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A STUDY OF ENERGY RELEASE IN ROCKET PROPELLANTS BY A PROJECTILE IMPACT METHOD

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ABSTRACT

A new technique has been developed for direct experimental measurement of detailed profiles of shock waves generated by projectile impact. The technique has made possible a clear definition of experimental requirements for generation of "square" waves in solid propellants.

Samples of granular ammonium perchlorate were subjected to square waves of measured durations and amplitudes, and the partly reacted residues were recovered for subsequent chemical analysis. The analytical procedures are discussed in some detail. The resulting data for decomposition of ammonium perchlorate are given as functions both of shock duration (8 to 21μsec.) and shock amplitudes (5 to 18 kbar). Extents of ClO_4^- decomposition range up to 14% but the extent of decomposition of NH_4^+ never exceeds 3%.

A laboratory-type composite propellant was also tested in a series of square-wave shock experiments. Threshold amplitudes for explosion were found and are given for several shock durations.

Plans for future work are briefly discussed.

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INTRODUCTION

This is the Second Annual Report on the subject program, covering the period from May 9, 1967 to May 9, 1968, written in lieu of the Seventh Quarterly Report.

The objective of the program is experimental measurement of rates of energy release in solid propellants subjected to strong shock waves. The method specifically developed for this study consists of impacting a propellant sample by a high-velocity projectile fired from a gun in such a way that both the amplitude and the duration of the shock wave are known and controllable over appreciable ranges. During the first year of the program a successful method was developed for impaction and subsequent non-destructive collection of the sample. Shocked, partly reacted samples were analyzed chemically to determine the extent of reaction which occurred under exposure to shock waves of known amplitudes, and preliminary analytical data were reported. Problems attending the generation of controlled shock waves and the non-destructive recovery were also discussed in detail in the First Annual Report.

During the second year of the program, progress has been made along three major lines of development. First, a new technique has been developed for direct experimental measurement of shock wave pressures in the range required by this program, i.e., up to about 18 kbar. This technique, utilizing a resistance gauge, has also revealed the detailed shape of the shock wave profile, and thus enabled us to define clearly the experimental requirements for generation of square waves. (Ref. 1 gives the scientific background concerning the shape of the shock wave.) Second, several series of shots have been fired, in which samples of pure ammonium perchlorate were exposed to square waves, recovered after exposure and analyzed chemically. These tests have generated a fairly extensive set of analytical data, and have thrown light on the applicability of several analytical techniques. Third, samples of a fuel-rich laboratory propellant

(ammonium perchlorate plus polyethylene) have been brought to explosion by exposure to square waves of varying pressures and durations. The results show well-defined explosion thresholds as functions of both shock pressure and duration.

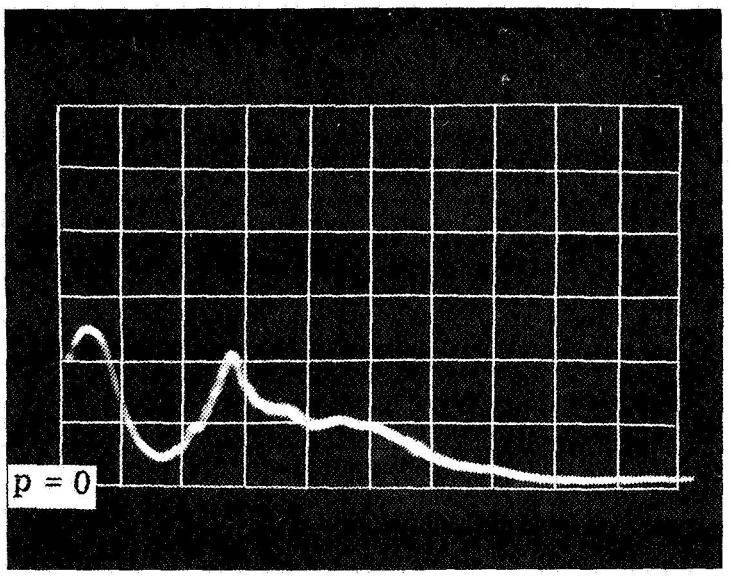
These three progress areas will now be discussed under separate headings.

I. WAVE SHAPE STUDIES

A detailed description of our high-amplitude wave shape studies by means of a carbon-resistor gauge is found in Reference 2. Only an abbreviated account and conclusions will be given here.

The carbon gauge is imbedded in a polyvinyl dichloride target at the normal location of the sample in our regular shots. The target is then placed inside a tubular target holder made of metal. One of the more significant results of these gauge tests is that the quality of this metal holder is very important. Figure 1 shows the oscilloscope record of a shot in which the target was placed inside a target holder made of mild steel, the inner diameter of which had been slightly enlarged in previous shots. Thus the lateral confinement of the target in this shot was not quite rigorous, and the gauge recorded a major rarefaction. The design of the target holder was then improved as shown schematically in Figure 2. The hardened steel in the new design is sufficiently strong to withstand shock pressures up to at least 18 kbar without any permanent deformation and with very little elastic deformation. Photographs of the disassembled and assembled target holder are shown in Figures 3 and 4. Thus the target is now rigidly confined, with the result that the gauge (or the sample) experiences only the passage of a single square wave, a most desirable experimental condition. A trace of the improved shape is reproduced in Figure 5.

Three important conclusions follow from these experiments. First, it has been shown that the carbon resistor gauge is a reliable instrument; it reproduces quantitatively the shape of the shock wave for periods up to at least 50μsec. For example, oscilloscope records obtained with the hardened-steel confinement (see Figure 5) always show a minor rarefaction which we believe to be caused by a slight elastic expansion of the steel. The rarefaction always occurs at 4μsec (within a fraction of a microsecond) after the initial arrival of the shock wave. Similarly, the small annular clearance between the polyvinyl dichloride target and the metal wall in imperfectly confined target assemblies



NOTE: Sweep Rate 0.2 cm/μsec;
Vertical Gain 0.1 v/cm.

