



Service through Science

GPO PRICE \$ \_\_\_\_\_

CFSTI PRICE(S) \$ \_\_\_\_\_

NASA Contractor  
Report No. 66395

Hard copy (HC) 3.00

Microfiche (MF) .65

ff 653 July 65

A STUDY OF ENERGY RELEASE IN ROCKET PROPELLANTS

BY A PROJECTILE IMPACT METHOD

by

Andrej Maček and Robert L. Durfee

Research Division  
Atlantic Research Corporation  
Alexandria, Virginia

Distribution of this report is provided in the interest of information exchange. Responsibility for its contents resides in the author or organization that prepared it.

FIRST ANNUAL REPORT ON THE PROGRAM NAS 1-6200  
REPORTING PERIOD: May 9, 1966 - May 9, 1967

**N67-35223**

FACILITY FORM 602

(ACCESSION NUMBER)

33

(PAGES)

(THRU)

1

(COP)

CR-66395  
(NASA CR OR TMX OR AD NUMBER)

27  
(CATEGORY)

June 9, 1967

ATLANTIC  RESEARCH

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

by

Andrej Maček and Robert L. Durfee

Research Division  
Atlantic Research Corporation  
Alexandria, Virginia

Distribution of this report is provided in the  
interest of information exchange. Responsibility  
for its contents resides in the author or  
organization that prepared it.

FIRST ANNUAL REPORT ON THE PROGRAM NAS 1-6200  
REPORTING PERIOD: May 9, 1966 - May 9, 1967

June 9, 1967

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

by

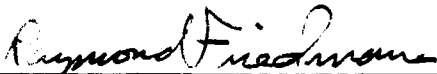
Andrej Maček and Robert L. Durfee

Research Division  
Atlantic Research Corporation  
Alexandria, Virginia

FIRST ANNUAL REPORT ON THE PROGRAM NAS 1-6200  
REPORTING PERIOD: May 9, 1966 - May 9, 1967

Working Group: Andrej Maček, Chief Investigator  
Robert L. Durfee  
Elmer W. Williams

Approved by:

  
Raymond Friedman  
Vice President

June 9, 1967

ABSTRACT

This is the first Annual Report on the subject program, covering the period of May 9, 1966 to May 9, 1967, written in lieu of the Fourth Quarterly Report.

The objective of the program is experimental measurement of the 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 an appreciable range. A successful method has been developed for non-destructive collection of the sample after the passage of the shock wave, and the shocked partly reacted samples have been chemically analyzed for the extent of reaction which occurred under exposure to known shock waves. Problems attending the generation of controlled shock waves and the non-destructive recovery are discussed in some detail in this Report.

The materials studied so far by this method were pressed samples of pure granular ammonium perchlorate and pressed mixtures of ammonium perchlorate/polyethylene powders. The upper limit of shock amplitudes studied so far in the program has been about 20 kbar. The shock durations were in the range of about 10 to 20 $\mu$ sec. The quantitative decomposition data on ammonium perchlorate are consistent with a model of high-pressure surface burning of individual grains in the pressed sample, in which only a certain fraction of the total grain area is ignited by the shock wave.

This program is sponsored by the NASA Langley Research Center, and is technically monitored by Dr. Andrew R. Saunders. A second year of the program is in progress now.

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	
I. INTRODUCTION . . . . .	1
II. TAILORING OF THE WAVE SHAPE. . . . .	2
III. SHOCK-HUGONIOTS AND PRESSURE DETERMINATION . . . . .	5
IV. EXPERIMENTAL ARRANGEMENT . . . . .	6
V. PRELIMINARY EXPERIMENTS. . . . .	7
VI. ANALYSIS OF SHOCKED SAMPLES . . . . .	10
VII. RESULTS . . . . .	11
A. Pure Ammonium Perchlorate ( $\rho_o \approx 1.7$ gm/cc). . . . .	11
B. Ammonium Perchlorate-Lithium Fluoride Mixtures ( $\rho_o \approx 1.7$ gm/cc). . . . .	12
C. Ammonium Perchlorate-Polyethylene (97/3) Mix- tures ( $\rho_o \approx 1.7$ gm/cc). . . . .	13
D. Ammonium Perchlorate-Polyethylene (90/10) Mixtures ( $\rho_o \approx 1.7$ gm/cc) . . . . .	13
E. Low-Density Ammonium Perchlorate ( $\rho_o = 1.2$ gm/cc). . . . .	13
VIII. DISCUSSION . . . . .	14
APPENDIX A	
APPENDIX B	
REFERENCES	
FIGURES	

## I. INTRODUCTION

A major gap in our understanding of the processes of initiation and propagation of explosions and detonations is caused by the lack of knowledge of reaction kinetics under appropriate conditions of very high pressure. The bridging of that gap is an essential prerequisite of progress in solving some of the most important problems in technology of propellants and explosives: transition from shock to detonation, transition from slow burning to detonation, explosion in rocket motors, and prediction of critical diameters for detonation. All of these demand the answer to one fundamental question: How rapidly does the fuel (propellant or explosive) react under a specified shock regime? No direct measurements of such rates are available, so that a common way of dealing theoretically with the problem has been the assumption of a homogeneous decomposition process based on low-pressure, usually subatmospheric, decomposition rate measurements. Such data, obtained under conditions enormously different from those prevailing under shock-loading, are essentially unsatisfactory. A somewhat more realistic approach, which applies to granular materials with known internal surface, is to estimate the rates of energy release on the basis of measured low-pressure surface-burning data extrapolated to high pressures in such a way that they are consistent with estimated detonation reaction times (1,2,3). However, even this approach involves a long extrapolation (from 100 to  $10^4$  or even  $10^5$  atm) based on an Arrhenius-type equation in which the crucial value of surface temperature must be estimated. Furthermore, there is no reasonable way of estimating the very important effective surface burning area during the transient shock-initiation stage. Evidently, a direct measurement of rates of energy release is becoming more and more desirable.

Two things are indispensable in any attempt at such measurements: generation of a shock wave of known duration and known (preferably but not necessarily uniform) pressure, and determination of the extent of chemical reaction which has taken place under such known shock-loading. The objective of the program described herein is experimental measurement of the

rates of energy release in solid propellants subjected to strong shock waves. The upper limit of the shock amplitudes studied so far in the program has been about 20 kbar.

The method specifically developed for this study is to impact a target assembly containing the propellant sample by a high-velocity projectile fired from a gun. This method differs from the previous attempts in two ways. First, the design of the projectile and the target is such that both the amplitude and the duration of the shock wave are known and controllable over an appreciable range. Second, the sample is recovered and analyzed after the test. The newly developed technique requires: (a) closely controlled geometry of the test components; (b) accurate matching of shock-impedances of the sample and its surroundings; (c) provision for non-destructive collection of the sample after the passage of the calibrated shock wave; and (d) quantitative chemical analysis of the shocked, partly reacted sample.

## II. TAILORING OF THE WAVE SHAPE

The impact of a rapidly travelling projectile upon the surface of a target will cause a strong shock wave to be propagated through the target material. The pressure-time history of any layer of the target sufficiently removed from the boundaries to be undisturbed by lateral rarefactions will be determined by the length of the projectile, by the velocity distribution within the projectile at the time of and for some time after the impact, and by the shock-compressibilities of both the projectile and target materials. An especially simple situation obtains if the mass velocity distribution within the projectile is uniform; this is true of a projectile fired from a gun, as in the present program, in contradistinction to explosively driven projectiles which travel in a pulsating fashion. In the simple case of uniform mass velocity distribution, the central portion of the target, for which one-dimensional shock parameters are valid, will be exposed to a "square wave" of constant amplitude  $P$  determined by the impact

velocity, and of duration  $\tau$  determined by the length of the projectile. Details of such an impact are given in Appendix A.

An idealized sketch of the wave-shaping experiment is shown in Fig. 1. Both the projectile and the target are made of the same material, chosen to match closely the shock-impedance of the propellant sample (see Section III), so that there is no spalling and virtually no reflections at the boundaries of the sample which could perturb the chemical kinetic measurements within the material. It is quite important that this be so, because recent work in shock-testing of explosive materials has revealed that boundary discontinuities - whether they cause shocks or rarefactions - may have a pronounced effect on the reactivity of the sample (4). The sample will be exposed to an accurate square wave if the geometry of the test is such that no lateral rarefactions can reach the sample until the rear-rarefaction has reached the projectile-target boundary. Assuming now that both compression and rarefaction waves travel at the same velocity  $U$  which is a function of pressure only, and keeping in mind that the duration of the shock wave is determined by the length of the projectile,  $\tau = \frac{2L}{U}$ , one can immediately write down the geometrical requirements for generation of a square wave in the sample by impact of a projectile of diameter  $D$  (see Fig. 1):

$$\begin{aligned} a &\geq 2L \\ d &= D - 2a \\ \rho &\leq U\tau = 2L \geq a \\ b &\geq L \end{aligned}$$

The last of the four requirements,  $b \geq L$ , would apply only if the downstream end of the target were free. However, if this were so, the target, after being exposed to the square wave, would travel at high speeds and in a violently pulsating fashion, a highly undesirable feature which would not only present difficult deceleration and recovery problems, but it would also spoil the experiment by subjecting the sample to a sequence of tension and compression pulses. Hence the need for an energy absorber. The energy absorber, again, has to match the impedance of the target so that the shock



wave passes into it without discontinuities. The correct size of the absorber then allows it to carry away the excess kinetic energy, leaving the target quiescent after the passage of the square wave. If the impact were elastic and shock conditions downstream of the target remained one-dimensional, an energy absorber exactly matching the dimensions of the projectile would be appropriate (see Appendix A). This is obviously not true even in the idealized design shown in Fig. 1. However, we found empirically that long (several diameters) segmented absorbers give excellent results: a downstream length of the system, depending on impact velocity, then flies off, leaving the upstream portions quiescent.

