N 70 30091

NASA CR-66926

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

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Prepared under Contract No. NAS1-8622
ATLANTIC RESEARCH CORPORATION
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Alexandria, Virginia

for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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FINAL REPORT: NAS1-8622

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December 23, 1969

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ABSTRACT

The objective of the program was a study of the rate of energy release in solid propellants by means of shock waves of known durations and known constant amplitudes. The data sought were measured decomposition rates in propellants under shock pressures of the order of 10 kbar.

The progress under this contract took place along three major lines:

(a) Instrumentation for a gauge allowing direct experimental determination of shock amplitude as a function of time was designed and perfected. The gauge was calibrated from 3.8 to 17.4 kbar.

(b) Four granular materials and a cast composite propellant, all based on ammonium perchlorate, were tested by being exposed to square-wave shockwaves with amplitudes ranging from 7.8 to 21.4 kbar, and durations ranging from 8 to 21 μsec. Granular samples were tested at two different pressed densities. Explosion thresholds were found to depend greatly on physical and chemical characteristics of samples.

(c) An accurate quantitative analysis for the perchlorate ion was developed, based on precipitation titration with tetraphenyl arsonium chloride. Samples shocked below the explosion threshold and subsequently recovered for chemical analysis showed only very small amounts of decomposition, never in excess of 2 percent.

Probable mechanisms of initiation of reaction by shock waves are briefly discussed. It is concluded that the four most important factors for initiation and buildup of chemical reaction are density of the sample, addition of burning-rate catalysts, shock pressure, and shock duration.

I. INTRODUCTION

This program was initiated in May of 1966. The first two years (May, 1966 - May, 1968) were funded under the contract No. NAS1-6200. The third year, which began in September, 1968, contract No. NAS1-8622, is essentially an extension of the previous work. The objective of the program is a study of the rate of energy release in solid propellants by means of shock waves of known durations and known constant amplitudes. The method specifically developed for this purpose is to impact a carefully designed target assembly containing the propellant sample by a cylindrical projectile fired from a gun. The shock pressure in the sample for a given projectile material, is determined by the velocity of the projectile. Shock pressures usually increase, and shock durations (for a given length) decrease with increasing projectile densities. Further, the design of the impact experiment is such that the shocked sample can be recovered and analyzed, thus yielding decomposition rate data. The crucial data sought in this program are <u>measured</u> decomposition (energy-release) rates in propellants under shock pressures of the order of 10 kbar. Two applications of the data so gathered would be (a) the assessment of hazards (especially non-detonative hazards) which arise when a large propellant grain is subjected to shocks; and (b) calculation of critical detonation diameters of the propellant.

Detailed accounts of the progress during the first two years can be found in the two Annual Reports and two publications generated under this program (1, 2, 3, 4). Very briefly, this progress can be summarized as follows:

(a) An experimental technique was developed whereby a sample of a solid propellant can be exposed to a "square-wave" shock of known amplitude P and known duration τ, and then recovered non-destructively for subsequent analysis. The shock wave in the propellant is generated by the impact of a projectile fired from a gun. A schematic representation of the impact experiment and a photograph of the gun assembly are shown in Figures 1 and 2 (see also Ref. 2).

(b) A pressure gauge operative under strong-shock conditions was perfected. The gauge consists of a carbon-resistor element which was found to change reproducibly with shock pressures in the kilobar range over relatively long durations (30-50μsec). This measurement technique has yielded experimental records of shock-wave profiles over the entire range of shock parameters encountered thus far in the program: amplitudes from 4 to 21 kbar, and durations from 8 to 21μsec..

(c) Small samples, ca. 0.3 gm, of powdered ammonium perchlorate (AP), pressed to 1.70-1.75 gm/cc density, were tested by the projectile-impact method. The retrieved samples were analyzed quantitatively by two methods. The perchlorate ion was titrated with tetraphenyl arsonium chloride, the end-point being determined conductometrically. This method revealed ClO_4^- losses under shock sometimes exceeding 10%; however, even as a rule, the data were rather scattered. Occasionally, they could not be correlated at all with general trends. Titration of NH_4^+ with base in the presence of formaldehyde gave more satisfactory results from the point of view of reproducibility; NH_4^+ losses in shocked samples so determined were always quite small, seldom in excess of 2%. The actual extent of the reaction under shock thus remained in doubt.

(d) Shock testing of a pressed propellant-like mixture, AP/polyethylene (87/13), revealed explosion thresholds in the range between 12 and 15 kbar, indicating the onset of substantial chemical reaction at well-defined shock pressure levels. Furthermore, threshold amplitudes were found to decrease with increasing durations τ, indicating that the concept of a finite rate of reaction, initiated by the incident shock and quenched by the rarefaction, is realistic.

The progress under contract NAS 1 - 8662 has been along three major lines:

(a) Instrumentation design for <u>measurement of shock parameters</u>, leading to complete quantitative definition of shockwaves generated in propellant samples.

(b) Shock testing of solid samples by square waves of varying amplitudes and durations, and determination of "explosion" thresholds. The samples so tested were: Reagent-grade ammonium perchlorate (AP), propellant-grade AP, reagent grade AP with small amounts of catalyzing additives, a propellant-like mixture of propellant-grade AP and polyethylene, and an actual composite (metallized) propellant.

(c) Development of a quantitative analysis technique for the perchlorate ion. Most of the samples listed in the previous paragraph, which were retrieved after exposure to shocks, were analyzed by this technique with the aim of determining the extent of (non-explosive) reaction having taken place under shocks of known amplitude and duration.

These three topics will now be described under separate headings.

II MEASUREMENT OF SHOCK PARAMETERS

The two shock parameters, amplitude P and duration τ, were determined in two ways. The first, somewhat less satisfactory method is based entirely on semi-empirical shock Hugoniots of the propellant sample and the plastic casing. The plastic was always polyvinyl dichloride (PVDC) with density of 1.53 gm/cc. The matter of these Hugoniots was discussed in detail in Refs. 1 and 3. The resulting plot of P vs. projectile-impact velocity, u, for PVDC projectiles, is reproduced in Figure 3; (all projectiles used in this program were made of PVDC). Duration τ in this method is assumed to be simply twice the transit time of a shockwave of amplitude P along the projectile. The two parameters are thus determined semi-empirically from a single measured datum, velocity u. This method was used exclusively in early stages of the program (Ref. 1 and 3).

Subsequent development of the carbon-resistor gauge (Ref. 2 and 4) was a major advance. It (a) allowed direct experimental measurement of τ; (b) revealed detailed shape of the shockwave; and (c) allowed an approximate experimental determination of P by the use of a calibration of a similar gauge at the Bureau of Mines. However, a direct calibration of our gauge was still not possible, because our circuitry did not allow a simultaneous measurement of impact velocity and of gauge resistance change. The last deficiency was removed during the current year. An account of the final experimental design and procedure follows.

In its travel from the gun muzzle to the target the projectile breaks successively two thin wires stretched across its path. The breaking of the two wires triggers two separate circuits, the first one serving the high-speed camera, and the second one the pressure gauge.

At the beginning of each shot the high-speed (Beckman & Whitley) framing camera, viewing the region between the gun muzzle and the target holder (see Figure 2), is manually set at the desired framing rate (usually 35,000 fps, corresponding to 28.6μ sec between frames) and the camera shutter is opened. Since the camera requires a high-intensity light source, it can be run for several minutes in subdued light without film exposure. The gun is now fired manually. The breaking of the first trigger wire, stretched across the muzzle of the gun 6 or 7 inches upstream of the target, actuates a high-intensity Xenon flash, the duration of which is 5.4msec. Since projectile velocities vary from 500 to 2,500 ft/sec, travel times between the muzzle and the target, about 0.2 to 1 msec, are always well within the available flash period. The resulting camera record shows the location of the projectile in a number of subsequent frames, and thus allows a good measurement of u. An example is shown in Figure 4.