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Figure 1. Oscillogram Obtained from the Carbon Resistor Gage upon Impact of a 0.72-Inch PVDC Projectile onto a PVDC Target with Delayed Lateral Confinement.

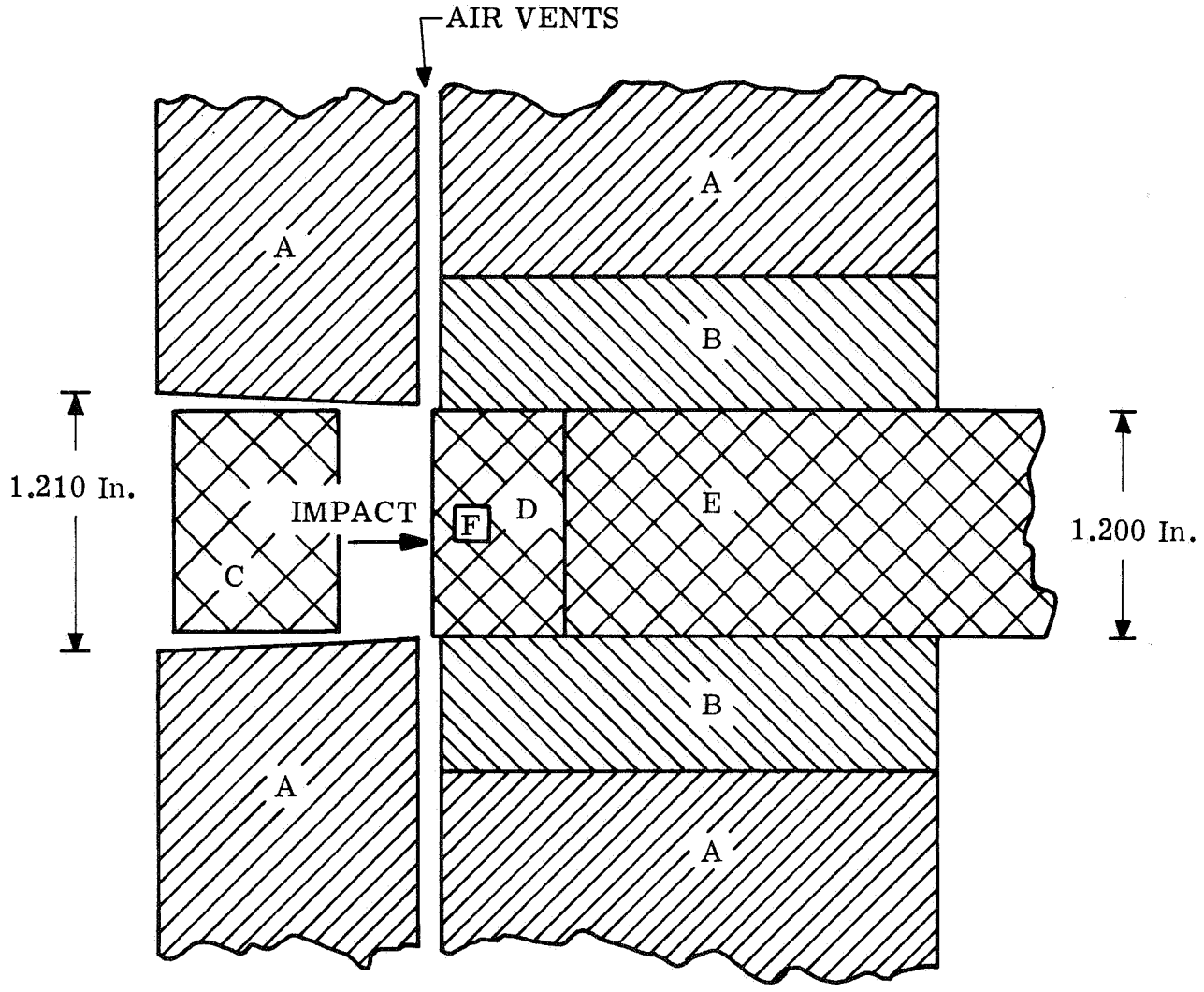
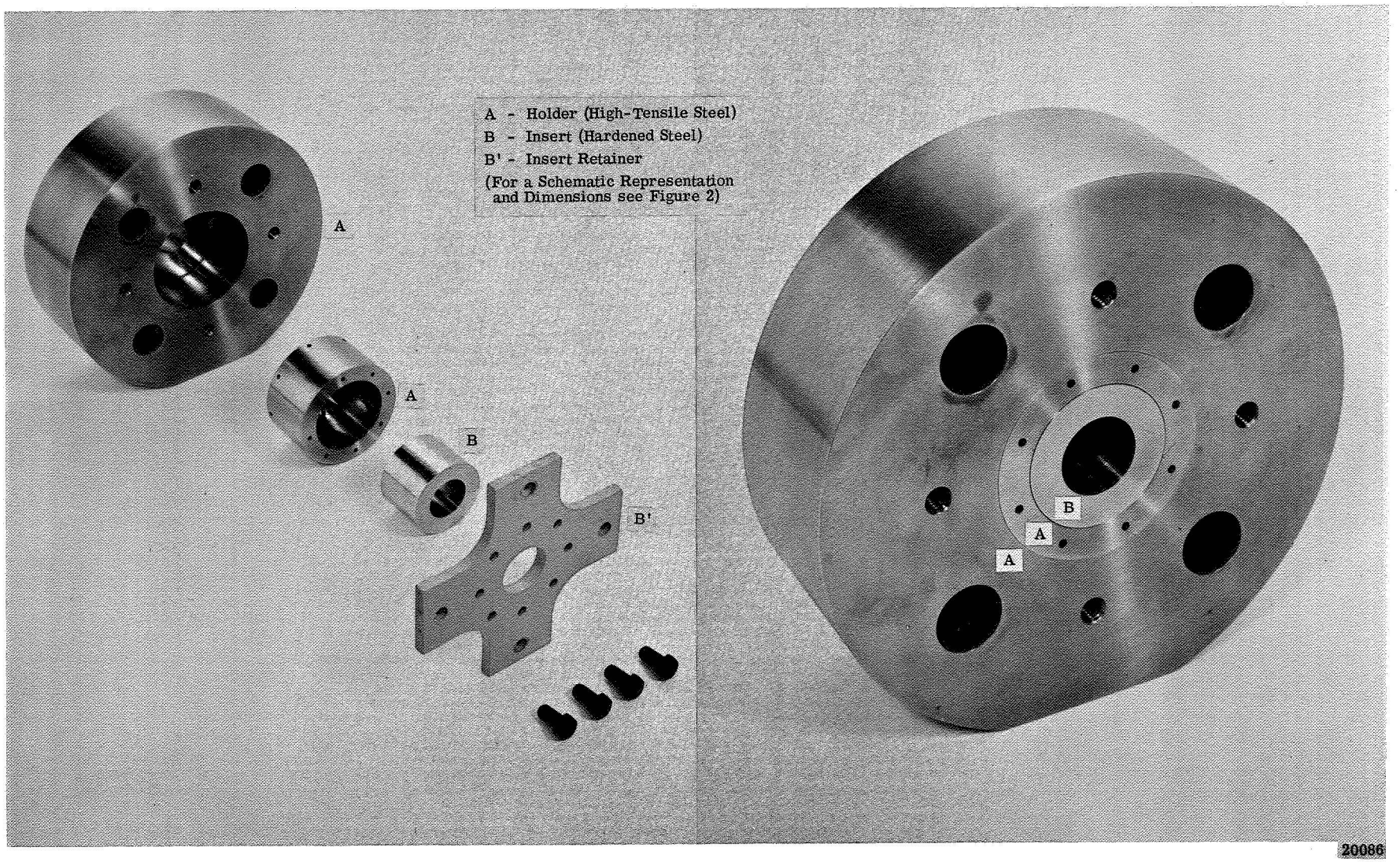


