Voidless density of AP/TNETB 80/20 is 1.913 g/cc

AP, N133

TNETB, X656 (ca. 10μ)

[b] Trace was cut by film join; two parts read separately; number given is average.

The AP in the mixture appears by the additivity rule to have a D_1 of 5.5 mm/µsec at $\rho_o = 1.904$. Eq. (1b), on the other hand, gives a value of 6.05 mm/µsec or 9% higher. Hence the AP in this mixture is behaving in much the same way it did in the analogous PETN mixture; i.e., it reacted sufficiently to make a contribution to the detonation velocity of the mixture, but the contribution was not as large as that indicated by extrapolation of Eq. (1b).

SUMMARY

Finely ground APs were used to derive the infinite diameter detonation velocity - loading density relation

$$D_1 \text{ (mm/µsec)} = 1.146 + 2.576\,\rho_o \qquad (1b)$$

over the range $0.55 \leq \rho_o \leq 1.0$ g/cc. The highest velocity actually measured was 4.86 mm/µsec observed in a confined charge at $\rho_o = 1.584$ g/cc (81.2% TMD). Various hydrodynamic-thermodynamic computions reproduce the slope of Eq. (1b), but some give D_1 values that are too high by 0.7 mm/µsec. None of these computations produce reasonable values of the detonation temperature which is estimated to lie between 2000°K and 1375°K, the adiabatic flame temperature.

Mixtures of AP/H.E., 80/20, detonate at 99% TMD. Results from diameter series give D_1 values for mixtures with HMX indicating an oxidation-reduction reaction. Although neither PETN nor TNETB mixtures appear to have such a reaction, the contribution of AP to their D_1 is less than that indicated by Eq. (1b). It is suggested that the additivity rule is not applicable to such mixtures at least for data obtained on charges with $d \leq 7.6$ cm.

The infinite diameter detonation velocity for TNETB is given by

$$D_1 \text{ (mm/µsec)} = 1.947 + 3.660\,\rho_o$$

and the diameter effect on D for this H.E. is very small in the range $2.54 \leq d \leq 7.62$ cm.

ACKNOWLEDGEMENT

We are indebted to many people for their help in this work. In particular, we should like to thank K. G. Shipp for preparing the recrystallized TNETB and N. L. Coleburn and T. P. Liddiard for supplying unpublished data.

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APPENDIX A

Effect of Discarding Two Data Points of Table 1

It was mentioned in the text that two values of D at d = 6.35 cm seemed out-of-line in Figure 1. When these two points are omitted from the least squares treatments, the results of Table A1 are obtained. The omission of these points reduced the q.m.e. of the D vs d^{-1} curve for ρ_o = 0.722 g/cc by a factor of about 3; it did not change the q.m.e. of the curve for ρ_o = 0.701 g/cc. The q.m.e. of the resulting D_1 vs ρ_o curves was reduced by a factor of about 2.6. The improvement is evident in the resultant curves, Figures A1 (ρ_o = 0.722) and A2, but does not seem large enough, compared to the experimental scatter, to justify discarding the points at d = 6.35 cm.

TABLE A1

RESULTS WITH OMISSION OF DATA AT d = 6.35 cm.

	D_i (mm/μsec)				-b cm mm/μsec	
ρ_o	Min.		Max.		Min.	Max.
0.722	2.936	(0.0167)	2.970	(0.0134)	3.661	3.768
0.701	2.910	(0.044)	2.944	(0.041)	2.373	2.480

Minimum $D_i = 1.057 + 2.620\ \rho_o$ (0.0146)

Maximum $D_i = 1.100 + 2.605\ \rho_o$ (0.0154)