The second trigger wire is placed at an accurately measured distance from the target. We chose arbitrarily a convenient distance of 1.27 inch (32.3mm). The breaking of the second wire triggers an oscilloscope sweep, as shown in the schematic diagram of the circuit, Figure 5. The travel time of the projectile from the oscilloscope trigger to target, determined by projectile velocity, thus is usually in the range of 40 to 200μsec. The sweep-speed of the oscilloscope was either 10 or 20μsec/cm. Since the carbon resistor is imbedded just below the surface of the target, as shown in Figure 1, its resistance changes, due to shock compression, almost immediately (about 1μsec) after impact. The signal from the resistor is now superposed on the sweep of the oscilloscope. An oscilloscope record is reproduced in Figure 6.

The oscilloscope-trigger circuitry presents two important advantages over previous arrangements. First, it is entirely independent of the other triggering system serving the camera, so that the two can be used simultaneously. The system thus allows a direct calibration of the gauge, as discussed in the next paragraph. Second, the oscilloscope timing from the trigger to the arrival of the shock at the gauge gives a redundant measure of the projectile velocity, u. The oscilloscope measurements were usually found to be in very good agreement (±2%) with simultaneous photographic measurements. However, it was also found that the oscilloscope circuit was subject to occasional faulty triggering. Thus, while this technique of velocity determination has been most useful in confirming the validity of camera measurements, the photographic technique remains more reliable of the two.

The gauge was calibrated by a series of 10 shots, in which impact velocities varied from 600 to 2,250 ft/sec. The corresponding impact pressures, determined by the Hugoniot reflection technique (see Figure 3 and Ref. 1 and 3), ranged from 3.8 to 17.4 kbar. The initial virtually discontinuous jump in resistance of the gauge recorded in these shots gives the direct measure of the incident shock wave amplitude. The plot of carbon-sensor resistances at incident shock pressures (i.e.peak deflections - see Fig 6) is given in Figure 7. The plot, of course, depends on the specific value of the resistance of the uncompressed sensor, R_o. However, since we always used a standard value of $R_o = 470 \pm 2$ ohm, a single curve suffices for all ten shots. The estimated experimental scatter of the data is ±2% in the high-pressure range and ±4% in the low-pressure range.

Records of the type reproduced in Figure 6, along with the calibration curve of Figure 7, give complete information about the shock regime acting on the region of the target where the gauge is imbedded. Thus when the sample is present in lieu of the gauge (see Figure 1), a complete pressure vs. time description in the sample is available. From this information, one can calculate the total shock impulse, $\int P dt$, to which a sample is exposed under a specified set of experimental conditions: specified impact velocity, projectile length, target geometry (e.g. degree of lateral confinement -- see Figure 1 of Ref. 2), etc.

III SHOCK TESTING OF AP AND PROPELLANT SAMPLES

Eight series of samples consisting of AP, AP with additives, and AP-type propellants were exposed to shocks of known parameters. The range of shock amplitudes was 7.8 to 21.4 kbar. Three different projectile lengths were used: 1.22, 1.83, and 3.18 cm. Approximate shock durations τ, as well as total shock impulses, are available for these shots from carbon-resistor data by methods discussed in Section II.

The geometry of the target assembly was uniform in all shots. The schematic diagram is shown in Figure 1. Note particularly that all targets were rigidly confined in hardened steel, so that lateral expansion of the sample under shock was negligible. The shape of the shock wave therefore was always a good approximation to an ideal square wave, which is adequately described by two parameters, P and τ. The cavities, machined out of the plastic, into which samples were loaded (not drawn to scale in Figure 1), were cylindrical in shape, and all of the same size: 1.219 cm in diameter, 0.762 cm in depth. Thus the sample volume was 0.889cc. With a loading density of 1.7 gm/cc, typical of many samples tested, the mass of the sample is about 1.5 gm. This is much larger than the samples used in previous years, which were only about 0.3 gm. The reason for the increase is that one of the major aims in this year's program was accurate chemical analysis of small extents of reaction which takes place under shock.

a. Propellant-Grade AP

The first series of tests was run on a sample of propellant-grade AP. The average particle diameter of the powder was 21μ. The powder was pressed into target cavities at maximum pressures which could be used without distortion of the plastic (about 15,000 psi). The mass, and therefore the density, of samples was determined by target weights before and after loading. Only samples falling within the range of 1.53±0.02 gm were accepted for testing. This corresponds to a loading density of 1.72gm/cc (88.2% of voidless).

Nineteen shots were fired. Projectile lengths used were 1.22, 1.83, and 3.18 cm, corresponding to approximately 8, 12 and 21 μsec shock durations (see above). Impact velocities ranged from 1,210 to 2,640 ft/sec, corresponding to impact pressures of 8.3 to 21.4 kbar (Figure 3).

The notation in the column of Tables I through VI, denoted "Mechanical Result," is as follows: A - no damage; B - cap loose (or off), no sign of reaction; C - cap loose (or off), signs of reaction; D - target sheared or ruptured. There is a possible ambiguity about results labelled "B". In cases where the target cap loosens without visible signs of reaction (smudging, scorching at sample surface), the effect may have been caused either by internal pressurization due to slow reaction, or by mechanical loosening under impact. Except for this qualification, the notation "A" through "D" clearly indicates increasing amounts of reaction.

In one shot the target cap was loose ("B"). The remaining 18 targets were retrived mechanically undamaged. Since in all types of results except "A", there is usually mechanical loss of the sample, only runs labelled "A" can be meaningfully analyzed for amounts of sample lost by chemical reaction. Most of the 18 undamaged samples in this series were subsequently analyzed chemically for the amount of perchlorate lost under shock exposure (see Section IV). Table I gives the complete listing of shock parameters and analytical data.

We conclude that the explosion threshold in this series was above 21.4 kbar (i.e., no explosion threshold was found even for 21 μsec duration).

b. Powdered AP/Polyethylene Mixtures

In the second series of shots powdered mixtures of propellant-grade AP (see Section IIIa) and polyethylene were tested. The average particle diameters of polyethylene powder were about 15μ. The mixture contained 87.4% of AP and 12.6% polyethylene by weight, i.e., it was approximately stoichiometric to HCl, H_2O, N_2 and CO. Pressed density, again, was controlled. The sample weight range was 1.335 ± 0.015gm, corresponding to

1.50gm/cc, or 86.7% of voidless density.

Two projectile lengths were used, 1.83 cm and 3.18 cm. Seventeen shots were fired with the shorter projectile (12μsec nominal shock duration) over an amplitude range of 10.2 to 18.1 kbar. Four shots were fired with the longer projectile (21μsec duration), ranging from 10.7 to 13.4 kbar. In view of the fact that approximate explosion thresholds had been found for this mixture in previous phases of this work (Ref. 2), the purpose of this rather extensive series of shots was twofold: (a) to determine amplitude thresholds more precisely, and (b) to obtain a series of mechanically undamaged samples which had been exposed to shock amplitudes near the explosion threshold for subsequent chemical analysis. The endeavour was successful. Shock parameters for explosion thresholds are shown in Figure 8, which also incorporates previous data from Ref. 2. Evidently, the threshold behavior is reproducible: 13.3 kbar for 12μsec and 11.7 kbar for 21μsec duration. Most samples which were retrieved below the explosion threshold were also analyzed chemically, as discussed in Section IV. Collected shock-parameter and analytical data are listed in Table II.

c. Low-Density Reagent-Grade AP

In view of the fact that neither of the two series of tests, the results of which are gathered in Tables I and II, had given evidence of substantial pre-explosion chemical reaction, test series IIIc through IIIg were designed to be short exploratory experiments with chemically pure AP, at two different pressed densities, and pure AP with additives. The purpose of tests at low densities and in the presence of additives was to induce reaction at low shock amplitudes.

The sample used in this series was reagent-grade AP, purchased from Fisher Chemical Co. The sample was carefully ground by hand and then analyzed micromerographically for particle size distribution. The weight mean diameter was found to be 30μ and the median diameter 32μ.