Figure 2. The Impact Experiment



Disassembled Target Holder

Assembled Target Holder

Figure 3. The Disassembled and the Assembled Target Holder Viewed from the Downstream (Exit) End.

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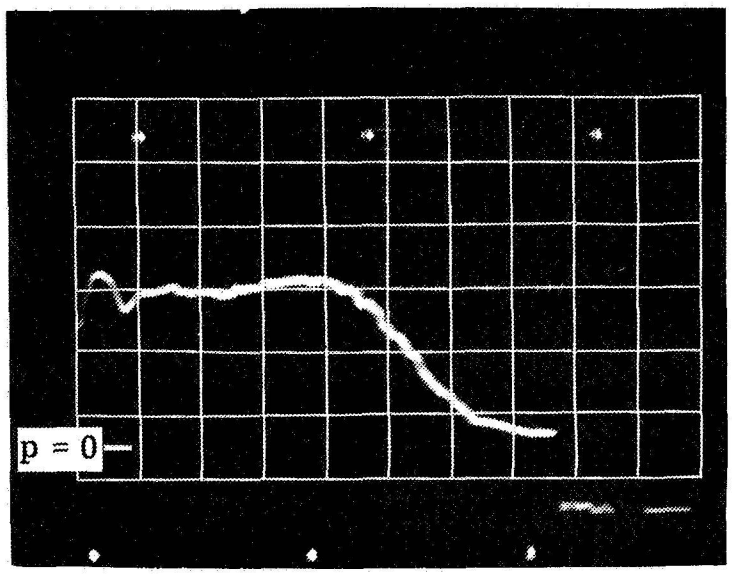
Figure 4. View of the Gun Muzzle with the Target Holder Attached.



NOTE: Sweep Rate 0.2 cm/μsec;
Vertical Gain 0.1 v/cm.

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Figure 5. Oscillogram Obtained from the Carbon Resistor Gage upon Impact of 1.25-Inch PVDC Projectile onto a Laterally Confined PVDC Target.

(see Figure 1) always gives an accurately reproducible wave pattern in replicate experiments. The bottom of the major rarefaction wave always occurs 8μsec after the arrival of the shock wave, again with reproducibility of a fraction of a microsecond, whereupon the pressure returns almost to the initial peak value. Furthermore, after the entire quantitatively reproducible sequence of events -- the first peak, the deep rarefaction in which pressure drops by a factor of three or four, the second steep increase by almost the same factor -- the oscilloscope trace settles to the original zero line. We conclude therefore that the gauge follows the pressure history even under conditions of widely and rapidly fluctuating amplitudes.

Second, it has been shown that, if the plastic target with the imbedded sample is indeed laterally confined, the sample will be exposed to a square wave as desired in our experimental technique and as predicted by the theory. Both the shock amplitude and duration are in excellent agreement with theoretical prediction.

Third, it has been found that the extent of ammonium perchlorate decomposition obtained with the new (hardened-steel) design is of the same order of magnitude but higher than that found previously under equivalent shock amplitudes. This can be seen by comparison of our new AP decomposition data, reported in section IIA below, with the data previously reported in Reference 1.