In the experimental work so far (see Section IV) no effort has been made to use projectiles sufficiently short to give strictly square waves, i.e.  $L/D < 0.25$ . Rather, we chose to use longer projectiles, which give longer shock durations  $\tau$  at the expense of the flatness of the pressure wave, and to minimize the effect of lateral rarefactions by massive confinement in steel. Thus in the actual experiments reported below the shock profile remained flat for a time of at least  $a/U \approx 4\mu\text{sec} < \tau$ , whereupon the pressure decreased to lower levels. Estimates of the pressure decrease are given in Appendix B. The quantitative work so far was done with total shock durations  $\tau$  of either  $\approx 12\mu\text{sec}$  or  $\approx 21\mu\text{sec}$ .

While working with short projectiles may also entail practical ballistic problems, the choice not to use them was made primarily because of the nature of the chemical kinetic problem. We found early in the program that the extent of decomposition of pressed granular ammonium perchlorate induced by the passage of the shock wave increases strongly with  $\tau$ , but only weakly with  $P$ , so that very high impact velocities would be needed with short projectiles. Fortunately, the very reason for avoiding short projectiles and thereby causing departures from square wave shapes, namely the small pressure-dependence of decomposition rates, makes the experimental results insensitive to pressure variations.

### III. SHOCK HUGONIOTS AND PRESSURE DETERMINATION

The shock amplitudes  $P$  were determined by the familiar Hugoniot reflection method described briefly in Appendix B. The numerical data needed for the construction of the required shock Hugoniots were those of Coleburn (5) for polyvinylidene chloride (Saran) and the ammonium perchlorate data of Salzman *et al.* (3).

In the early part of the program Saran was used as the material for projectiles, targets, and energy absorbers. While this material was found to perform satisfactorily at low impact velocities, it shows its limitations at higher velocities: it cracks, it chars extensively (no doubt because of the air shock), and there is evidence of a slight reaction with ammonium perchlorate. Saran was therefore replaced by its isomer, polyvinyl dichloride (PVDC) which is much more resistant both physically and chemically. All of the quantitative data reported in Section VII were obtained with PVDC as the impedance-matching material.

No experimental shock-compressibility data are available for PVDC. However, its structure is very similar to that of Saran, and the density of the material used in our experiments,  $\rho_0 = 1.53$  gm/cc, is less than 5% lower than that of Saran used in Coleburn's experiments ( $\rho_0 = 1.60$  gm/cc). Therefore, to construct the shock Hugoniot of PVDC, we used the straight line fit of experimental  $U$  vs.  $u$  data for Saran (Fig. 2) and the density of PVDC. In view of the great similarity of the two materials the PVDC Hugoniot so constructed (Fig. 3) is probably as good as the experimental Saran data.

The propellants used so far in this program were pressed samples of pure ammonium perchlorate, of ammonium perchlorate with an inert additive (LiF), and of granular ammonium perchlorate/polyethylene mixtures. Except for a very few low-density shots, all of the samples were pressed to a relatively high density of about 1.7 gm/cc. A common Hugoniot for all these materials was therefore constructed on the same basis as that of PVDC, namely from the experimental Saran data corrected for the density difference (Fig. 3). This procedure introduces an error, whose magnitude can be esti-

mated as follows: When the same procedure is extrapolated all the way to the crystal density of ammonium perchlorate (1.95 gm/cc), the calculated pressures fall 12% below the measured values of Ref. 3. Since our extrapolation is not nearly so large, and since according to the Hugoniot reflection technique the boundary adjustment pressure between PVDC and the sample is about half-way between the two respective Hugoniots (see Appendix B), our pressure determinations for high-density samples should be accurate within a few percent. A plot of shock pressures in the sample of 1.7 gm/cc density, calculated on this basis, vs. impact velocity is shown in Fig. 4.

Estimates of Hugoniots for low-density pressed materials are much less accurate. In order to set a lower limit to the shock pressures in 1.2 gm/cc ammonium perchlorate samples, we used a "locked-solid" procedure (see Ref. 6), which assumes no resistance to compression up to the crystal density, and the experimental data (3) beyond that. The Hugoniot so constructed is also shown in Fig. 3.

#### IV. EXPERIMENTAL ARRANGEMENT

The gun was a 30.5 mm caliber smoothbore. The projectiles fired so far in the program were right circular cylinders machined out of a plastic (PVDC or Saran), 30.5 mm in diameter, and either 18.3 or 31.8 mm long. Two to five grams of a commercial gun powder were used to attain projectile velocities of 800-2500 ft/sec.

The main diagnostic piece of equipment was a high-speed Beckman & Whitley camera. This instrument records 220 frames on standard 33 mm film with minimum time of 28.6 $\mu$ sec between frames, and minimum effective exposure time of 0.75 $\mu$ sec per frame. Illumination at these high photographic speeds was provided by a special Beckman & Whitley Xenon flash lamp, which emits high-intensity light flashes of 2.7, 5.4, or 10.8 msec duration. The high-speed camera with diffuse backlighting by the Xenon flash proved very satisfactory both for observation of projectile orientations during flight,

and for projectile velocity measurements. The distance from the gun muzzle to the target was 18 cm. No tumbling or tilting difficulties were encountered.

The target and the energy absorber, both 30.5 mm in diameter (Fig. 5), were made out of the same material as the projectile. The cylindrical sample well, machined in the center of the target facing the gun, was 6.1 mm in diameter and 6.1 mm deep so that the mass of the sample at 1.7 gm/cc pressed density was about 0.3 gm. The entire target assembly (target with cap and energy absorber) was recessed into the target holder, steel or brass, so that both the target and the projectile were confined laterally at the instant of impact. The opening of the target holder facing the gun was slightly enlarged (to 31.0 mm diameter) so that the projectile could enter without contacting the metal face. The inner diameter of the holder then tapered down to the gun (and target) diameter over a length of 24.4 mm, so that the angle of the taper was extremely small. Measurement of the projectile velocities before and after passage through empty target holder showed that there is virtually no deceleration due to friction in this geometry.

The granular samples of pure ammonium perchlorate or ammonium perchlorate with additives (see Section VII) were pressed into the sample well at 16,000 psi. The pressed samples were protected from the air shock during impact by target caps 3.2 mm thick. The caps, made of the same plastic as the targets, were firmly glued (see Fig. 5).

## V. PRELIMINARY EXPERIMENTS

### A. Testing Series Performed at Exotech, Inc.

The first series of tests was done at the Exotech, Inc. facilities at Rockville, Maryland. The objectives of this series were: (a) Study of mechanical behavior of Saran and of pressed samples under high-pressure shock conditions. In order to distinguish mechanical damage due to shock from that due to chemical energy release, we ran duplicate shots with ammonium per-

chlorate and potassium chloride, an inert salt of virtually same crystal density. (b) Study of decomposition of pressed ammonium perchlorate at different impact velocities and different projectile designs.

This early work was done before the Atlantic Research Corporation facility (see Fig. 5) was constructed. The gun barrel and the projectile diameters were 20 mm. The gun range, including the barrel and the target, was evacuated to ca. 0.2 torr. The distance from the barrel to the target was 23 feet. Projectile velocities were measured by time intervals between the muzzle flash and impact on the target, determined with a signal from a solar cell, and a phonograph cartridge pickup respectively. Impact velocities ranged from 1150 to 1900 ft/sec, corresponding to a pressure range in Saran from 7.7 to 13.8 kbar.

Saran was used as the projectile and target material in all shots. It was found that the projectile length/diameter ratio had to be 0.8 or higher for stable flight in vacuum. The pattern of impact on the target was generally reproducible within about 2 mm so that a target diameter of 25 mm was necessary. Since the sample well, 4 mm in diameter and 8 mm deep, was always in the center of the target, the hits were generally somewhat off-center.

Two different projectile designs were used. In the first design, the L/D ratio of the projectile face was kept at the ideal low value of 0.2 (i.e. 4 mm length), but for ballistic purposes the projectile had a rather long tubular extension. This design correctly eliminates lateral rarefactions and thus generates a good square wave of  $\tau \sim 2.5\mu\text{sec}$ . However, following the passage of the square wave the sample experiences additional irregular pulses as parts of the tubular extension, whose mass unfortunately is comparable to that of the projectile face, collapse onto the target. In the second design, the projectiles were solid cylinders, either 14 mm or 16 mm long. In this geometry the duration of the shock wave is well defined, but one must expect that after a flat pressure plateau of a few microseconds, the pressure will decrease because of lateral rarefaction.

In this series of tests only qualitative indications of reaction in ammonium perchlorate were possible. There was mechanical loss of sample in every shot, because the energy-absorbing technique had not yet been developed. Thus no quantitative chemical analysis was possible.

Twenty-one shots were fired, twelve with ammonium perchlorate and nine with potassium chloride as test samples. The results of the series indicated that some ammonium perchlorate was decomposed at shock pressures somewhat below 10 kbar, and, furthermore, that the reaction was more pronounced with solid projectiles than with hollow ones. The series also yielded very valuable information toward the design of the Atlantic Research Corporation gun facility (need for accurate hits and hence desirability of a shorter gun to target distance, design of energy-absorbers, etc.).