Four shots were fired with pure AP pressed to a relatively low density of 1.51$\pm$0.015gm/cc (77-78% of voidless). Projectile lengths were 3.18 cm. No mechanical damage was found at 12.9, 14.4, and 15.4 kbar. Explosion occurred at 17.0 kbar. The three retrieved samples were also analyzed chemically (see Section IV). The data are collected in Table IIIa.

A probable explosion threshold can therefore be assigned between 15.5 and 17.0 kbar (for 21μsec duration). A slight uncertainty remains, however, because the pressed density of the sample in shot No. 35B was 2-3% lower than the average of the other three shots. At any rate, this series demonstrates that pure AP at these pressed densities has a reasonably low explosion threshold.

d. High-Density Reagent-Grade AP

Three shots were fired with the material described in Section IIIc, but pressed to a higher density, ρ_o = 1.73$\pm$0.01gm/cc. No explosion threshold was found. The results are listed in Table IIIb.

e. High-Density AP - Cu 0202 Mixture

Five shots were fired with a powdered mixture of 97.5% reagent-grade AP and 2.5% of a commercial "copper chromite" catalyst (Harshaw Chemicals Cu0202). The reason for using this mixture is that Cu0202 is known to be very efficient in increasing the burning rate of AP; addition of a few percent of the catalyst increases the burning rate several times (Ref. 5). Moreover, Cu0202 was found to be quite effective in catalyzing the high-temperature decomposition kinetics of AP (Ref. 6).

The pressed density in this series was the highest attainable without distortion of the plastic cavity; it ranged between 1.70 and 1.75gm/cc. The projectile lengths in all five shots were 3.18cm. Two of the samples exploded. Three were retrieved. Two of the latter three were analyzed (see Section IV). The data are collected in Table IVa. The explosion threshold appears to be between 10.2 and 13.4 kbar for 21μsec duration.

f. Low-Density AP - Cu0202 Mixture

Three shots were fired with the AP/Cu0202 (97.5/2.5) mixture, described in Section IIId. However, in this series the pressed density was substantially lower, only about 78% of the voidless value. Shock pressures ranged from 8.7 to 15.4 kbar. Shock durations were 21μsec. Explosion occurred in all cases. The data are collected in Table IVb.

Tables IV and VI show substantial catalytic effect of Cu0202 as far as explosion threshold is concerned. The low-density mixture was the most sensitive sample studied in this program.

g. AP-Cu0202 - Carbon Mixture

Four shots were fired with a mixture containing 95% AP, 4% carbon, and 1% Cu0202. The reason was that addition of carbon had been found to decrease drastically the ignition temperature of AP (Ref. 7). The pressed density of these samples was rather high and very uniform: $\rho_o = 1.738 \pm 0.007$gm/cc.

The results are collected in Table V. Three samples were collected undamaged, and were analyzed (Section IV). The fourth one, at a high shock amplitude, exploded. Comparison with the results of Table V indicates that carbon is less effective in inducing reaction in AP under shock than Cu0202. Thus it is possible that the crucial requirement for inducement of substantial reaction under shock is not efficient ignition of AP grains, but rather the rate of subsequent surface decomposition.

h. Composite Propellant

In the final series, shock tests were performed on an actual composite propellant. The propellant consisted of AP, PBAN binder, and aluminum. The propellant was prepared and loaded into plastic (PVDC) capsules provided by Atlantic Research Corporation, by U. S. Naval Ordnance Station, Indian Head, Maryland.

Twenty-five samples were prepared, twenty-one of which were subsequently shock-tested in the same way as samples described in Sections IIIa through IIIg. In view of the fact that difficulties were experienced in casting the propellant directly into plastic capsules, which is the preferred procedure, only three samples were prepared in that fashion. The remainder were pre-cast into cardboard sleeves, and the cast specimens were pressed lightly into plastic capsules. A small amount of glue was used to eliminate cavities between the specimen and the plastic. Most samples so prepared had an unfortunate feature, in that they did not fill the sample cavity entirely. While an attempt was made to correct this deficiency by filling the space with plastic, the density of these samples remained unknown. Moreover, the density of the specimens (sample plus glue) which did not need this correction, determined from weight difference before and after loading, was 5 to 8% lower than in the case of samples cast directly into capsules. Undetected voids in these samples must therefore be suspected. In view of the fact that work with the composite propellant performed in another program (Ref. 8), disclosed the crucial importance of voidlessness, only the results of the three tests with high-density (1.76-1.79gm/cc) samples are quantitatively reliable.

The data are collected in Table VI. Probably the most important result of this series is the establishment of the high degree of stability of the cast propellant, as shown by runs 88-B, 113-B, and 119-B, none of which exhibited any obvious reaction (part a of Table VI). It is noteworthy that the sample in shot 119-B was exposed to a shock impulse near the upper limit of the current technique.

Part b of Table VI lists the results with pre-cast samples. Densities of specimens, in the few cases where they could be determined, are given in the second column; in the absence of other evidence, it must be assumed that densities of other specimens were not necessarily any higher. Under these circumstances, no quantitative meaning can be assigned to mechanical results observed (last column). However, it may be pointed out that in at least some cases (shots 84-B and 121-B) there was no definite sign of reaction even at very high shock impulse levels. It can be presumed then that substantial reactions observed in other shots (77-B, 83-B) was due to undetected imperfections in the sample.

No quantitative chemical analyses were made in this series.

IV QUANTITATIVE CHEMICAL ANALYSIS

It was noted previously (Ref. 2) that the experimental technique employed in the present program places stringent demands on the quantitative analysis of samples which had been exposed to a shockwave and then retrieved mechanically undamaged. This is so, because the analysis is necessarily based on a small difference between the original quantity of the (unreacted) sample, and the recovered residue. A substantial effort, therefore, was devoted during the current year toward an improved method of analysis for perchlorate ion. Several techniques were tested and abandoned before a sufficiently accurate method was adopted. A brief description of the unsuccessful methods follows. All of these methods are modifications aimed at improvement of the tetraphenyl arsonium chloride precipitation titration.

The conductometric titration procedure suffered from the slowness of precipitate formation. Addition of large amounts of an electrolyte speeded up the procedure, but it was found that the strongly enhanced conductance of the solution made it difficult to detect the endpoint with sufficient precision.

An amperiometric titration with tetraphenyl arsonium chloride and an added electrolyte was considered with the view of accurate endpoint detection. This method depends upon the appearance of a polarographic wave once excess tetraphenyl arsonium chloride is present beyond the endpoint. However, a polarogram run on tetraphenyl arsonium chloride showed a poorly defined reduction wave, considered inadequate for titration.

Several perchlorate titrations were attempted by means of a rotating platinum electrode, but the endpoint was not sharply enough defined to give results superior to those obtained in our previous work.

The applicability of a potentiometric endpoint procedure was investigated in a simple experiment. A titration of perchlorate with tetraphenyl arsonium chloride was run using a platinum-calomel electrode and a potentiometer readout. No distinct potential change was observed at the endpoint. The experiment was then repeated with a polarized electrode pair, again with negative results.

The method finally adopted employs a specific-ion electrode. First we found that specific-ion electrodes do not have sufficient precision for direct measurement of ClO_4^-. However, they are very suitable for the detection of endpoint. The success of this method depends on the fact that the perchlorate-specific electrode (Orion Research) is subject to interference from chloride. Thus, when the electrode is used against a double-junction calomel reference in the precipitation titration of perchlorate with tetraphenyl arsonium chloride, its potential is controlled by the concentration of perchlorate ion until the equivalence point is reached, whereupon the potential shifts to that resulting from Cl^- interference; the addition of Cl^- enhances the response. The result is the familar "S-shaped" potentiometric titration curve, which can be handled by an automatic titrator.

This method, when used on pure samples of AP, gave the following results: 0.6 percent maximum deviations in individual runs; 0.3-0.4 percent average deviations of three or more runs. Averages of three or more runs were used in all the reported analyses.