II. ANALYSIS OF AMMONIUM PERCHLORATE SAMPLES

Three series of projectile-impact tests were run on samples of pure ammonium perchlorate (AP). AP samples, weighing 0.31-0.34 gm, were granular material with average grain diameters of 15 microns, pressed to about 1.7 gm/cc density. Targets were rigidly confined, having been force-fitted into the hardened steel target holder, as shown in Figure 2. In these three series the impacting projectiles were 0.480", 0.720" and 1.250" long respectively, corresponding to shock durations of 8, 12, and 21μsec. Periodic control tests were also run with carbon-resistor gauges, which ascertained that shock-wave profiles were "square" as shown in Figure 5.

Shocked, partly reacted AP samples were examined in three ways: by quantitative chemical analysis for the ClO_4^- ion; by quantitative chemical analysis for the NH_4^+ ion; and by direct weighing of the retrieved residue. These tests will be described now.

A. The Perchlorate Ion Analysis

Since our technique involves difference measurements between the amount of AP originally present in the sample and the amount left after exposure shock, and since this difference is never very large (probably never more than 15%), accurate analysis for residual AP is difficult. Of the several potentially applicable methods for ClO_4^- found in the literature, only the reaction of ClO_4^- with tetraphenyl arsonium chloride has been found useful. A perchlorate-specific electrode was tried, but was found to lack sufficient accuracy. A method based on decolorization of a copper pyridinium complex proved over-sensitive to time and temperature. Direct weighing of AP washed from the target was unsuccessful because of losses during solvent evaporation and is not specific for perchlorate. Reduction of AP with measured excess of a titanium reagent followed by titration of excess reagent was not tried, because it is also not specific for ClO_4^-. However, such reduction may prove useful for determination of total residual chlorine, which may also shed light on the cause of discrepancy between the results of ClO_4^- and NH_4^+ analysis (see Section IV).

Shocked AP samples were therefore analyzed for perchlorate ion by a conductometric titration procedure. Each sample was washed from its plastic target and diluted to a standard volume. Aliquots of this solution were then titrated with a standard solution (0.01 M) of tetraphenyl arsonium chloride. In the conductometric endpoint procedure, the conductance of the solution is measured following incremental additions of titrant. The conductance values are plotted against corresponding volume of added reagent, and the equivalence point is indicated by a change in slope of the resulting linear plot. This analysis gave results which were reproducible to $\pm 1\%$ with pure AP, but which were somewhat less reproducible with partly decomposed AP samples. An alternative,

gravimetric, procedure was attempted using the same reagent. In this procedure, tetraphenylarsonium chloride is added in excess to the perchlorate sample and the resulting precipitate is filtered, washed and weighed. The method gave consistently high results and was found to be generally unsatisfactory.

AP decomposition data from the conductometric titration procedure are plotted in Figures 6, 7, and 8. These are raw data expressed as percent decomposition versus impact velocity for 0.480, 0.720 and 1.250-inch projectiles respectively. The curves are reasonably well defined, although some scatter is evidenced in the data for the 0.720-inch projectiles.* The persistent analytical problems stem from the attempt to measure the relatively small changes in total recovered perchlorate due to decomposition.

It was previously suggested[1] that the impact shock ignites the surface of individual grains of AP within the body of the sample. Grain surfaces then regress and flame spreads as a function of shock pressure p, during the shock duration τ, whereupon the reaction is quenched by the arrival of the rarefraction wave. If this is true, then the linear regression rate, R, can be written:

$$R = B\ p^{\alpha} \tag{1}$$

and the amount, n, reacted under shock of duration τ will be:

$$n = A\ p^{\alpha}\tau \tag{2}$$

where A and B are constants. A plot of log n/τ vs log p should give a line of slope α. This function is plotted in Figure 9, a composite plot for all three sets of data. A detailed account of the manner in which impact velocities in Figures 6, 7, and 8 are translated into shock pressures is given in Reference 1. The correlation is not bad except for a few stray points. The value of α is high (>2). This is not surprising in view of the fact that the area of the internal burning surface is likely to increase with pressure.

*An additional set of four shots with 0.720-inch projectiles, not included in Figure 7, produced stray results. These were all fired on the same day and are presumed to reflect a systematic error in weighing, pressing, velocity measurement, or analysis. The data are: 2180 fps, 3.0% reacted; 1865 fps, 5.9%; 2180, 7.1%; and 2180 fps, 2.8%.