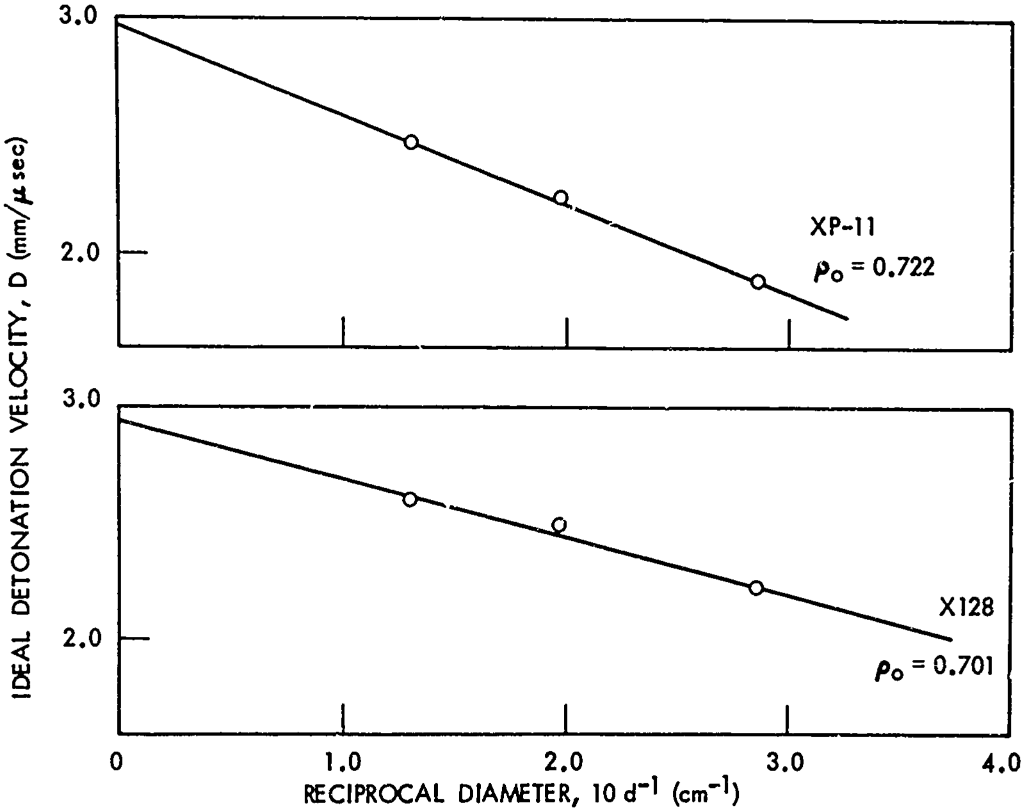

FIG. A1 D_i VS d^{-1} CURVES FROM DATA OF TABLE A1

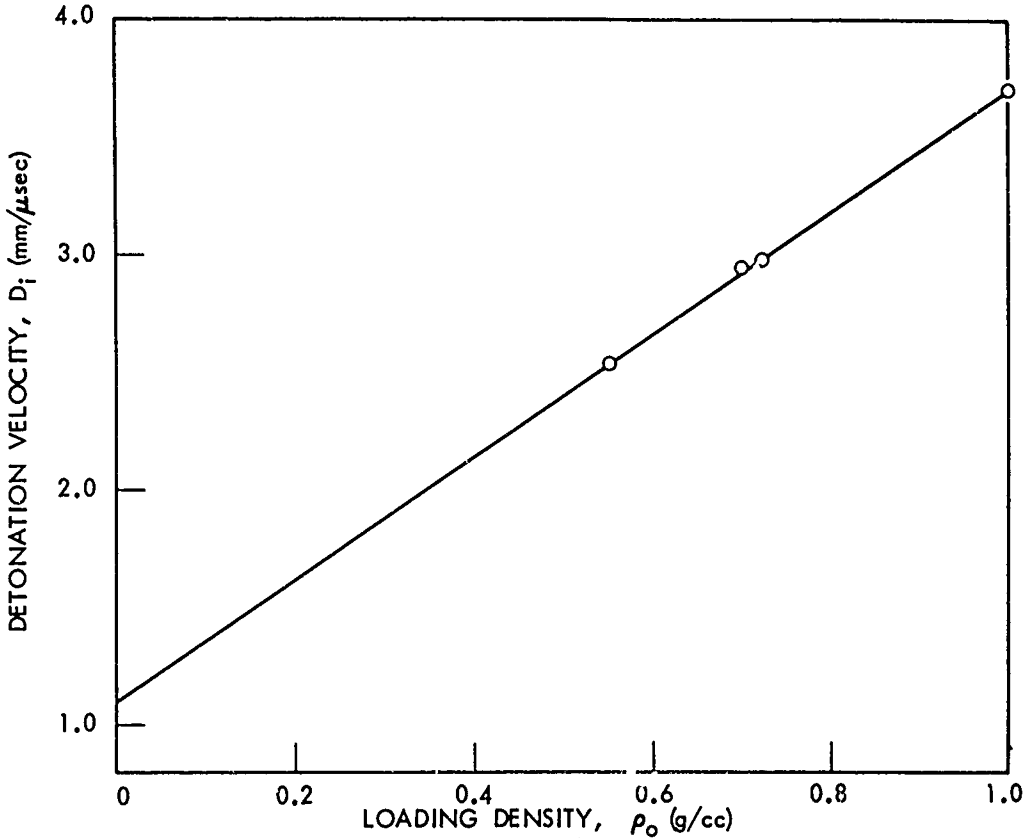

FIG. A-2 D_i VS ρ_o CURVE FROM DATA OF TABLES 1 AND A1

APPENDIX B

APPARENT AGEING EFFECT OF AP

A small sample of XP-17 was stored for a year after the original study[1] was completed. The results on charges (ρ_0 = 0.685 g/cc) prepared from this aged sample are as follows:

Shot No.	d(in.)	D mm/μsec Aged	 Original*
400	1.0	F(1.39)	1.88
393	1 3/8	1.955	2.10
392	2.0	2.140	2.28

* From smoothed curves of Ref. (1).

XP-11 after some months storage became mildly caked and had to be rolled before it could be used to make charges. After caking, a 2 in. diam charge at ρ_0 = 0.722 g/cc showed D of 2.24 mm/μsec compared to the precaking value of 2.35 mm/μsec (Ref. 2, smoothed data).

Lot N-128 was fired at ρ_0 = 0.701 g/cc and d = 2.0 in. about three weeks after it was received and again a month later. Results were:

Shot No.	D(mm/μsec)	Date
412	2.665	5/31/67
414	2.497	6/27/67

None of the changes noted are large enough to be conclusive except the failure of the one inch diam charge of aged XP-17. However, all changes are in the direction of lowered D with increased age. Future work will explore this trend, particularly at low densities and with freshly ground material, conditions which might be expected to favor the largest charges.

APPENDIX C

DATA FROM PRELIMINARY WORK ON AP/HMX MIXTURES

Since supplies of HMX of various particle size were on hand, exploratory work on AP/H.E. mixes was carried out with this H.E. On the basis of this work, as noted in the text, it was found that more uniform charges could be prepared from the 80/20 mixes than from the 90/10 although both showed some agglomerates of the fine H.E.

Table C1 contains all data obtained in the preliminary work. Comparison of shots 471 and 472 with 473 and 474 indicates that a fine H.E. is more effective than a coarse in extending the detonability range of the AP/HMX, 90/10, mixtures; hence fine H.E.s were used for the remainder of the work. However, it should be noted that (1) the coarser HMX mix could be compacted to a slightly higher % TMD (1% higher) than the finer HMX mix, an effect of coarse particles frequently observed in compaction, and (2) the higher % TMD rather than the coarser HMX might be responsible for the failure of the 2.54 cm diameter charges to detonate at ρ_0 = 1.765 g/cc (90.8% TMD).

Where the raw data can be compared, the finer AP resulted in a slightly higher D at the same charge diameter and a slightly lower density; compare shot 458 with 464 and 457 with 462. For this reason as well as in hope of obtaining better dry mixing, fine AP was used in the subsequent work.