#### B. Preliminary Experiments at Atlantic Research Corporation

Upon completion of the Atlantic Research Corporation test facility, more than 40 preliminary shots in various geometries similar to that shown in Fig. 5 were fired with high-speed photographic coverage. Distance from gun to target was 18 cm. The primary objectives were: (a) Determination of the required projectile L/D ratio. (b) Determination of the projectile velocity curve vs. gunpowder weight. (c) Observation of behavior of Saran under high-velocity impact. (d) Design of the energy-absorber which would allow quantitative retrieval of the shocked sample. The samples were pressed powders of ammonium perchlorate or inert potassium chloride.

All the projectiles were solid cylinders 30.5 mm in diameter. It was found that L/D ratios of 1.25, 0.8, 0.6, and 0.5 (no lower ratios were tried) gave straight trajectories without tumbling or tilting.

Saran was found to perform well up to about 8 kbar. Above that pressure both the projectiles and the targets cracked extensively, projectiles even shattered occasionally, and the plastic adjacent to ammonium perchlorate was slightly attacked chemically.

Qualitative results confirmed the findings of the earlier work (Section V-A) that decomposition of ammonium perchlorate begins at shock

pressures below 10 kbar. It was also found that the extent of decomposition in pressed granular ammonium perchlorate increases strongly with decreasing particle size. This is consistent with the surface-burning model (Section VIII).

Three important modifications were adopted as the result of these studies. First, Saran was replaced by the much stronger and less reactive polyvinyl dichloride. Second, the target was redesigned with the firmly glued cap to protect the sample from the air shock and to prevent mechanical loss of the sample. Third, long segmented energy absorbers were adopted and found to be very effective for quantitative recovery of test samples. In the subsequent work, reported in Sections VI and VII, 54 shots yielding quantitative data were fired with experimental arrangement as shown in Fig. 5. The sample recovery in these latter shots was excellent. The recovered samples were analyzed chemically by the methods described in Section VI.

## VI. ANALYSIS OF SHOCKED SAMPLES

The samples were analyzed for the total amount of ammonium perchlorate remaining after exposure to the shock wave by a volumetric-conductometric method (7). The total recovered solid sample was dissolved in a measured amount of distilled water (usually 250cc). Aliquot portions (10cc) of the solution were then titrated with tetraphenyl arsonium chloride, which precipitates ammonium perchlorate, and the conductivity of the solution was measured during titration. The end point of the titration is shown by a discontinuous increase in the conductivity of the solution. The scatter of experimental data by this technique amounted to maximum errors of  $\pm 0.8\%$ .

Lithium fluoride, an inert powder, was admixed to some ammonium perchlorate samples to verify the assumption that there was no mechanical loss of the powder during shock and recovery. The quantitative analysis of lithium fluoride was made by measuring the total amount of lithium in the sample by means of a flame photometer. The maximum error in this determination was  $\pm 1.5\%$ .

## VII. RESULTS

Five series of experiments were run, all with pressed samples of granular materials: ammonium perchlorate (AP) with an average particle diameter of about  $15\mu$ ; polyethylene (PE), average particle diameter about  $10\mu$ ; and lithium fluoride (LiF), average particle diameter less than  $10\mu$ . The specific surface of AP samples, measured by the BET adsorption technique with nitrogen as adsorbant, was  $3040 \text{ cm}^2/\text{gm}$ . The geometrical surface of spheres of  $15\mu$  diameter with  $1.95 \text{ gm/cc}$  density is  $2045 \text{ cm}^2/\text{gm}$ . The five series of tests were: pure AP at  $88 \pm 4\%$  of the crystal density; AP/LiF (95/5) mixtures at  $88 \pm 4\%$  of the crystal density; AP/PE (97/3) at  $90.5 \pm 2\%$  of the crystal density; AP/PE (90/10) at  $96 \pm 3\%$  of the crystal density; and pure AP at about 60% of the crystal density.

All of the results in the following paragraphs are reported in terms of directly measured data, i.e., the amount of AP lost as a function of impact velocity. Since, in all cases, the impedance-matching material was PVDC, the corresponding shock pressure can be read directly from the curve in Fig. 4 for all shots except those with low-density AP (Section VII-E). Two projectile lengths were used, 18.3 mm and 31.8 mm. The corresponding durations  $\tau$  decrease slightly with increasing impact velocities, because of increasing values of shock velocity  $U$ . Since over our experimental range the shock velocities are always about  $3 \text{ mm}/\mu\text{sec}$ , the approximate values of  $\tau$  in all experiments are 12 and  $21\mu\text{sec}$  respectively. More exact values for each individual shot can easily be calculated from experimental shock Hugoniot data (Fig. 2).

### A. Pure Ammonium Perchlorate ( $\rho_0 \approx 1.7 \text{ gm/cc}$ )

Eight shots were fired at impact velocities ranging from 1250 to 2010 ft/sec, corresponding to shock pressures from 8.8 to 15.4 kbar. The weight-loss data are plotted in Fig. 6. An inspection of these results shows two things. (a) Except for one shot out of eight, the data are self-consistent well within  $\pm 1\%$ . (b) The amount of AP reacted is markedly higher in shots with long projectiles ( $\tau \approx 21\mu\text{sec}$ ) than in shots with short projectiles ( $\tau \approx 12\mu\text{sec}$ ). Indeed, in two of the four long-duration shots, at



1785 and 1920 ft/sec respectively, gas evolution was sufficient to shear off the target cover, so that most of the sample was lost in both these shots. This type of occurrence is marked by a vertical arrow, indicating an unknown, but relatively large, amount of reaction. No ruptures were observed with short projectiles.

B. Ammonium Perchlorate - Lithium Fluoride Mixtures ( $\rho_0 \approx 1.7$  gm/cc)

To verify that the loss of perchlorate was not partly mechanical, 16 shots were fired in which a non-reactive powder was added to the sample. Impact velocities ranged from 810 to 2290 ft/sec, corresponding to shock pressures in the sample of 5.3 - 18.1 kbar. Lithium fluoride was chosen because of its stability, and because it lends itself to flame-photometric analysis.

Except for a small effect of dilution, these samples should be expected to give the same results as pure perchlorate. This expectation was confirmed; the data are plotted in Fig. 6 along with the results for pure perchlorate. The only difference between the two series is that some samples with LiF showed slightly less loss, especially with long projectiles at high impact velocities. In 14 out of 15 shots, the targets with partly reacted samples were recovered with no apparent mechanical loss. In one shot the glue broke, the cap loosened and there was mechanical loss. The recovered incomplete portion was analyzed, and the significance of this result is discussed below.

The quantitative analysis of lithium fluoride in recovered samples yielded recovery data ranging from 98.6 to 101.4%, i.e., it gave complete recovery results within the experimental scatter of  $\pm 1.5\%$ . The same samples yielded ammonium perchlorate recovery range from 93.6 to 99.7%, indicating appreciable losses. We conclude that there was no mechanical loss, except of course in the case of the partially opened sample, where the loss was obvious. In this sample the loss of LiF was 11.9%, and the loss of AP 18.6%. The extent of reaction in AP, calculated on the assumption that the percentage loss of LiF equals the percentage of the mechanical loss of the total

sample, is 7.8%. This datum is included in Fig. 6 (in parenthesis), and it lines up well with the rest of the comparable data. This technique, therefore, appears promising for determination of quantitative data on the extent of reaction in ammonium perchlorate even in the cases where the total (solid) sample is not recovered.

C. Ammonium Perchlorate/Polyethylene (97/3) Mixture ( $\rho_0 \approx 1.7$  gm/cc)

As a step toward evaluation of composite propellants, pressed samples of ammonium perchlorate containing a little polyethylene powder were tested. Eleven shots were fired at 800-2350 ft/sec (5.2 - 18.4 kbar). Ten of these are plotted in Fig. 7. In one test the analysis for ammonium perchlorate loss gave an inordinately large value, about 18%, so that it could not be included in the plot. In four tests, three with long projectiles and one with short, there was sufficient gas evolution to break off the target cap.

Evidently, addition of the fuel increased substantially the reactivity of the samples. Also, a substantially larger extent of AP decomposition is again evident with longer shock-durations.

D. Ammonium Perchlorate/Polyethylene (90/10) Mixtures ( $\rho_0 \approx 1.7$  gm/cc)

Sixteen shots were fired with AP/PE mixtures approximately stoichiometric to HCl, H<sub>2</sub>O, CO<sub>2</sub>, and N<sub>2</sub> at 1070 to 2320 ft/sec (7.5 to 18.3 kbar). In one shot the glue broke, and the sample was lost. The other 15 samples were recovered and analyzed. The results are plotted in Fig. 8.

These samples were obviously relatively unreactive. We believe that this is so because of their relatively low porosity, on the average only 4%.

E. Low-Density Ammonium Perchlorate ( $\rho_0 = 1.2$  gm/cc)

To check the effect of porosity, three lightly pressed pure AP samples (ca. 40% porosity) were exposed to shocks of about 12 $\mu$ sec duration.

These samples proved very sensitive. The target cap broke in two shots, at 1630 and 1670 ft/sec respectively, despite the fact that shock-pressures in the samples must have been quite low -- according to the "locked-solid" Hugoniot as low as 4.5 kbar (see Section III), although in reality probably somewhat higher. Analysis of the third shot at 1070 ft/sec yielded 0.7% loss, indicating little or no reaction. However, the low-limit estimate of the corresponding pressure is only 2.5 kbar.

### VIII. DISCUSSION

The above experimental results are consistent with a model of high-pressure surface burning of individual grains in the pressed sample, in which only a certain fraction of the total grain area is ignited. The grain surface then regresses and the flame spreads at a rate which is a function of shock pressure  $P$ , during the shock duration  $\tau$ , whereupon the reaction is quenched by the arrival of the rarefaction wave. No homogeneous component to the reaction rate need be considered. While no specific data relating the shock temperature to the shock pressure inside the grain appear to be available for ammonium perchlorate, general considerations indicate clearly that this temperature must remain far too low for any appreciable homogeneous reaction.