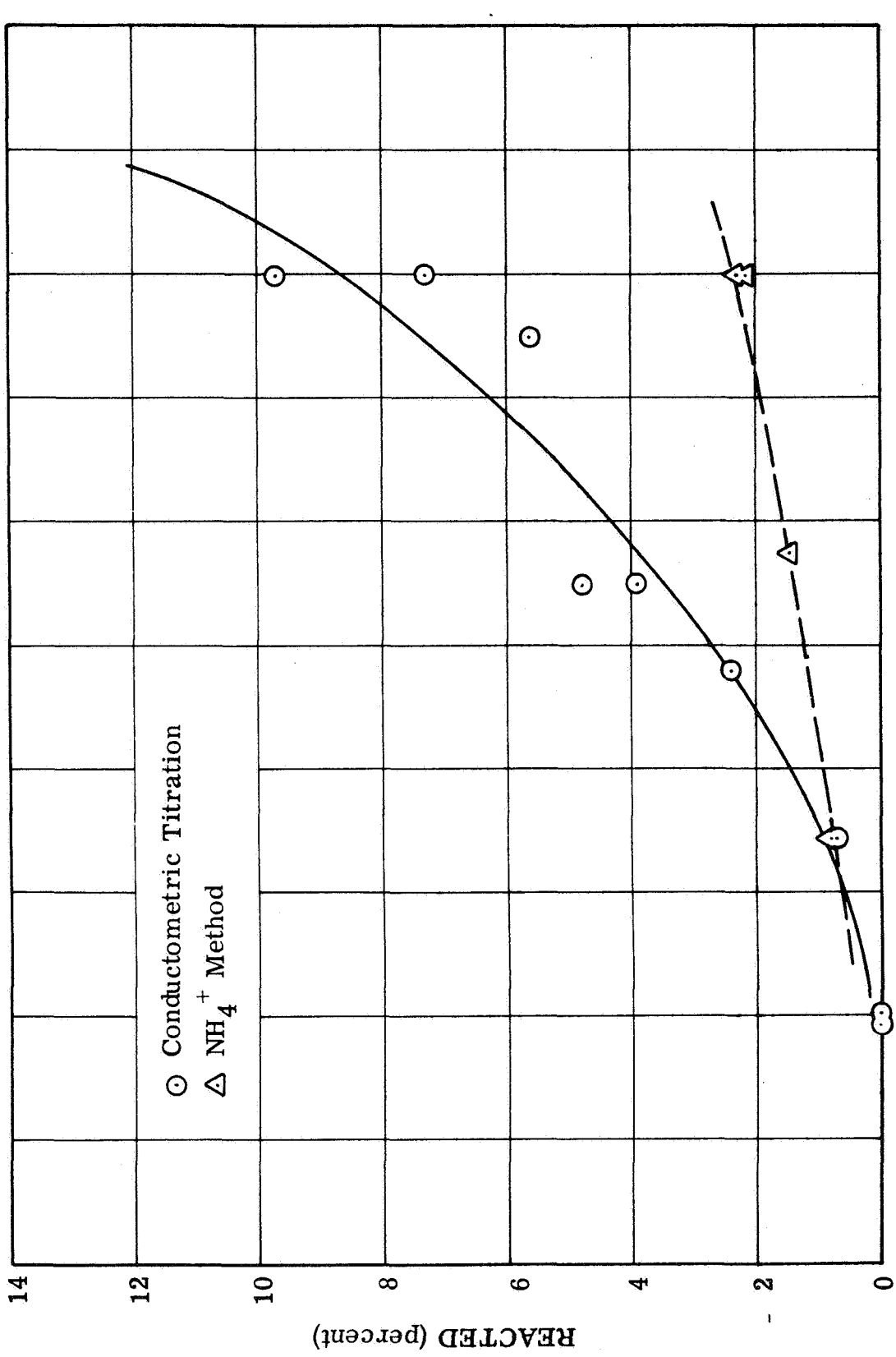

Figure 6. Percent Reaction Versus Impact Velocity, 0.480-Inch Projectiles.

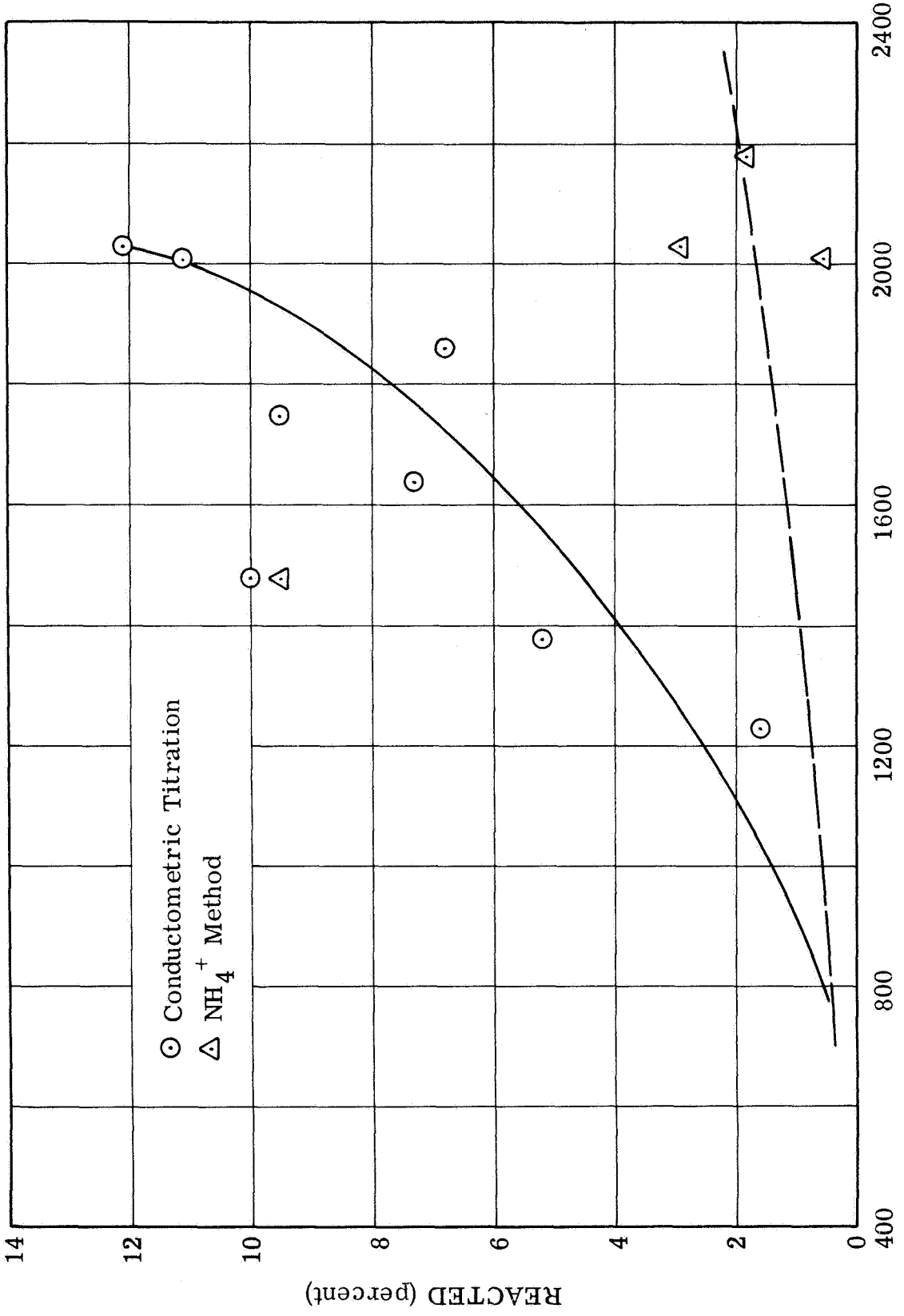

Figure 7. Percent Reaction Vs. Impact Velocity, 0.720-Inch Projectiles.