In view of the fact that in the reaction under shock partial reduction of perchlorate cannot be excluded, tests were run on interference with chlorate. None was found. A sample consisting of 1.500g AP and 0.300g $KClO_3$ analyzed to an equivalent of 1.498 g AP. The method, evidently, cannot be subject to interference of chloride either.

The method was also used for analysis of perchlorate in the presence of substantial amounts of polyethylene powder (Section IIIb). A prepared mixture containing 87.4% AP and 12.6% polyethylene analyzed to 87.34±0.25% AP in an average of six runs. Similarly good results were obtained with AP/Cu0202 and AP/carbon/Cu0202 mixtures.

We conclude that the method, as used in this program, is reliable within ±0.4 percent. In view of the fact that somewhat larger errors were experienced in a few analyses of shocked samples (manifested by results which showed more perchlorate than the amount originally present -- see negative "losses" in Tables I through V), we have carefully examined the experimental procedure for possible errors other than those of chemical analysis. The weighing errors are less than 0.1% and can therefore be neglected. However, the preparation of pressed samples involves smoothing out (sanding) of the surface of the samples; this process involves slight losses of the plastic capsule, which in the end-result tend to shift analytical data to higher values. The maximum error so introduced can be 0.3%. The cumulative error, in the direction of finding too much ClO_4^-, therefore may conceivably be as high as 0.7% (but, of course, is usually less). Thus any entries in Table I-V which show "losses" between -0.7 and +0.4%, may be due to experimental errors. Losses higher than 0.4% should be considered real (chemical reaction). A "loss" lower than -0.7% (Shot 5-B, Table I) cannot be accounted for.

Only mechanically undamaged residues of samples were analyzed (result "A" in that the last columns of Tables I-V). Result "D" usually means gross, or even total, loss of sample. Result "C" means small, but visible loss. Result "B" usually does not entail visible loss, but such (mechanical) loss must always be suspected.

An inspection of Tables I-V reveals a general type of result: mechanically undamaged samples show very little loss when analyzed, never in excess of 2 percent. We conclude that the decomposition reaction under shock loading either proceeds to a very limited extent only, or builds up rapidly toward explosion. It must be emphasized, however, that this conclusion applies only to pressed samples of pure AP, or AP with additives which, even at relatively high densities, contained a substantial void volume (at least 10%). Results with consolidated propellant samples (Table VI) remain inconclusive as far as chemical reaction is concerned.

The second conclusion is that such extents of reaction as are found by chemical analysis to have taken place under shock loading cannot be correlated with shock parameters (amplitude, impulse, energy). To be sure, the small amounts of reaction found, coupled with experimental error limits, do not leave much room for discrimination among the results. Nevertheless, a comparison of pairs of results, such as 12-B and 15-B in Table I, 40-B and 25-B in Table II, etc., suggest an erratic initial reaction.

V. CONCLUSIONS

1. The extent of chemical reaction under shockwaves of specified amplitude and duration for various AP-containing mixtures can be judged qualitatively be the occurrence of explosion and quantitatively by chemical analysis of the sample retrieved. "Explosion" means an extent of reaction sufficient to rupture the plastic capsule containing the sample. Since quantitative chemical analysis never revealed more than 2% decomposition of perchlorate, it can only be stated that the extent of reaction leading to explosion is in excess of 2%.

2. No explosion thresholds were found for AP --- either propellant-grade, or reagent grade --- when pressed to about 90% of voidless density. Maximum shock impulses employed in these tests were as follows: 21.4 kbar for 8 μsec, 18.6 kbar for 12 μsec, and 17.1 kbar for 21 μsec in the case of propellant-grade material; 17.6 kbar for 21 μsec in the case of reagent-grade material. Thus, no difference in shock sensitivity between the two grades has been found; it must be pointed out, however, that no exten-

sive effort was made to establish a threshold for reagent-grade AP, so that the data on that material are very meager.

3. An extensive series of tests on AP/polyethylene powdered mixture pressed to 87% of voidless density gave explosion threshold amplitudes which decrease with increasing shock durations. This result indicates that the concept of a finite rate of reaction, initiated by the incident shock and quenched by the rarefaction, is realistic.

4. Decreased densities of pressed powdered charges have a strong effect on sensitivity, both for pure AP and for AP with a catalyst (Cu0202).

5. Addition of Cu0202, a catalyst which is known to accelerate deflagration of AP in strand-burner experiments, increases markedly the shock sensitivity of AP, both at high (88% of voidless) and low (78% of voidless) density. On the other hand, no definite lowering of the explosion threshold was found upon addition of carbon, which had been reported to facilitate ignition of AP. These results suggest that the rate of surface decomposition after ignition, rather than the process of ignition itself, is crucial in determining buildup to explosion.

6. The extent of pre-explosion reaction found by precipitation titration of ClO_4^- under NAS1-8622 agrees with NH_4^+ analysis performed in earlier stages of this program (2% or less in both cases). Thus the chemical analysis of shocked samples indicates that the decomposition reaction under shock loading either proceeds to a limited extent only, or builds up rapidly toward explosion.

7. All of the results are consistent with the hypothesis that the chemical reaction initiated by the shock wave is a decomposition reaction taking place at the surfaces of individual grains (i.e. throughout the body of the granular charge). The subject of such reactions in porous media has been studied extensively both for AP and for explosives (9, 10, 11). Despite the many studies, the exact initiation mechanism is not known. Two processes which probably contribute toward initiation are (a) adiabatic compression of interstitial gas, followed by heat conduction from the

gas into grains, and (b) generation of high temperatures at grain surfaces by stagnation of grains, accelerated by the shockwave, against other grains. It may be pointed out that in either of the two cases, ignition times are apt to be very short; it can be shown, for example, that both compression of the gas and the ensuing heat transfer into the solid can be accomplished in a fraction of a microsecond. Thus, it does not appear probable that, in experiments lasting for 10 μsec or more, ignition lags will be decisive in the buildup of explosion.

These considerations, combined with our experimental results, suggest the following probable sequence of events in our experiments: (a) Whenever there is surface ignition of the grains, it takes place almost immediately upon arrival of the shockwave. It appears quite possible that ignition occurs at all shock-pressure levels employed in this work (i.e. down to about 8 kbar). It is also possible that ignition occurs at random points throughout the granular bed. (b) The subsequent developments depend on the rate of deflagration of ignited grains, and possibly on the rate of propagation of the reaction from grain to grain. The four principal factors determining (enhancing) the extent of the reaction, and therefore chiefly responsible for occurence of explosions are: (a) decreasing density of the pressed charge; (b) addition of burning-rate catalysts; (c) increased shock pressure; (d) increased shock duration.

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TABLE I

SHOCK DATA ON PROPELLANT-GRADE AP

$\rho_o = 1.72 \pm 0.02$ gm/cc

Shot	τ (μsec)	Velocity (ft/sec)	Press. (kbar)	Mech. Result*	% Loss**
9-B	8	1205	8.3	A	0.6
23-B	8	1380	9.8	A	NA***
11-B	8	(1300-1500)****	9-11	A	0.1
12-B	8	1480	10.7	A	1.6
13-B	8	2300	18.1	B	NA
14-B	8	2350	18.6	A	0.3
15-B	8	2640	21.4	A	0.1
3-B	12	1435	10.2	A	1.1
4-B	12	1610	11.8	A	0.8
5-B	12	1895	14.4	A	-1.0 (?)
6-B	12	1955	14.9	A	-0.1
8-B	12	2300	18.1	A	0.8
7-B	12	2350	18.6	A	0.3
16-B	21	1480	10.7	A	0.3
19-B	21	1610	11.8	A	NA
17-B	21	1670	12.3	A	-0.7
18-B	21	1780	13.4	A	NA
20-B	21	1895	14.4	A	NA
21-B	21	2185	17.1	A	0.3

* A-no damage; B-cap loose. See Section IIIa.