A very rough estimate is possible of the burning area involved in our experimental work. According to available published information (extrapolation of low-pressure burning rates consistent with rough measurement of detonation reaction times), the linear burning rates for ammonium perchlorate should be between 50 and 150 cm/sec at 10 kbar (1,2,3). At this pressure, our experiments with high-density AP ( $\sim 1.7$  gm/cc) show about 2% reaction in about 10  $\mu$ sec. Assuming now that ignition is instantaneous, if the entire geometrical area were involved in deflagration, the burning rate would have to be only about 0.5 cm/sec, i.e., at least two orders of magnitude below the expected value. In other words, our high-density results are consistent with the picture in which less than 1% of the total surface is ignited by the incident shock wave. According to the same model, the results of the three low-density shots (Section VII-E) show that the effective burning area increases markedly with increasing porosity of the pressed sample.

APPENDIX A

Let the projectile in Fig. 1 travel forward, i.e., from left to right, at the initial velocity  $u_p$ , and let  $t = 0$  denote the instant at which it contacts the target. At  $t = 0$  the pressure at the interface between the projectile and the target rises discontinuously from  $p = 0$  to  $p = P$ . From the time  $t = 0$  on, a shock wave of amplitude  $P$  travels forward into the target at velocity  $U_T$ , and another shock wave of the same amplitude  $P$  travels backward into the projectile at velocity  $U_p - u_p$  relative to an outside observer, where  $U_p$  is the normal velocity in the projectile of a shock of amplitude  $P$ . The interface travels forward at velocity  $u_T < u_p$ .

This situation persists until at  $t = \frac{\tau}{2} = \frac{L}{U_p}$  the backward shock reaches the rear end of the projectile. A rarefaction wave in which pressure drops from  $P$  to 0 now travels forward into the projectile at a velocity very nearly equal to  $U_p$ . Consequently, the velocity of the rarefaction wave relative to an outside observer is  $U_p + u_T$ , and the particle velocity behind the rarefaction wave is  $2 u_T - u_p$ . The rarefaction wave traverses the length  $L$  of the projectile in another time interval  $\frac{L}{U_p} = \frac{\tau}{2}$ . The net result of this process is that the interface is subjected to a square wave of amplitude  $P$  and duration  $\tau$ . It is easy to see that every other vertical cross-section of the sample in Fig. 1 will be subject to the same pressure-time regime providing the system is one-dimensional, i.e., provided that during time  $\tau$  the sample is not affected by lateral rarefactions. The geometry necessary for this condition, i.e., required to maintain constant values of  $P$  and  $\tau$  in the sample, is specified in Section II.

The physics of impact is simplified in an important way in the special case of equal projectile and target impedances (i.e., the same material for both parts of the system). In that case  $U_p = U_T \equiv U$ ,  $u_T = \frac{1}{2} u_p$  (see Appendix B), and the particle velocity behind the rarefaction wave is  $2 u_T - u_p = 0$ . This means that the projectile, having transferred all of its kinetic energy to the target, remains stationary after the impact. Now if the target is backed by an energy-absorbing segment made of the same material as the projectile and the target, the shock wave will pass into the absorber

without discontinuities. Furthermore, if the absorber exceeds a critical length, it will take all of kinetic energy, leaving also the target stationary. Since even in the geometry shown in Fig. 1, where the sample is exposed to an accurate (one-dimensional) square wave, the entire system is evidently not one-dimensional, the calculation of the critical length of the energy absorber would be a difficult two-dimensional problem. In the one-dimensional problem, valid in the limit of low impact velocities or of infinite lateral confinement, the shock wave is propagated at the constant velocity  $U$  and the associated particle velocity  $u_T = \frac{1}{2} u_p$  all the way to the far end of the energy absorber, regardless of its length. At that end, the free surface velocity assumes the value  $2 u_T = u_p$ . A rarefaction wave now travels backward from the free end, and it meets the forward travelling rarefaction after a time  $\frac{\tau}{2}$ . A segment of the energy-absorber, therefore, which acquires a permanent velocity ( $u_p$ ) is  $U \times \frac{\tau}{2} = L$ , i.e., precisely the length of the projectile, while the rest of the system remains stationary.

In the experimental work reported in Sections IV and V an empirical approach was taken toward the design of an energy-absorbing system. It was found that long segmented absorbers work well even at high impact velocities.

APPENDIX B

The method for calculating the pressure  $P$  and the duration  $\tau$  of the shock wave in the propellant is shown in Fig. 9.

Assume first that the projectile, the target, and the propellant sample all have the same shock-compressibility, described by curve A. Let the velocity of impact be  $u_p$ . Since, upon impact, two shock waves of velocity  $U$  relative to the propagating medium travel in opposite directions from the interface, the pressure  $P_A$  at the interface is defined by the intersection of A and its mirror-image reflection  $A^-$ .

Consider next the case in which the shock-impedance of the sample, given by curve B, is somewhat higher than that of the projectile. In this case the particle velocity in the sample, defined by the intersection of B and  $A^-$  is somewhat less than  $\frac{u_p}{2}$ , and the corresponding pressure  $P_B$  is somewhat higher than  $P_A$ . If on the other hand the sample has a lower shock impedance than the projectile (curve D), the relative values of pressures and particle velocities are reversed:  $u_c > \frac{1}{2} u_p$ , and  $P_c < P_A$ . These two cases correspond to the two experimental situations, with high and low density pressed samples respectively (see Fig. 3).

Finally, consider the initial adjustment conditions in the cylindrical geometry at the lateral boundary between the target and the high-density metal holder (see Figs. 3 and 5). The shock Hugoniot of the metal is shown as curve M in Fig. 9. Since at the instant of impact there is no radial component of velocity at the target-metal boundary, one can treat the problem conveniently by shifting the metal Hugoniot by an amount  $\frac{u_p}{2}$  on the abscissae to position M'. Thus the pressure  $P_A$  in the target will impart to the metal an initial radial particle velocity  $u_M - \frac{u_p}{2}$ , with the resulting pressure drop at the interface to the value  $P_M$ . For the experimental pair of materials, steel and PVDC (Fig. 3), the pressure drop from  $P_A$  to  $P_M$  is about 12% over the entire range of impact velocities. It must be pointed out that the experimental Hugoniot for steel in Fig. 3 is drawn

from data taken at very high pressures, i.e., in the plastic flow region (8). If the pressure is so low that the metal still exhibits appreciable elastic strength, the pressure drop  $P_A - P_M$  will be less. This is probably true in much of our experimental work.

Thus in the experimental arrangement used so far in this program (Fig. 5) the initial shock pressure  $P$  in the sample will be maintained over the time interval necessary for the radial rarefaction wave to travel from the steel boundary to the sample, about  $4\mu\text{sec}$ . Thereupon, the pressure will drop to a lower value because of radial yield of the steel holder ( $0.88P$  on the assumption of purely plastic yield), and it may continue to decrease if there is continued two-dimensional cylindrical flow. However, our experimental results (Section VII) indicate that high shock pressures must be maintained in the sample for durations exceeding  $12\mu\text{sec}$ , because amounts of chemical reaction induced by  $21\mu\text{sec}$  shock waves are always substantially larger than amounts induced by  $12\mu\text{sec}$  shocks.

REFERENCES

1. W. H. Andersen and R. E. Pesante, Eighth Symposium (International) on Combustion, p. 705. Academic Press, 1962.
2. W. H. Andersen and R. F. Chaiken, ARS Journal 31, 1379 (1961).
3. P. K. Salzman, O. R. Irwin, and W. H. Andersen, AIAA Journal 3, 2230 (1965).
4. F. C. Gibson, C. R. Summers, C. R. Mason, and R. W. Van Dolah, Third Detonation Symposium, ONR, Princeton, New Jersey, September 1960.
5. N. L. Coleburn, Private Communication.
6. M. G. Salvadori, R. Skalak, and P. Weidlinger, J. Eng. Mech. Div., ASCE Proc., April 1960, p. 77; M. W. Evans, C. M. Ablow, B. O. Reese, and A. B. Amster: Proceed. Intern. Conf. on Sensitivity and Hazards of Explosives, London, October 1963.
7. R. J. Baczuk and W. T. Bolleter, Anal. Chem. 39, 93 (1967).
8. M. H. Rice et al, Solid State Physics, Vol. 6, ed. F. Seitz and P. Turnball, pp. 61-62, Academic Press, New York 1958.



Figure 1. The Idealized Experiment.