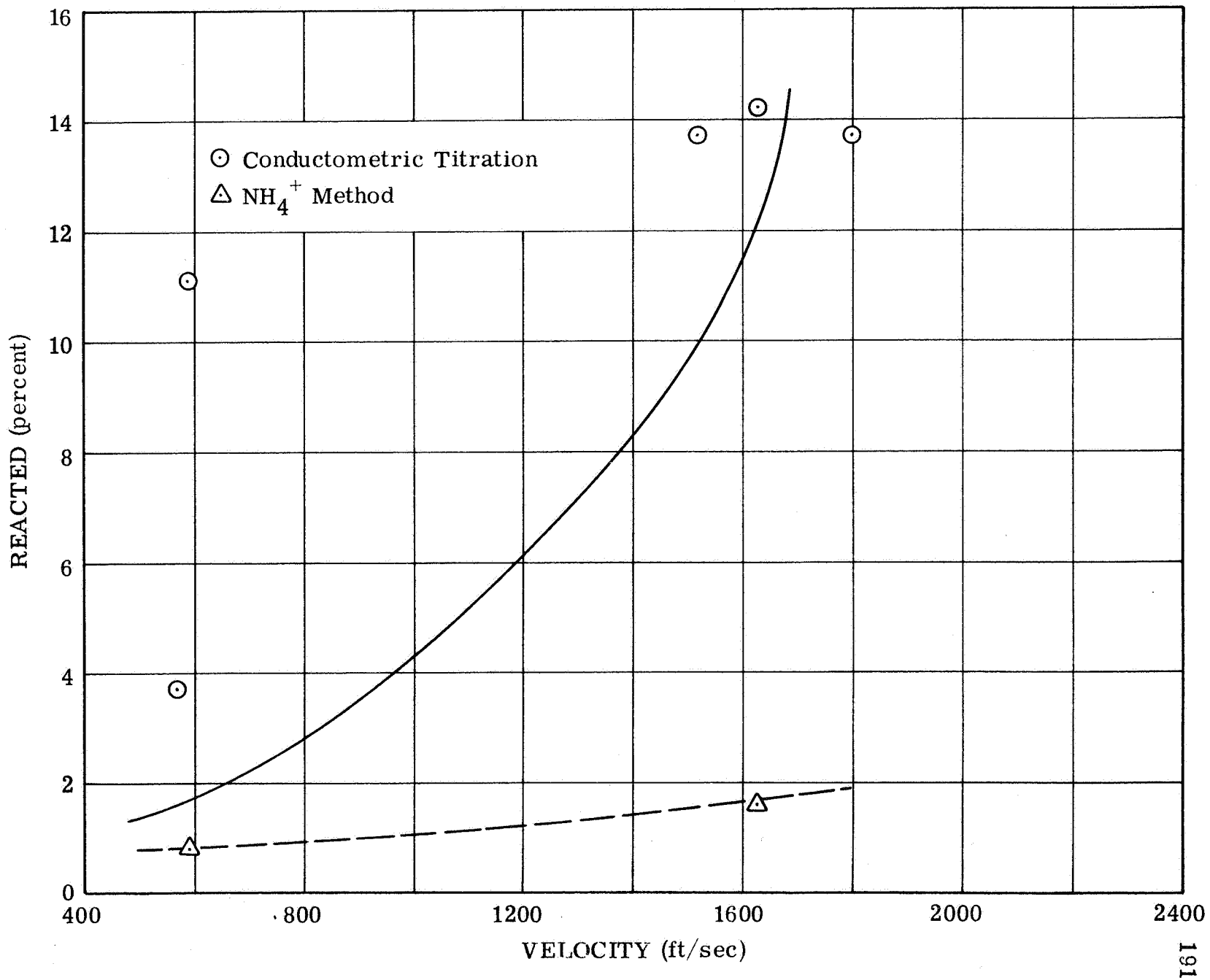

Figure 8. Percent Reaction Versus Impact Velocity, 1.250-Inch Projectiles.