The overall gradient of the D vs ρ_0 curve for 2.54 cm diameter charge of AP/HMX, 90/10, is about 1.64 mm μsec^{-1} cc g^{-1}. (See Figure C1). This is about comparable to the slopes found for AP alone (1.8 to 2.28 for d of 3.81 to 7.62 cm).*[2] As pointed out above, however, the high density point may be close to the failure limit, and consequently the curve may not be linear over the entire range. It should also be noted that this AP alone is not detonable in a 2.54 diameter charge at any density, and we have been able to detonate our finest AP only up to about 81% TMD.

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* Data for AP,N126, which is slightly finer than AP,N127.

APPENDIX C (Cont'd)

Non-linearity is exhibited by the D vs ρ_o data of the 80/20 mixture (d = 2.54 cm) also plotted in Figure C1. The slope is approximately 4.43 in the range 87.5-92.4% TMD but the curve appears to bend over between 92.4 and 95.9% TMD. This might be experimental error in the last point, or a high density behavior comparable to that of TNT, high bulk density NQ, or AP itself. In any event addition of HMX to AP extends its detonability in 2.54 cm diameter charges from about 51% TMD to at least 88.8% (10% HMX) and 95.9% (20% HMX).

There are also data for three D vs d series in Table C1. These are plotted in Figure C2 where each of the three curves shows the break indicating an oxidation-reduction reaction, as discussed in the text. Although the finer AP appears to produce larger D at any given ρ_o and d, it does not seem to affect the D_i value.

The additivity rule was not applied to these results because it is not quantitatively descriptive of porous mixtures. The additivity rule[24] gives the ideal detonation velocity of a mixture as

$$D_{iv} = \sum_j x_j D_{vj} \qquad (C1)$$

where x is mass fraction and the subscripts i, j and v refer to ideal (infinite diameter), component j, and voidless density, respectively. At 100% TMD, Eq. (C1) gives the detonation velocity of cyclotol mixtures to 0.3%. When an analogous approximation is used for porous charges, the component and mixture velocities must be computed at the same % TMD, but the approximation becomes poorer as the % TMD decreases. Thus at 70% TMD, the D_i computed for the mixture from known ideal velocities of the components is about 1% low. The error increases at lower % TMD.

When this approximation is used to compute the velocity of one component from the measured velocity of the mixture and known velocities for other components, the error is roughly twice that of the inverse procedure. Hence our effort to obtain mixtures of % TMD $\geq$ 95 before applying the additivity rule.