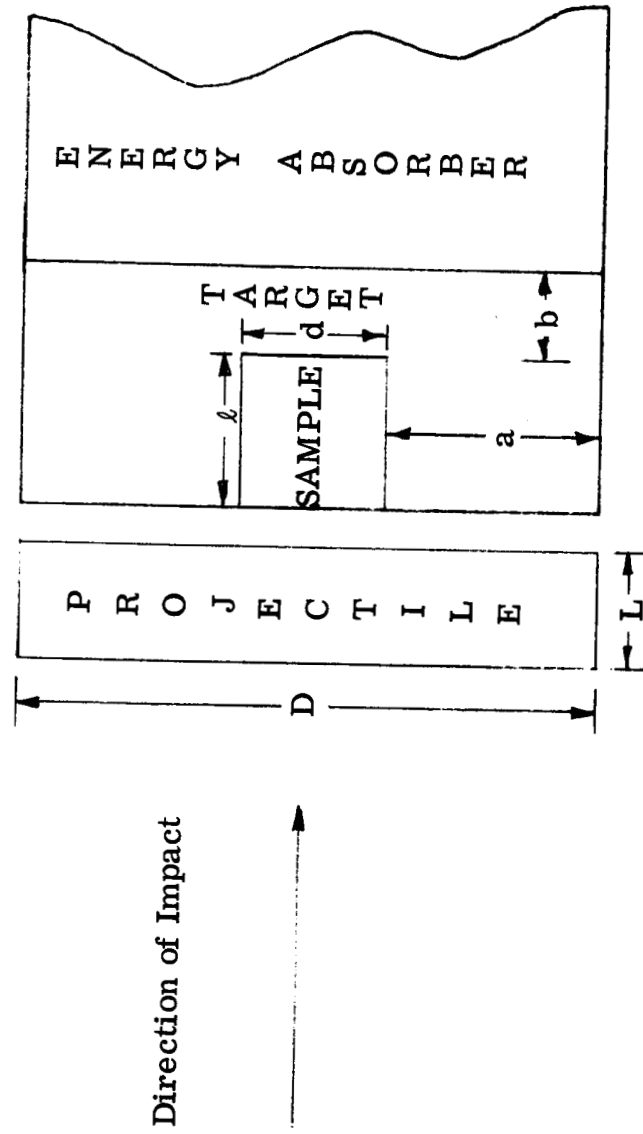


Figure 2. Experimental Shock Velocity Versus Particle Velocity Data for Saran (Ref. 5 ).

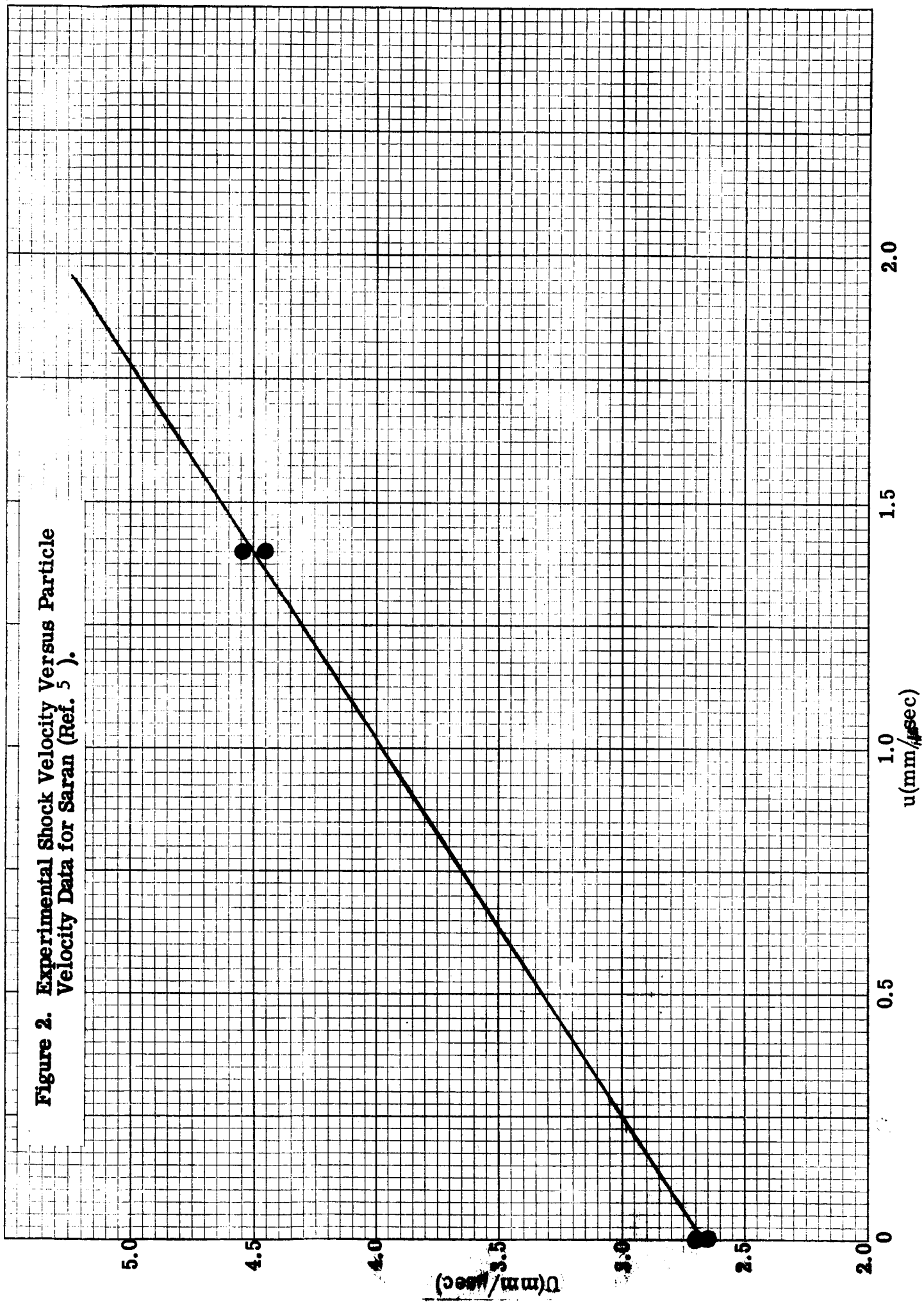


Figure 3. Shock Hugoniot.

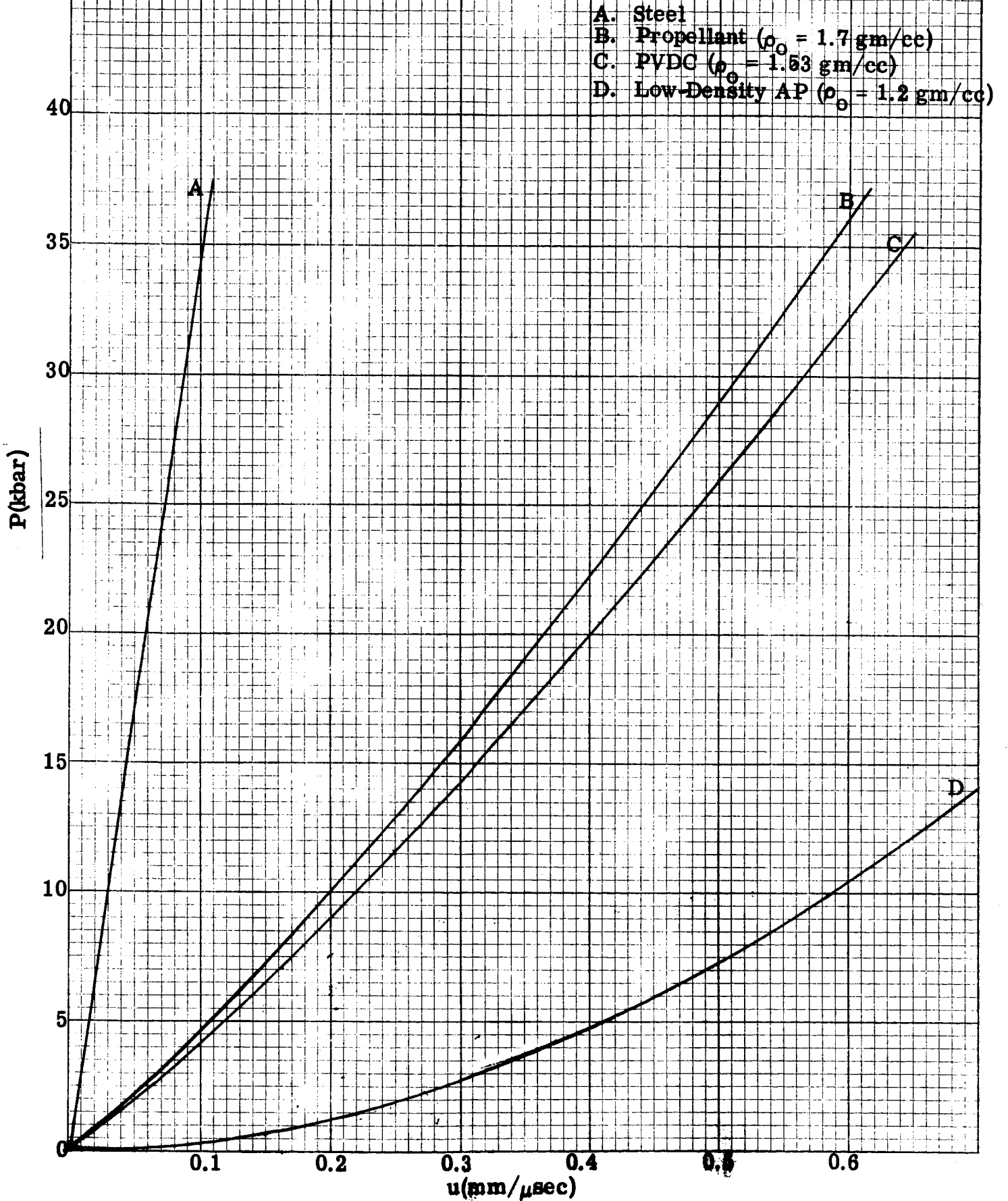


Figure 4. Shock Pressure in Sample ( $\rho_0 = 1.7 \text{ gm/cc}$ )  
Versus Impact Velocity.