** Based on perchlorate analysis. See section IV.

*** NA - not analyzed.

**** Camera failure; velocity estimated.

TABLE II

SHOCK DATA ON AP/PE MIXTURES (87.3% AP)

$\rho_o = 1.50 \pm 0.015$ gm/cc (86.7 ± 0.9% of voidless)

Shot	τ (μsec)	Velocity (ft/sec)	P (kbar)	Mech. Result*	%Loss**
28-B	12	1435	10.3	A	1.6
53-B	12	1550	11.3	A	NA
33-B	12	1670	12.4	A	0.2
36-B	12	1670	12.4	A	0.0
40-B	12	1670	12.4	A	-0.1
25-B	12	1720	12.8	A	1.8
48-B	12	1725	12.9	A	1.2
31-B	12	1780	13.4	A	-0.3
29-B	12	1895	14.4	D	---
49-B	12	1900	14.4	D	---
27-B	12	2070	16.0	D	---
30-B	12	2125	16.5	D	---
45-B	12	2150	16.7	D	---
46-B	12	2150	16.7	D	---
32-B	12	2150	16.7	D	---
39-B	12	2240	17.6	D	---
26-B	12	2300	18.1	D	---
71-B	21	1480	10.7	A	NA
68-B	21	1665	12.4	D	---
70-B	21	1665	12.4	D	---
69-B	21	1780	13.4	A	NA

* A - no damage; D - target ruptured. See Section IIIa.

** Based on perchlorate analysis. See Section IV.

TABLE III

REAGENT-GRADE AP (32μ diameter)

a. $\rho_o = 1.51 \pm 0.015$ gm/cc

Shot	τ (μsec)	Velocity (ft/sec)	Pressure (kbar)	Mech. Result*	% Loss**
37-B	21	1730	12.9	A	0.3
38-B	21	1900	14.4	A	0.1
41-B	21	2010	15.4	A	0.9
35-B	21	2180	17.0	D	---

b. $\rho_o = 1.73 \pm 0.01$ gm/cc

Shot	τ (μsec)	Velocity (ft/sec)	Pressure (kbar)	Mech. Result*	% Loss**
64-B	21	2010	15.4	B	---
66-B	21	2120	16.4	A	0.1
67-B	21	2240	17.6	A	-0.5

*A - no damage; B - cap loose; D - target ruptured. See Section IIIa.

**Based on perchlorate analysis. See Section IV.

TABLE IV

AP/CuO2O2 (97.5/2.5)

a. $\rho_o = 1.725 \pm 0.025$ gm/cc

Shot	τ (μsec)	Velocity (ft/sec)	Pressure (kbar)	Mech. Result*	%Loss**
43-B	21	1150	7.8	A	0.1
50-B	21	(1100-1300)***	7.5-9.0	A	-0.1
59-B	21	1435	10.3	A	-0.5
44-B	21	1780	13.4	D	---
42-B	21	1900	14.4	D	---

b. $\rho = 1.52$ gm/cc

Shot	τ (μsec)	Velocity (ft/sec)	Pressure (kbar)	Mech. Result*
56-B	21	1260	8.8	D
55-B	21	(1400-1700)***	10-12.5	D
51-B	21	2100	16.3	D

* A - no damage; D - target ruptured. See section IIIa.

** Based on perchlorate analysis. See Section IV.

*** Camera failure; velocity estimated.

TABLE V

AP/C/CuO2O2 (95/4/1)

$\rho_o = 1.738 \pm 0.007$ gm/cc

Shot	τ (μsec)	Velocity (ft/sec)	Pressure (kbar)	Mech. Result *	% Loss **
61-B	21	1610	11.8	A	-0.4
60-B	21	1720	12.8	A	-0.6
62-B	21	2070	15.9	A	0.0
63-B	21	2410	19.2	D	---

* A - no damage; D - target ruptured. See Section IIIa.

** Based on perchlorate analysis. See Section IV.

TABLE VI

COMPOSITE PROPELLANT

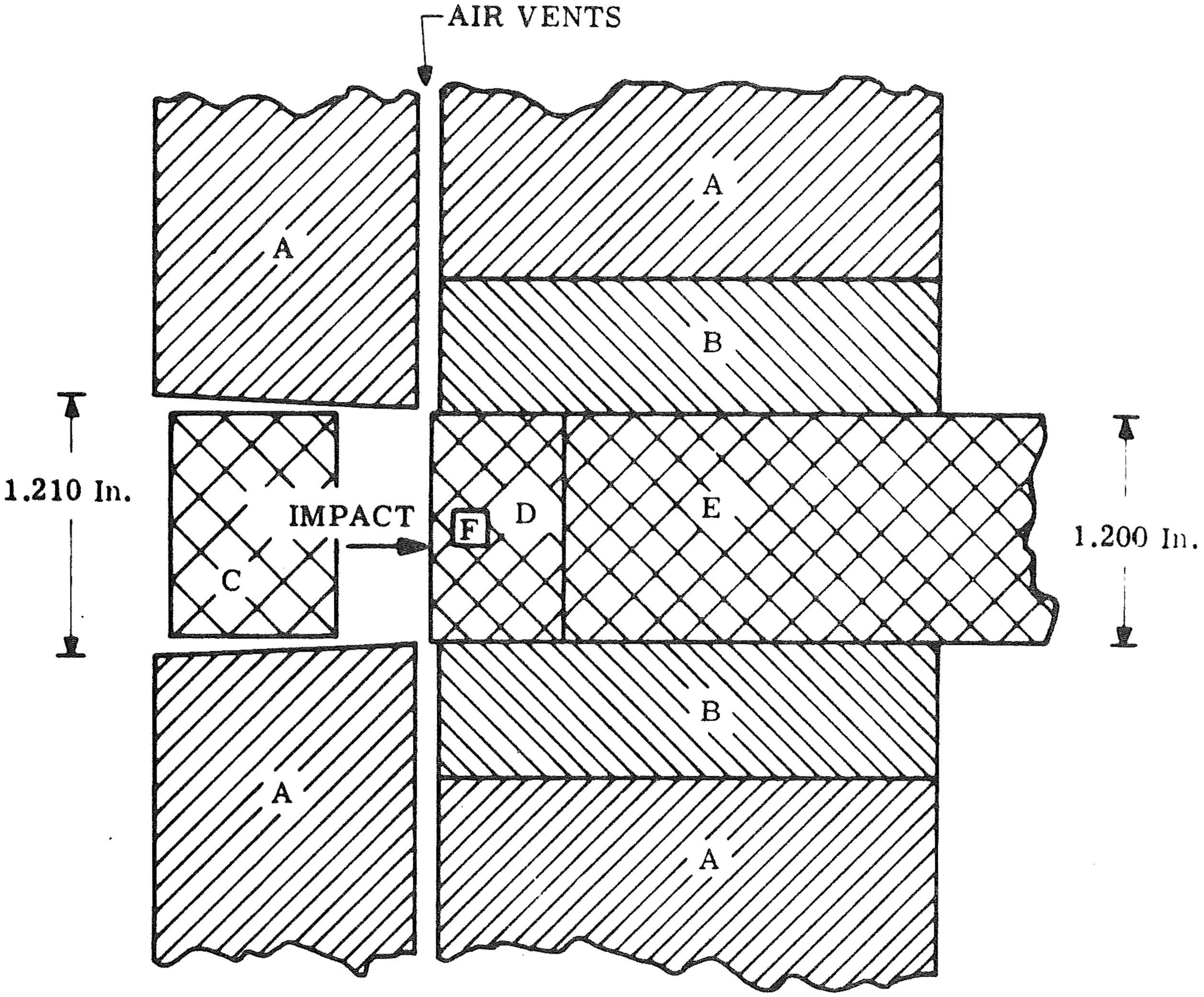
a. Samples Cast into Plastic

Shot	ρ (gm/cc)	τ (μsec)	Velocity (kbar)	Pressure (kbar)	Mech. Result*
88-B	1.762	12	1150	7.8	A
113-B	1.781	21	1895	14.2	A
119-B	1.786	21	2470	19.8	A
			b. Pre-Cast Samples		
80-B	1.643	12	1835	13.8	A
89-B	F	12	1890	14.2	A
79-B	1.670	12	1950	14.9	A
99-B	F	12	2010	15.4	B
81-B	1.675	12	2070	16.0	A
91-B	F	12	2070	16.0	A
90-B	F	12	2300	18.2	B
95-B	F	12	2410	19.2	C
100-B	F	12	(∿2400)**	∿19	C
92-B	F	21	1550	11.3	A
112-B	F	21	1720	12.8	C
115-B	F	21	1830	13.8	A
87-B	F	21	1900	14.4	C
77-B	F	21	2050	15.8	D
114-B	F	21	2180	17.0	A
83-B	F	21	2300	18.1	D
84-B	F	21	2300	18.1	B
121-B	F	21	2470	19.7	B

* A - no damage; B - cap loose; C - reaction; D - target ruptured. See Section IIIa.