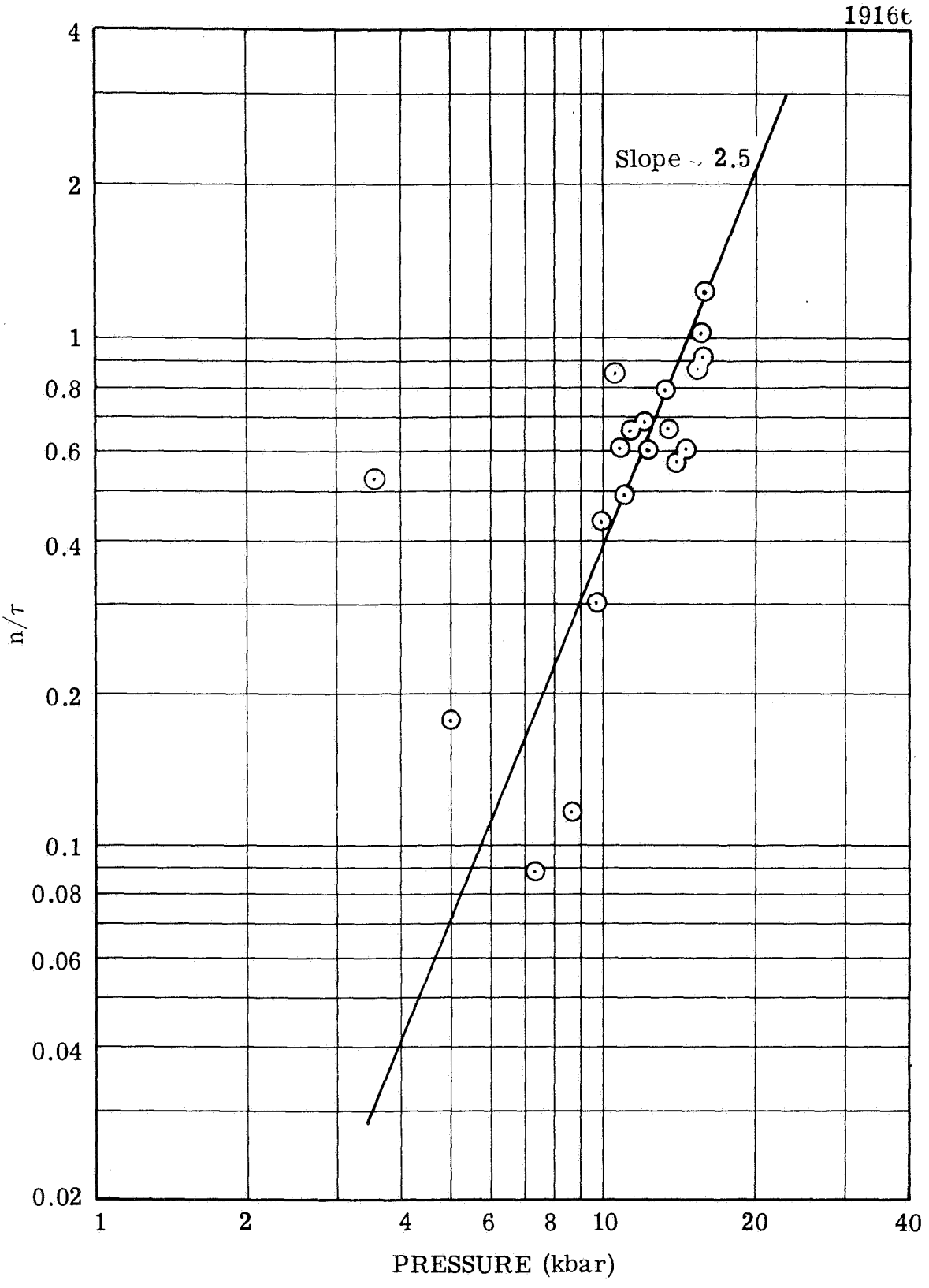

Figure 9. Composite Plot of Log n/τ Versus Log p.

B. The Ammonium Ion Analysis

The chemical analysis of recovered AP was also approached by measuring the quantity of ammonium ion in the shocked samples. The method is known as the formol titration and is based on the reaction of ammonium ion with formaldehyde to liberate an amount of acid equivalent to the ammonium ion initially present. The liberated acid is subsequently titrated by a simple acidimetric procedure.

A relatively few samples were analyzed by this method and the results are shown in Figures 6, 7, and 8 along with the conductometric data. The results are seen to be consistently lower than those from the perchlorate analysis, implying that decomposition of the perchlorate ion proceeds to a greater degree than that of the ammonium ion when AP is subjected to impact.

C. Weighing of Shocked AP Samples

Several shocked AP samples were carefully removed from the plastic target, and weighed. This test was not done routinely, because it is usually difficult to separate quantitatively the sample from the plastic.

The results, compared with the original weight of the sample, show that the mass loss is only 0-3%, always substantially less than the equivalent perchlorate loss found by the conductometric method (see Section IIA).

D. Discussion of Analytical Results

The implication of the results described in Sections II A, B, and C is that under these extremely high pressures the perchlorate ion decomposes to a greater extent than the ammonium ion, and also that a substantial portion of decomposition products is retained within the solid sample. It also appears that decomposition of AP does not proceed to thermodynamic equilibrium products, which would be largely HCl, H_2O, O_2, and N_2.

No firm explanation can be offered for these facts. It is possible that perchlorate undergoes stepwise reduction to chlorate, chlorite, hypochlorite, or chloride ions. If so, the chlorine-containing intermediates may interfere with the ClO_4^- analysis causing the relatively large scatter of data, reported in Section IIA. It is also possible that some decomposition products (e.g. HCl, Cl_2, H_2O, or NH_3) become adsorbed on the large internal surface of the partly decomposed solid sample. It is hoped that future work will shed light on these problems.

III. TESTING OF A FUEL-RICH PROPELLANT

A laboratory propellant was prepared by careful mixing of the AP powder, used in tests described in Section II, and a polyethylene (PE) powder with average particle diameters in the range between 10 and 15 microns. The mixture was AP/PE (87/13) by weight, i.e. it was roughly stoichiometric to H_2O, CO, HCl, and N_2. Testing of such a mixture was desirable, because the mixture is physically quite similar to pure pressed AP samples, thus linking the study to our previous work, but chemically very much akin to practical composite propellants. In particular, the mixture is much more energetic than pure AP so that its combustion yields very much higher temperatures and very much more reducing gaseous products.

The testing procedure was the same as in the case of pure AP (Section II), except that the samples were much larger, 1.34 ±0.01 gm. Two slightly different pressed densities were used, corresponding to 86 and 89% of voidless values. Three projectile lengths were used, corresponding to shock-durations τ of 8, 12, and 21μsec. Shock pressures ranged from 6.0 to 15.5 kbar. Targets were again force-fitted into hardened steel, so that samples were exposed to "square" waves.