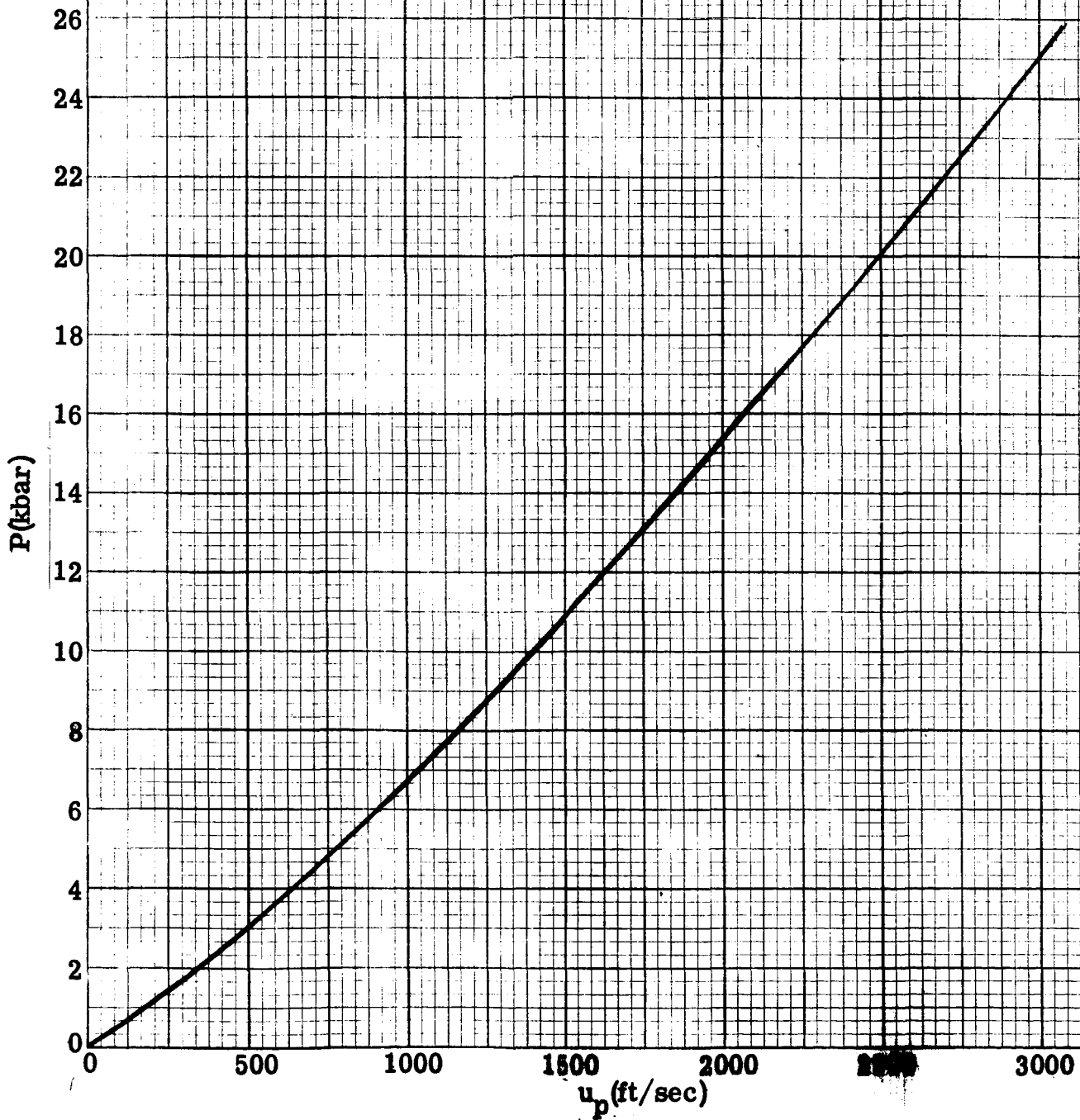


Figure 5. Experimental Arrangement.

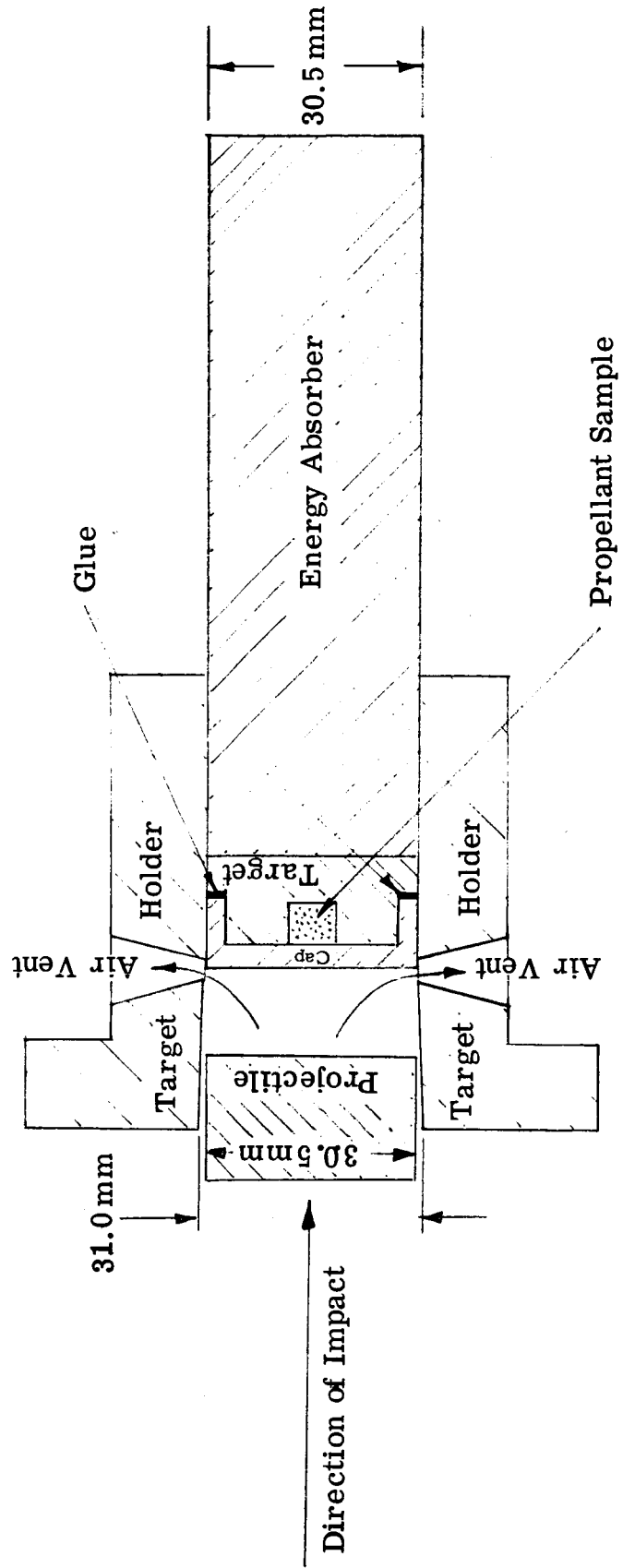
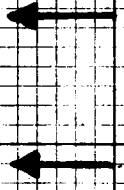


Figure 6. Weight Loss Versus Impact Velocity for Pure AP and AP/LiF Mixtures ( $\rho_0 \approx 1.7 \text{ gm/cc}$ ).

○ Pure AP.	Projectile Length: 18.3mm
● Pure AP.	Projectile Length: 31.8mm
□ AP/LiF(95/5).	Projectile Length: 18.3mm
■ AP/LiF(95/5).	Projectile Length: 31.8mm



(B)