F - Surface filled; density unknown.

** Camera failure; velocity estimated.



A = HOLDER (HIGH-TENSILE STEEL)
B = INSERT (HARDENED STEEL)
C = PROJECTILE (POLYVINYL DICHLORIDE)
D = TARGET (POLYVINYL DICHLORIDE)
E = ENERGY ABSORBER (POLYVINYL DICHLORIDE)
F = SAMPLE OR GAUGE

1/26

The Impact Experiment

Figure 1

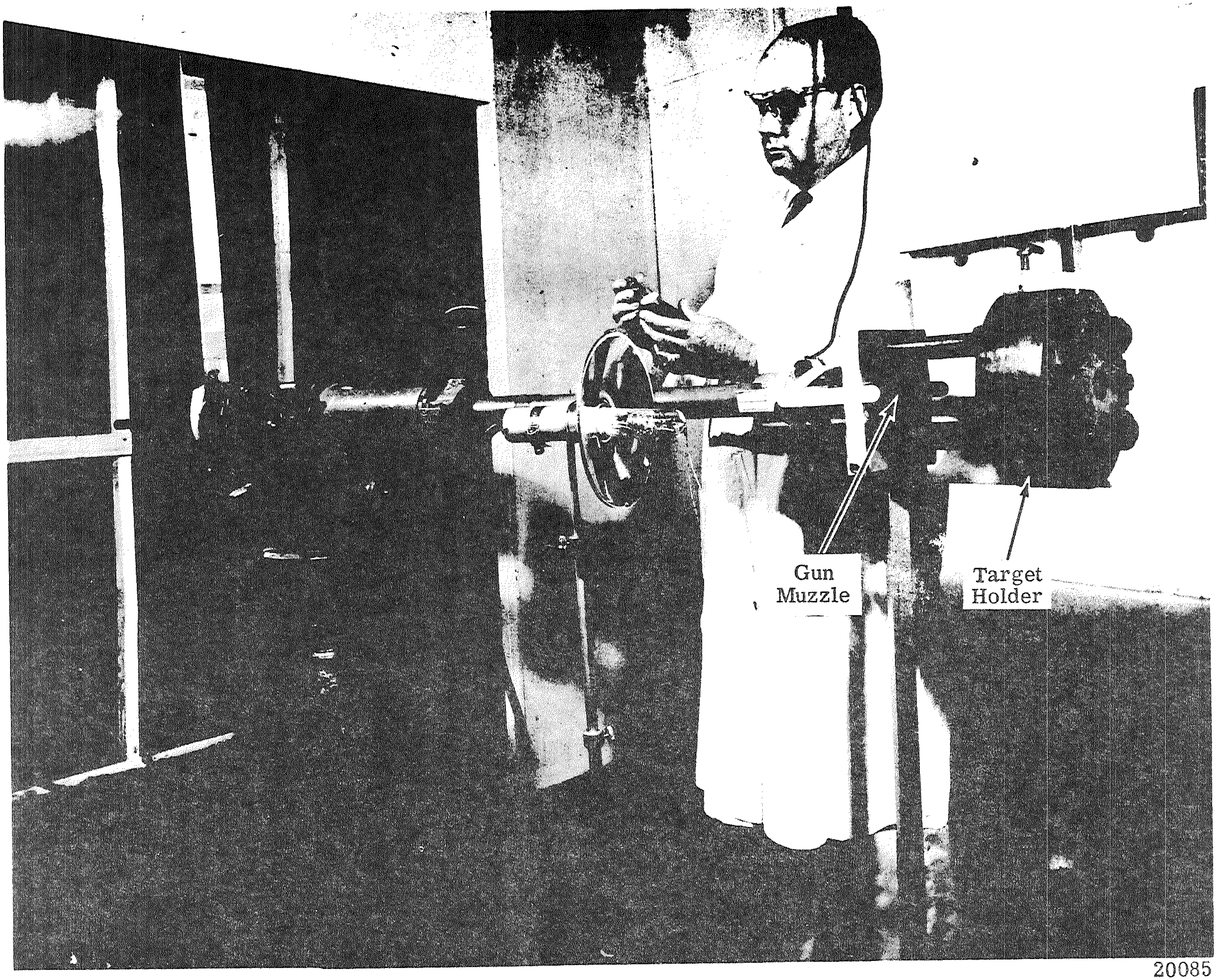
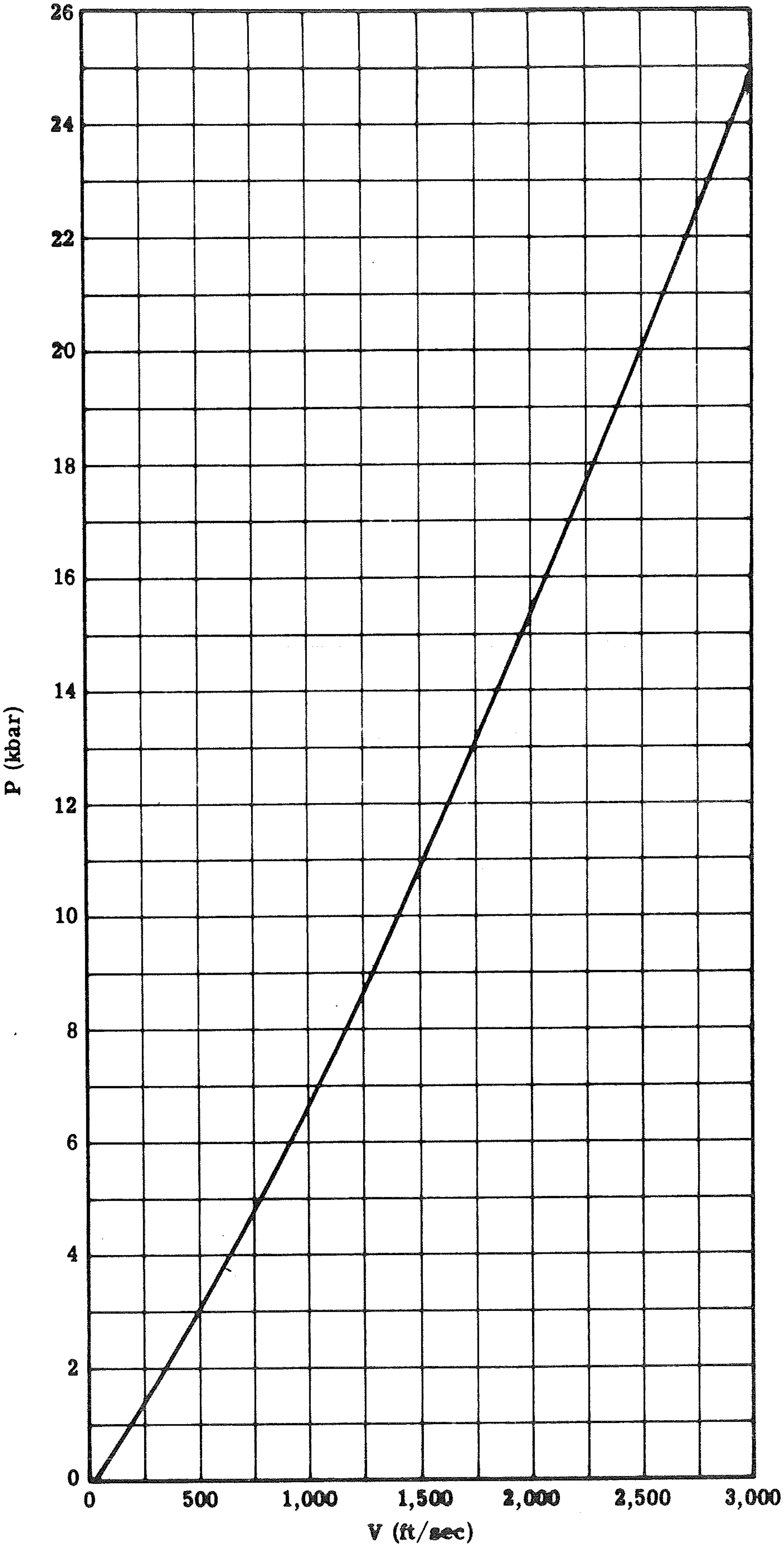
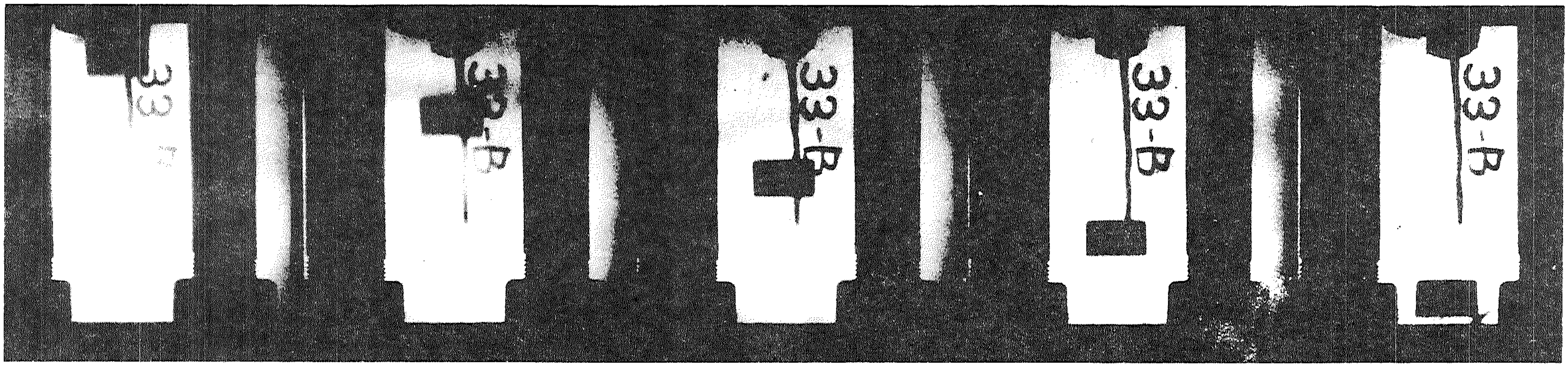