In 13 out of a total of 28 shots the chemical reaction in the sample was sufficient to break the plastic casing. The shock amplitude at which this occurs is well-defined, and it varies both with shock duration τ and with the pressed density, i.e. porosity, of the sample. "Explosion" thresholds obtained in this way are plotted in Fig.10. Variation of threshold

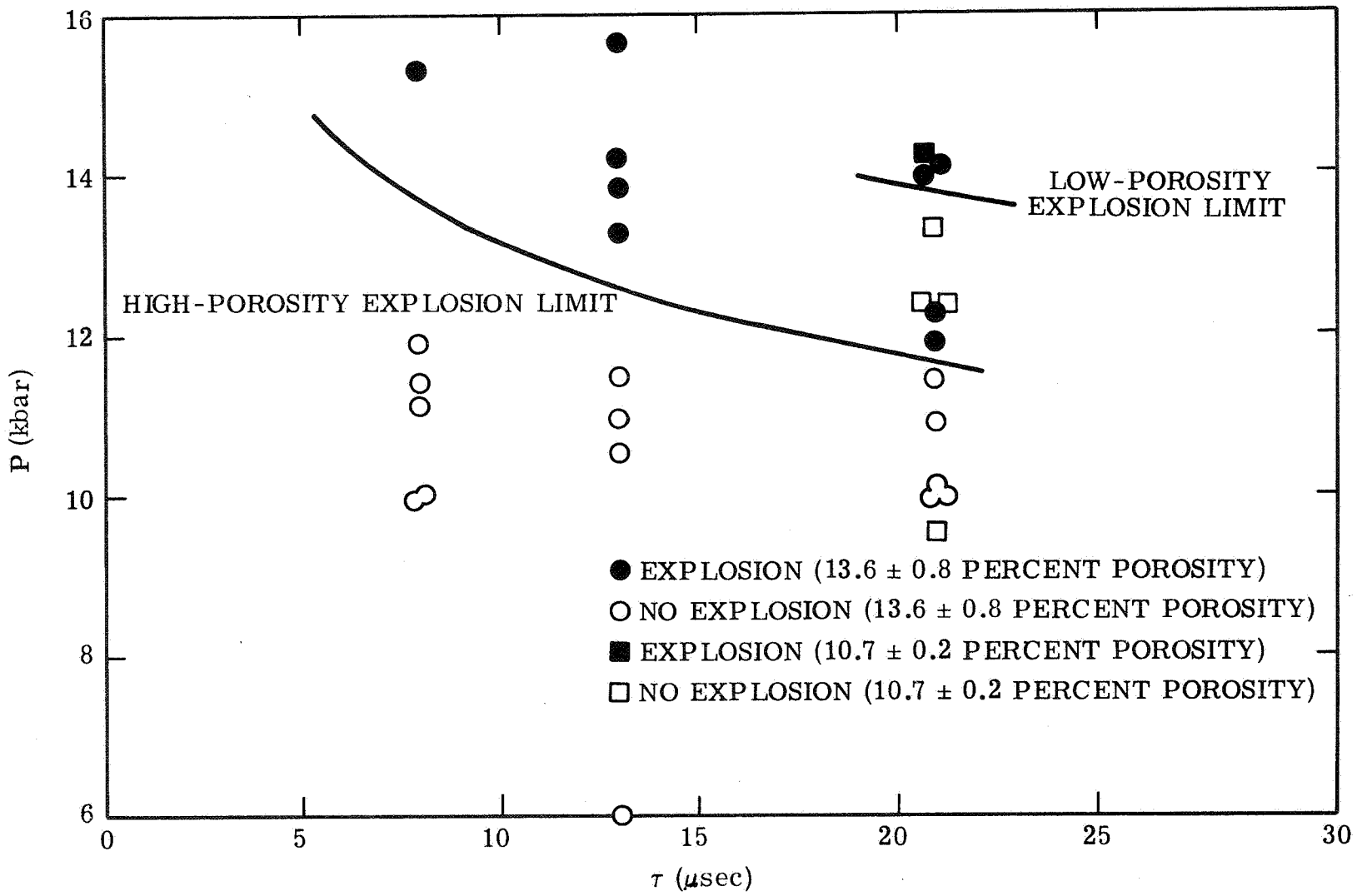

Figure 10. Square-Wave Shock Testing of AP/POLYETHYLENE (87/13).

pressure with τ and with porosity follows the expected pattern.

The existence of thresholds indicates that the decomposition reaction induced by our projectile impact method is reproducible. It also suggests that the amount of gas evolution, in the pressure range of our experiments, is substantially more for the AP/PE mixture than it is for pure AP samples. However, large samples of pure AP (1-1.5 gm) will have to be tested to verify the second conclusion.

IV. PLANS FOR FUTURE WORK

Another year's effort under a new contract has begun on September 25, 1968.

In the new effort better accuracy will be sought for chemical analysis of the extent of ClO_4^- decomposition under calibrated shock experiments. We propose to do this first simply by increasing the sample size. If this does not improve the reproducibility, other analytical techniques will be attempted. In addition, confirmatory evidence about the suspected formation of chlorine-containing intermediates will be sought by analysis of total chlorine contained in the shocked sample. Similar techniques will be applied toward chemical analysis both of powdered AP/PE mixtures, and of a service propellant. Theoretical implications of new experimental data covering the development of detonation will be examined.

REFERENCES

1. A. Maček and R. L. Durfee: "A Study of Energy Release in Rocket Propellants by a Projectile Impact Method." Paper 68-150, 1968, AIAA. See also the First Annual Report on the Program NAS1-6200, Atlantic Research Corporation, June 9, 1967.

2. R. L. Durfee and A. Maćek: "Generation and Measurement of High-Amplitude Square Shocks in Solids." AIAA Journal 6, 977 (1968).