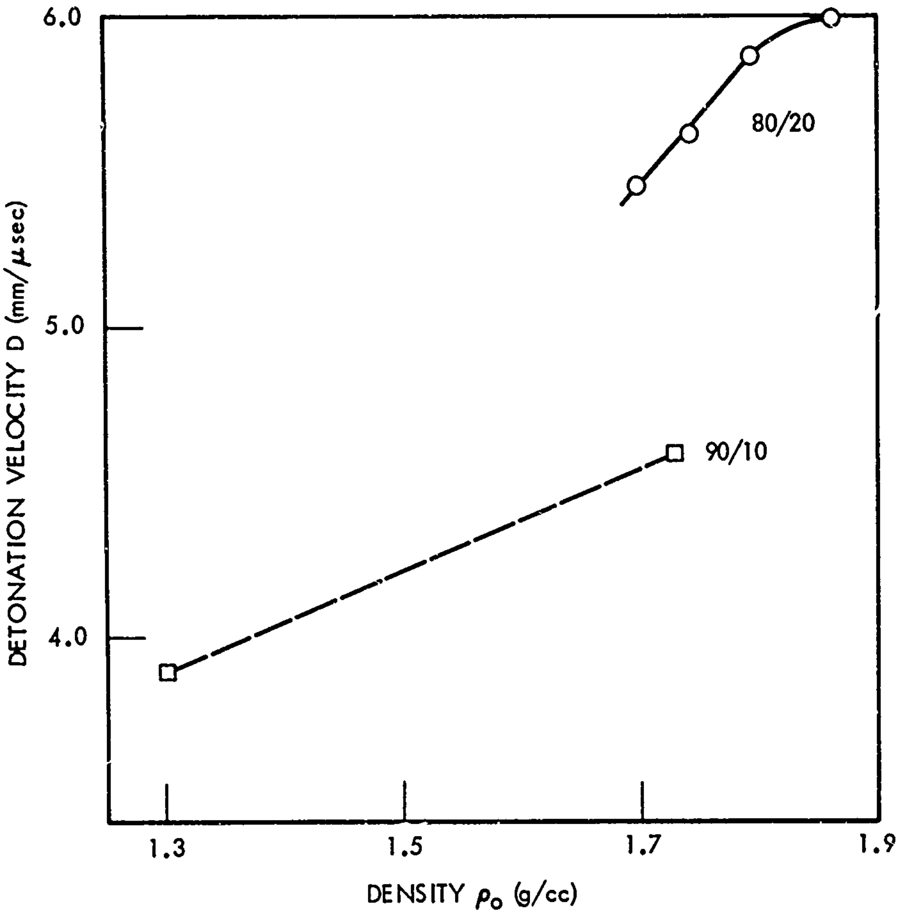

FIG. C1 D VS ρ_o CURVES FOR AP/HMX AT $d = 2.54$ cm

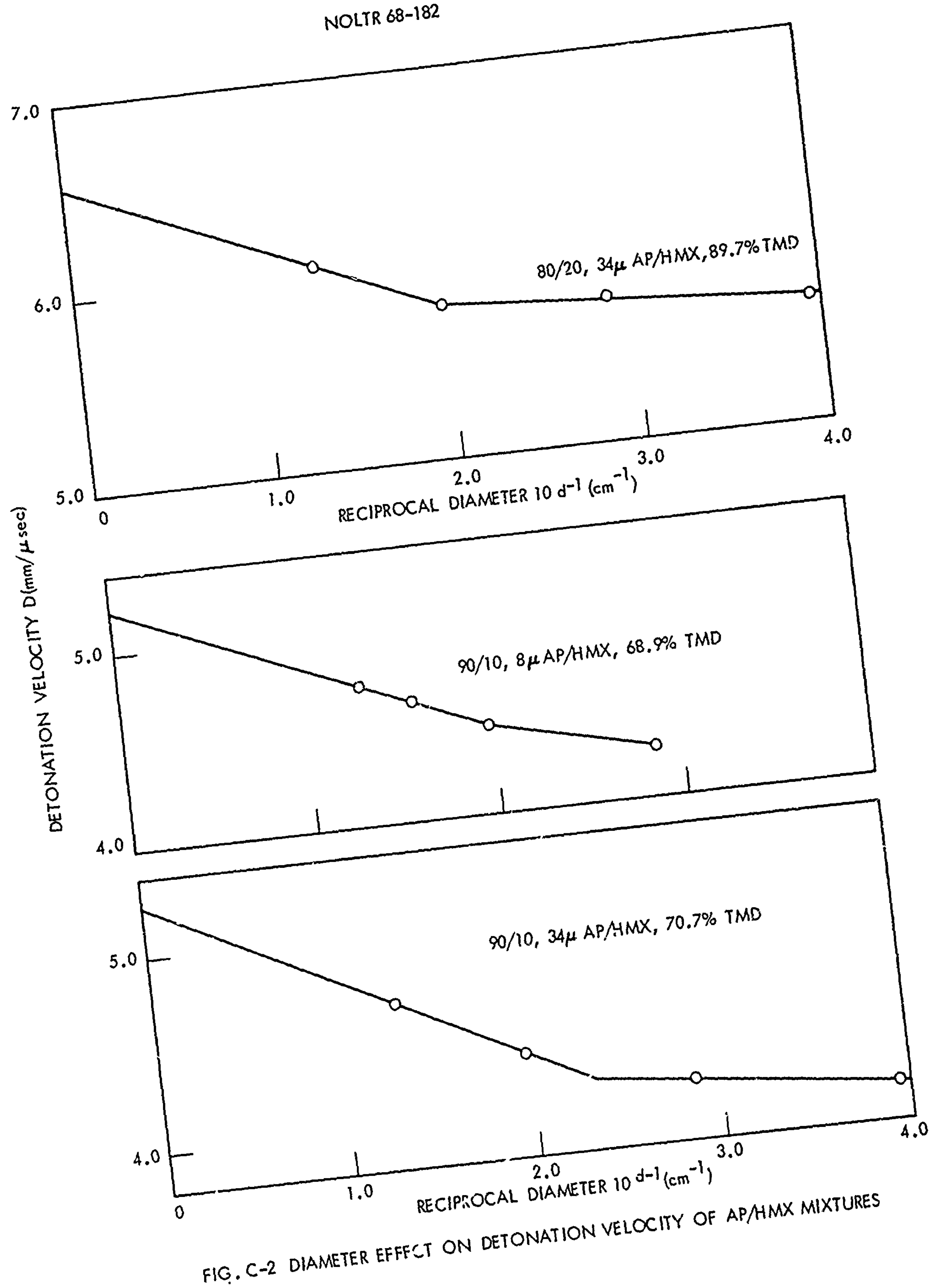

FIG. C-2 DIAMETER EFFECT ON DETONATION VELOCITY OF AP/HMX MIXTURES

TABLE C1

PRELIMINARY UNCORRECTED SHOT DATA ON MIXTURES OF AP/HMX

Shot No.	AP	HMX	d cm	ρ_o g/cc	D mm/μsec		Shot No.	AP	HMX	d cm	ρ_o g/cc	D mm/μsec
					90/10 (ρ_v = 1.945 g/cc)							
455	N127	X586	2.54	1.3011	3.888	$(3.993)^a$	471	N127	X585	2.54	1.771	F, δ ~10 cm
457	↓	↓	3.50	1.3761	4.103		472	↓	↓	↓	1.761	F, δ ~10 cm
456	↓	↓	5.08	1.2881	4.179	$(4.322)^b$						
458	↓	↓	7.62	1.3481	4.596	$(4.641)^b$	473	N127	X586	2.54	1.731	4.645
							474	↓	↓	↓	1.731	4.528
462	N128	X586	3.50	1.3461	4.262							
465	↓	↓	5.08	1.3391	4.442							
463	↓	↓	6.35	1.3381	4.614							
464	↓	↓	7.62	1.3411	4.712							
			Av.	1.341								
					80/20 (ρ_v = 1.940 g/cc)							
492	127	X586	2.54	1.7411	5.623							
493	↓	↓	3.50	1.7431	5.735		485	N127	X586	2.54	1.701	5.502
494	↓	↓	5.08	(1.7581)	5.870	$(5.785)^c$	486	↓	↓	↓	1.701	5.405
495	↓	↓	3.72	1.7391	6.053		504	↓	↓	↓	1.791	5.872
			Av.	1.741			505	↓	↓	↓	1.861	5.987

HMX, X585, average particle size of 640μ by sieve analysis.

HMX, X586, average particle size of 14μ by sieve analysis.

AP, N127, 28μ   AP, N128, 7.8μ.

a Corrected to $\rho_o = 1.376$ g/cc

b Corrected to $\rho_o = 1.376$, same slope used.

c Corrected to $\rho_o = 1.74$ g/cc

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13. ABSTRACT

Work with finely ground AP led to the infinite diameter relationship

$$D_i(\text{mm}/\mu\text{sec}) = 1.146 + 2.576\,\rho_0$$

over the range $0.55 \leq \rho_0 \leq 1.0$ g/cc. D and ρ_0 are, respectively, detonation velocity and charge density. The quadratic mean error found was 0.040 mm/μsec. Several computations of D_i as a function of ρ_0 are summarized and compared with the experimental data. Estimated limits on the detonation temperatures are proposed.

Detonation velocity measurements were made on AP/H.E. mixtures containing 20% of HMX, PETN, and TNETB. They indicated an oxidation-reduction reaction for AP/HMX only. The AP in the other two mixtures contributed to the detonation velocity, but the additivity rule does not seem applicable to mixtures of AP with organic H.E.

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14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
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Ammonium perchlorate (AP)						
AP/HE mixtures						
Detonation velocity						
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TNETB, ideal detonation velocity						

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