Figure 2. View of the Gun Muzzle with the Target Holder Attached.



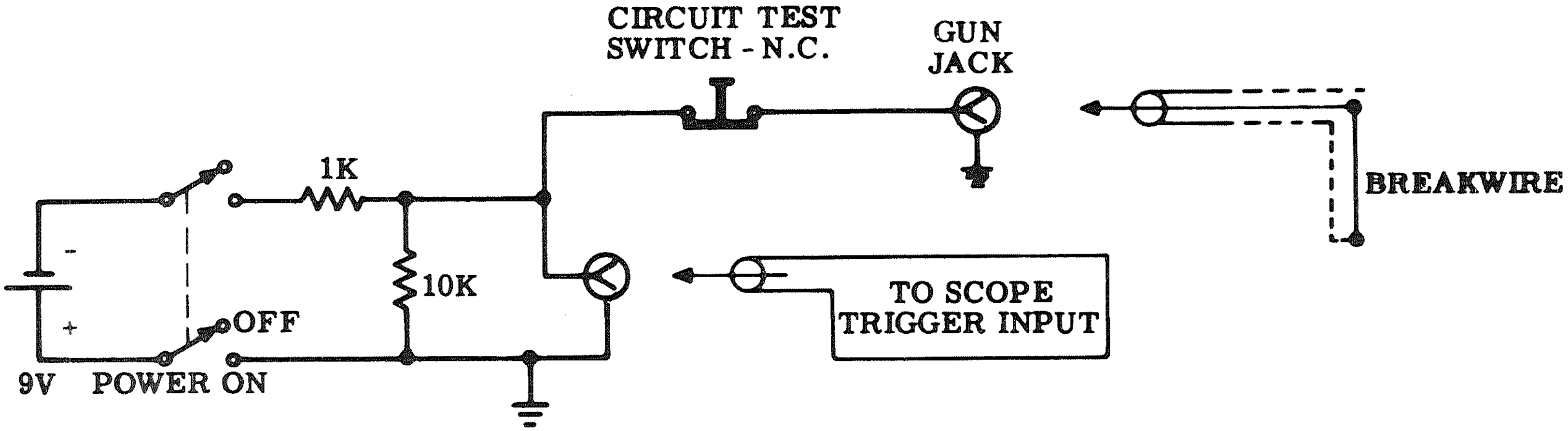
24209

SHOCK PRESSURE VERSUS IMPACT VELOCITY
Figure 3



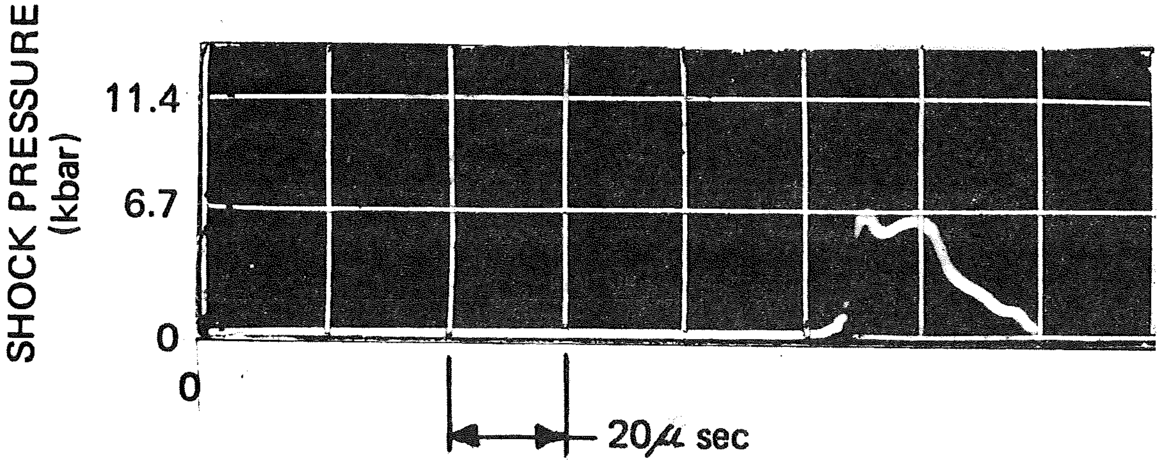
24321

Figure 4. Projectile in Flight Between Gun and Target, Velocity = 1,670 ft/sec, 57.2 μsec Between Frames.