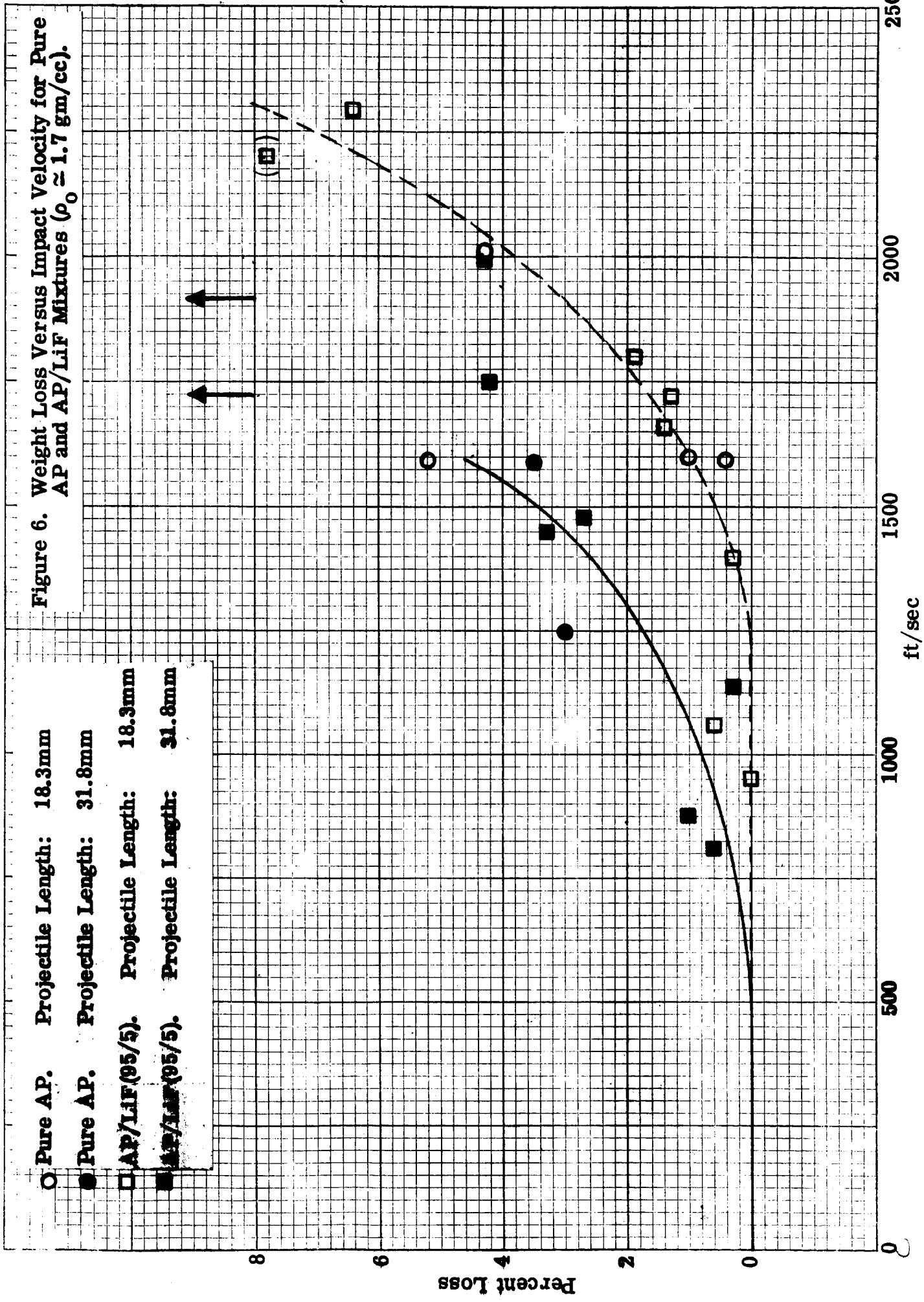
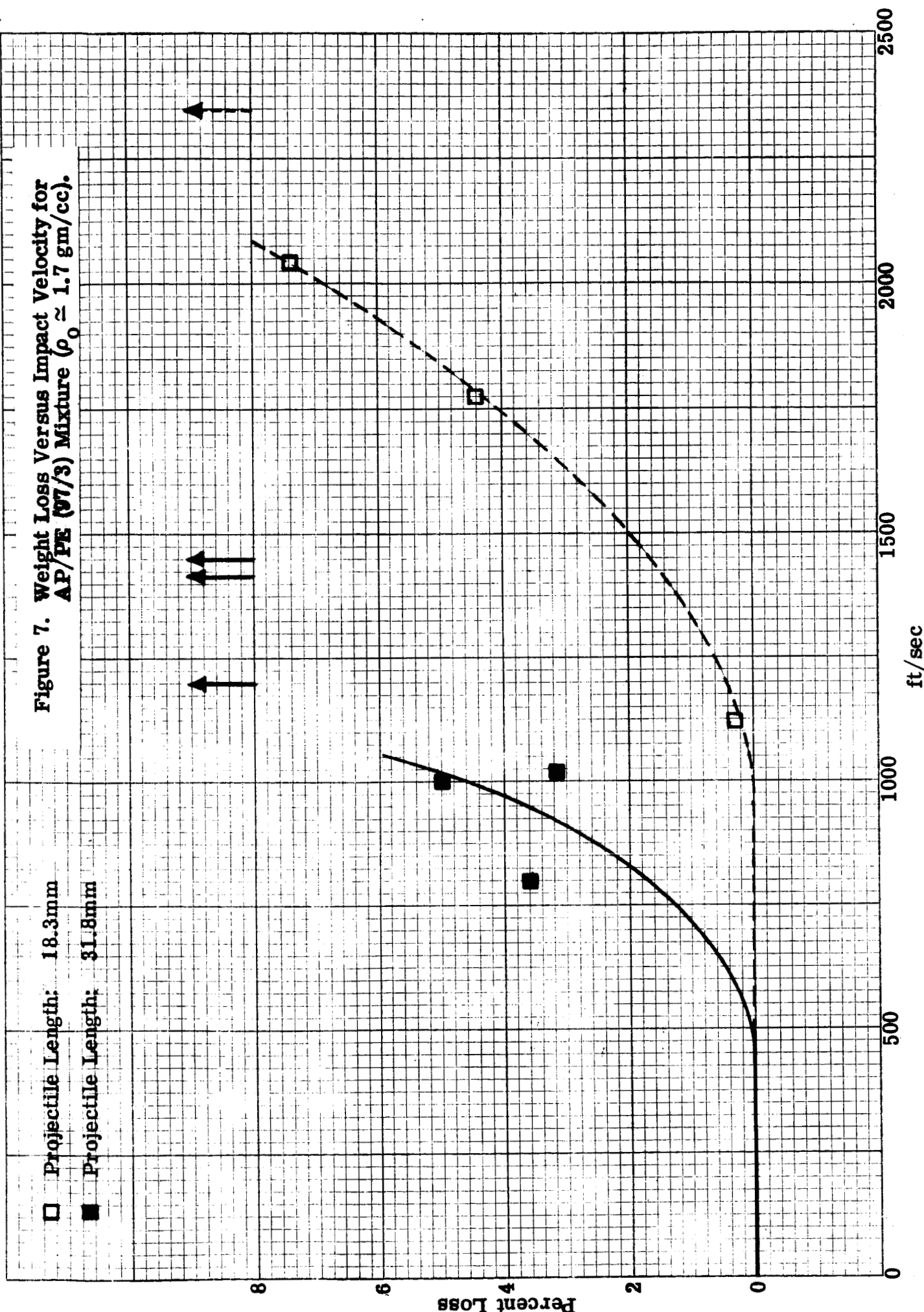


Figure 7. Weight Loss Versus Impact Velocity for AP/PE (97/3) Mixture ( $\rho_0 \approx 1.7 \text{ gm/cc}$ ).