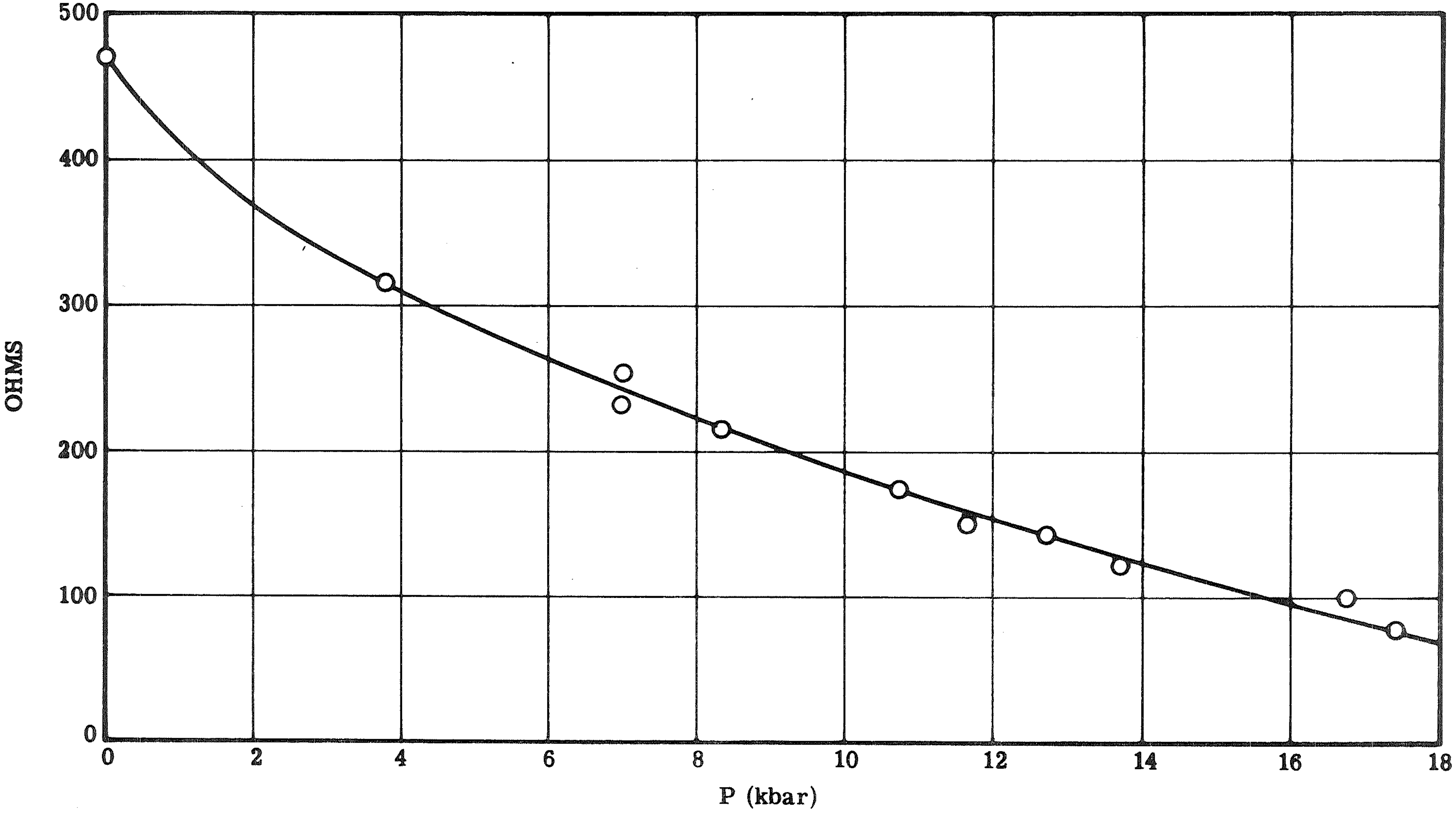
OSCILLOSCOPE SWEEP - TRIGGER GENERATOR

Figure 5



24322

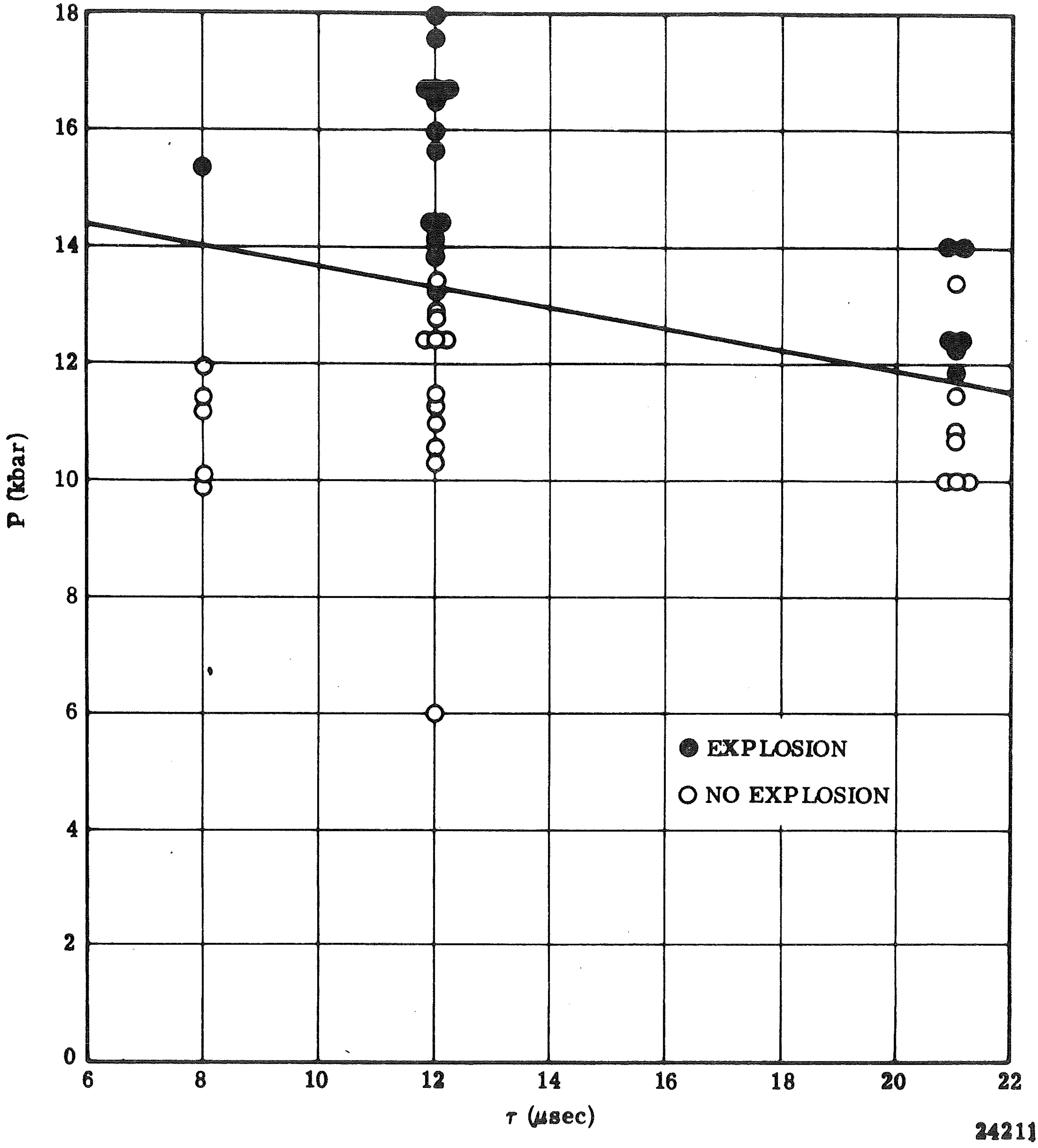
Figure 6. Oscilloscope Record of a Pressure-Gauge Signal, Impact Velocity: 1,035 ft/sec.



24210

CARBON-SENSOR RESISTANCE VERSUS SHOCK PRESSURE

Figure 7



EXPLOSION THRESHOLD FOR AP/POLYETHYLENE MIXTURE

Figure 8

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