**Figure 8. Weight Loss Versus Impact Velocity for AP/PE (90/10) Mixture ( $\rho_0 \approx 1.7 \text{ gm/cc}$ ).**

○ Projectile Length: 18.3mm  
 ● Projectile Length: 31.8mm

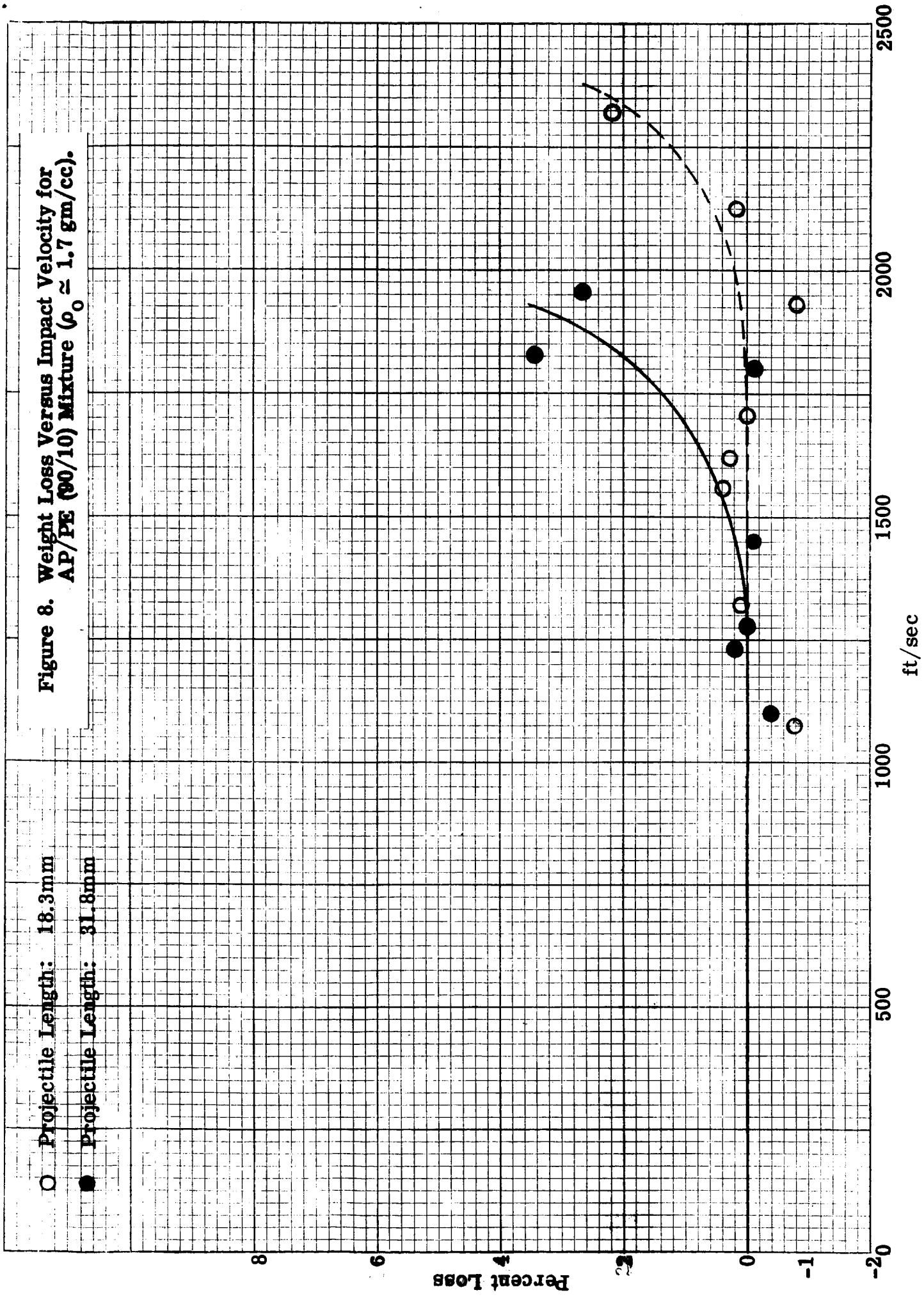
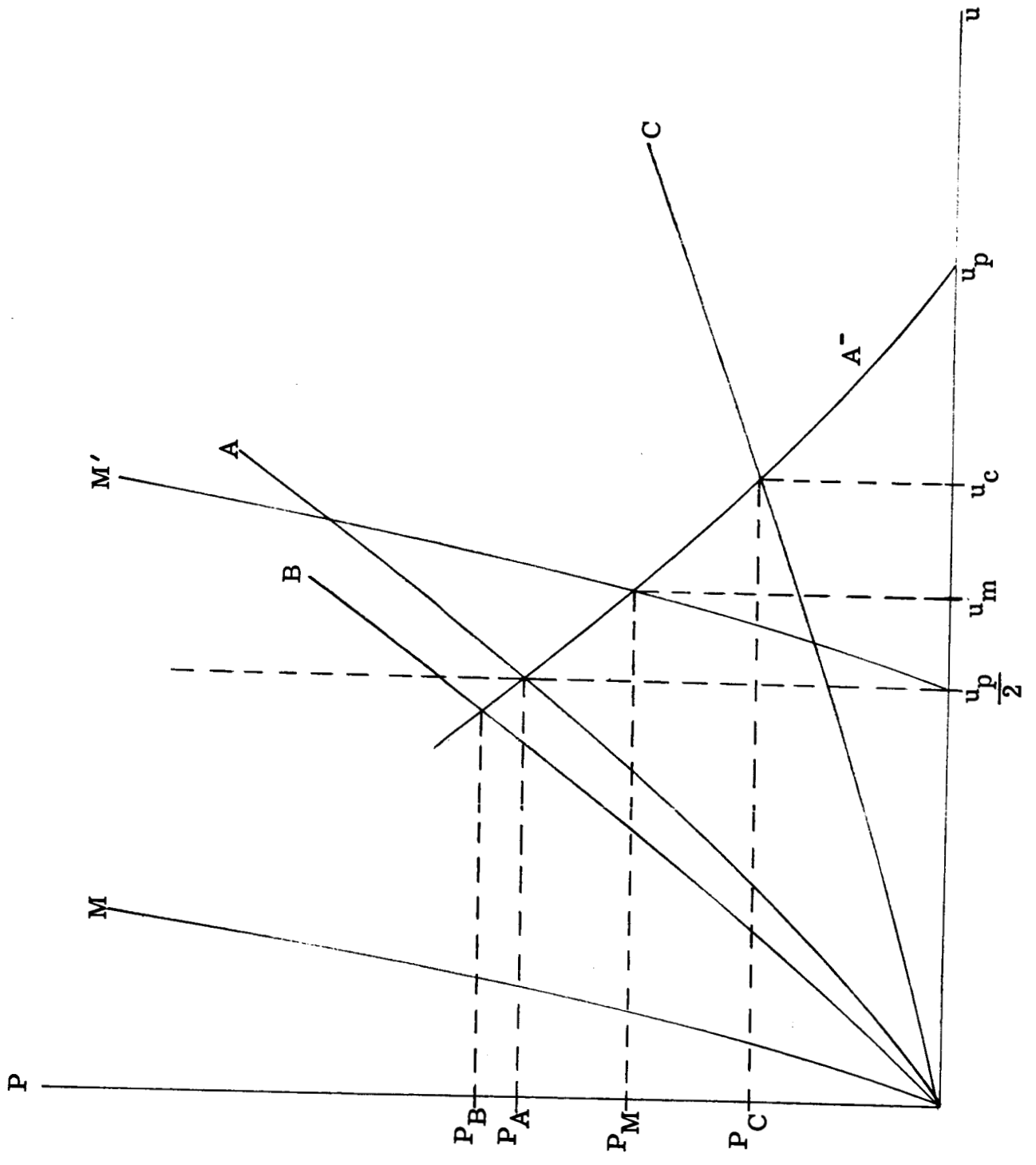




Figure 9. The Hugoniot Reflection Method.



NASA CR-66395

DISTRIBUTION LIST

NAS1-6200

	<u>Copies</u>
NASA Langley Research Center Langley Station Hampton, Virginia 23365 Attention: Contracting Officer	1
Dr. Andrew R. Saunders, Mail Stop 217	5
Research Reports Division, Mail Stop 122	1
R. L. Zavasky, Mail Stop 107	1
Robert L. Swain	1
NASA Ames Research Center Moffett Field, California 94035 Attention: Library	1
NASA Flight Research Center P.O. Box 273 Edwards, California 93523 Attention: Library	1
NASA Goddard Space Flight Center Greenbelt, Maryland 20771 Attention: Library	1
Jet Propulsion Laboratory 4800 Oak Grove Drive Pasadena, California 91103 Attention: Library	1
NASA Manned Spacecraft Center Houston, Texas 77001 Attention: Library	1
Marshall Space Flight Center Huntsville, Alabama 35812 Attention: Library Alton L. Wheeler	1 1
NASA Western Operations Office 150 Pico Boulevard Santa Monica, California 90406 Attention: Library Eugene F. Wyszpolski	1 1

DISTRIBUTION LIST

NAS1-6200

	<u>Copies</u>
NASA Wallops Station Wallops Island, Virginia 23337 Attention: Library	1
NASA Electronics Research Center 575 Technology Square Cambridge, Massachusetts 02139 Attention: Library	1
NASA Lewis Research Center 21000 Brookpark Road Cleveland, Ohio 44135 Attention: Library, Mail Stop 3-7 James L. Kramer	1 1
NASA John F. Kennedy Space Center Kennedy Space Center, Florida 32899 Attention: Code ATS-132	1
NASA Michoud Assembly Facility P. O. Box 26078 New Orleans, Louisiana 70126 Attention: Mr. Henry Quintin, Code I-Mich-D	1
National Aeronautics and Space Administration Scientific and Technical Information Facility P. O. Box 33 College Park, Maryland 20740	25 plus reproducible
Chemical Propulsion Information Agency Applied Physics Laboratory 8621 Georgia Avenue Silver Spring, Maryland 20910	1
U. S. Naval Ordnance Test Station China Lake, California 93557 Attention: Mr. Edward W. Price (Code 5008) Dr. Alvin S. Gordon	1 1
Office of Naval Research Navy Department Washington, D. C. 20360 Attention: Mr. Roland D. Jackel, 429 Dr. Ralph Roberts	1 1

NASA CR-66395  
DISTRIBUTION LIST

NAS1-6200

	<u>Copies</u>
Air Force Rocket Propulsion Laboratory Edwards Air Force Base, California 93523 Attention: Mr. Richard Spann	1
Air Force Office of Scientific Res. (SREP) Propulsion Division Washington, D. C. 20333 Attention: Dr. Bernard T. Wolfson	1
Air Force Systems Command Research And Technology Div. (RTGS) Bolling Air Force Base Washington, D. C. 20332 Attention: Dr. Leon Green, Jr.	1
National Aeronautics and Space Administration Lewis Research Center 21000 Brookpark Road Cleveland, Ohio 44135 Attention: Dr. Richard J. Priem Dr. Louis A. Povinelli	1 1
United Technology Center P. O. Box 358 Sunnyvale, California 94088 Attention: Dr. Robert Brown	1
Rocketdyne, Division of North American Aviation, Inc. Solid Propellant Operations P. O. Box 548 McGregor, Texas 76657 Attention: S. C. Britton	1
Chemical Propulsion Information Agency The Johns Hopkins University Applied Physics Laboratory 8621 Georgia Avenue Silver Spring, Maryland 20910 Attention: Dr. Robert H. Cantrell	1
Stanford Research Institute 333 Ravenswood Avenue Manlo Park, California 94025 Attention: Dr. L. Seely Dr. M. W. Evans	1 1

DISTRIBUTION LIST

NAS1-6200

	<u>Copies</u>
California Institute of Technology Pasadena, California Attention: Dr. Frank E. Marble Professor B. H. Sage	1 1
University of California Department of Aerospace Engineering Das Diego, California 92106 Attention: Dr. Stanford S. Penner Dr. F. A. Williams	1 1
Princeton University Forrestal Research Center Princeton, New Jersey Attention: Dr. Martin Summerfield Dr. Irvin Glassman	1 1
Rohm and Haas Company Redstone Arsenal Huntsville, Alabama 35812 Attention: Dr. William A. Wood	1
Stevens Institute of Technology Department of Mechanical Engineering Hoboken, New Jersey 07030 Attention: Dr. Robert F. McAlevy, III	1
Aero Chem. Research Laboratories, Inc. Princeton, New Jersey 08540 Attention: Dr. H. F. Calcote	1
U. S. Naval Ordnance Laboratory White Oak, Maryland 20903 Attention: Dr. S. J. Jacobs Dr. D. Price Dr. J. A. Ablard N. L. Coleburn	1 1 1 1
U. S. Naval Ordnance Station Indian Head, Maryland Attention: Dr. Martin Zimmer	1
Naval Air Systems Command Washington, D. C. 20360 Attention: Dr. O. H. Johnson	1

DISTRIBUTION LIST

NAS1-6200

	<u>Copies</u>
Aerojet-General Corporation Downey, California Attention: R. F. Chaiken P. K. Salzman	1 1
Harvard University Cambridge, Massachusetts Attention: Prof. Howard Emmons	1
Lawrence Radiation Laboratory Livermore, California Attention: Dr. Frank Walker	1
Ordnance Systems Command Washington, D. C. 20360 Attention: B. Drimmer	1
Ordnance Research and Development Co. 6856 Tujunga Ave., North Hollywood, Calif. 91605 Attention: T. P. Lirra	1