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SHOCK RESPONSE OF FILLED PLASTICS (U)

by

E. G. Johnson and M. L. Pandow

June 1967

U. S. ARMY MISSILE COMMAND
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ROHM AND HAAS COMPANY
REDSTONE RESEARCH LABORATORIES
HUNTSVILLE, ALABAMA 35807

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SHOCK RESPONSE OF FILLED PLASTICS

ABSTRACT

A method of determining shock Hugoniots of opaque media by means of microwave interferometry is described. This method has been used to determine shock Hugoniots for solid propellants, propellants with dummy oxidizer, and inert binders. It was found that the shock response of solids-filled elastomeric polymers is the same as that of the continuous phase alone, at loadings as high as 75 wt. % solids. It was also found that ammonium perchlorate decomposes exothermally under shock, even in nondetonable propellants; and because of this decomposition, truly non-reactive shock Hugoniots cannot be obtained on live-oxidizer formulations, at least not at shock strengths above 10 kbar.

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SHOCK RESPONSE OF FILLED PLASTICS

INTRODUCTION

Solid propellants represent quasi-stable compositions of matter which, owing to the presence of premixed oxidizer and fuel, present certain unique potential hazards in use. Although no properly consolidated solid-propellant motor has been known to detonate upon normal thermal initiation,* nevertheless certain propellants are capable of sustaining classical stable, high-velocity detonation when subjected to very strong shocks such as those created by an explosion or high-energy impact. Even those fuel-binder composite types which do not sustain detonation in ordinary charge sizes generate blasts of considerable magnitude. Recent tests by Aerojet for the Air Force in very-large-diameter charges of fuel-binder propellant have shown such large explosive equivalents and short reaction times as to reduce the whole question of whether or not true detonation occurs to one of only academic interest.

A knowledge of the physical and chemical nature of the shock response of components is necessary for analysis of the mechanism of the process of initiation of detonation. The high pressures and high loading rates characteristic of shocks (in this discussion, always supersonic) cannot be simulated by conventional pseudo-steady-state equilibrium methods usually employed for measurement of such properties as compressibility. Moreover, the behavior of a composite propellant

*This is not to say case rupture and explosions do not occur owing to changes in deflagration rate or burning surface or both, arising from such causes as combustion instability, grain break-up, case-bond failure, etc. What is referred to here is a reaction-supported shock through the propellant with decimation of confining materials, which are impelled at supersonic velocities, and formation of sharp, intense blast waves.

probably could not be adequately inferred from that of the respective constituents, even if such data were available. The solution of the equation of state across the shock front (the Hugoniot relation) can only be inferred by indirect means. In the sections which follow, the method by which the shock Hugoniot may be derived and the experimental techniques for making velocity measurements in opaque media by means of microwave interferometry are briefly reviewed. Results with simulated propellant at different solids loading are discussed which indicate that, in the truly non-reactive case (with dummy oxidizer), the shock response is unaffected by the presence of dispersed solids and is therefore that of the continuous phase alone. Preliminary data are also given which suggest that live oxidizer reacts sufficiently to make some energy contributions to the shock, even in the non-detonating case.

BACKGROUND

Hugoniot Relations

A factor of prime importance in consideration of the mechanism of shock initiation of detonable materials is the amount of energy transmitted to the material by the initiating shock wave. The relation based on hydrodynamic models which describe the change in specific internal energy, e, in a non-reactive shock front is known as the Hugoniot relation; in terms of pressure, P, and specific volume, τ

$$e_1 - e_0 = \tfrac{1}{2}(P_1 + P_0)(\tau_0 - \tau_1) \qquad (1)$$

For a shock wave of a given velocity in a given medium this energy change is a constant. Consequently, the Hugoniot relation can be expressed as a graph of any two variables of state, and measurement of any two of these variables gives a complete description of the shock Hugoniot.

The combinations of variables most commonly used to describe the Hugoniot are particle velocity and shock velocity (u, U), shock velocity and pressure (U, P), and pressure and volume (P, τ). These quantities are interrelated through the following expressions, where ρ_0 is the mass density ahead of the shock:

$$P = \rho_0 u U \qquad (2)(1)\dagger$$

$$P = \rho_0 U^2 (1 - \frac{\tau}{\tau_0}) \qquad (3)(1)$$

Measurement of Shock Hugoniots

The quantities which can be measured for the determination of the shock Hugoniot are the shock velocity and the particle velocity. The shock velocity is directly observable by any technique which registers the time-displacement of the shock front in the medium. The particle velocity must be derived by an indirect technique. Two methods have been used, both of which involve certain assumptions in the calculation of the particle velocity.

With the first method, the free-surface velocity, U_{FS}, of the material through which a shock has passed is measured ([2,3]). It is assumed that

$$u = \tfrac{1}{2} U_{FS} \qquad (4)([3])$$

In the second method, a shock wave is passed through the material under investigation and then into an adjacent material of a known Hugoniot. It is assumed that the impedance-mismatch equation relating incident and transmitted shock conditions

$$\frac{u_i}{u_f} = \frac{\rho_f U_f + \rho_i U_i}{2\rho_i U_i} \qquad (5)$$

holds at the interface between the two materials. The shock velocity is measured on both sides of the interface and u_f is determined from the known Hugoniot; u_i can then be calculated from Eq. 5.

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†Numbers in parentheses in the text indicate references at end of report.

Shock Hugoniots have been determined for many non-reactive materials; water ([5]), a number of organic liquids ([2]), several metals ([3]), Plexiglas®**([6]) are among the more important ones. There have also been attempts to determine the non-reactive Hugoniot of detonable materials ([7]), either by using shock pressures below that necessary for initiation or by working in geometries in which the material will not detonate. Since some chemical reaction does take place in the material behind the shock front and since such reactions may be very rapid ([8]), doubt arises as to whether or not a truly non-reactive Hugoniot is being measured. To answer this question a series of experiments was initiated in which aluminum-loaded plastic and simulated propellants were studied.

EXPERIMENTAL RESULTS

Measurements on Inert Binders

Initial measurements, which have already been reported ([9]), were made on an unfilled, inert methacrylate binder (Table I), and on the same binder loaded 20% by weight with aluminum. Two sizes of aluminum were used: one having a weight-median particle diameter, d_m, of 6μ, with a 90% range of 2.5μ to 11μ, and one having a d_m of 105μ, with a 90% range of 84μ to 115μ. The experimental method used was the impedance-mismatch technique. Shock velocities were measured in the samples and Plexiglas by microwave interferometry (See below).

The results of the experiments showed no difference between the particle-velocity–shock-velocity relationships for the pure binder and for the binder containing either of the two aluminum particle sizes. The data also agreed with the relationship for Plexiglas (Fig. 1).

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Table I

Inert Binder Composition Used for Hugoniot Studies

Ingredient	Function	Weight Per Cent
Paraplex® P-13[a]	resin	75
Santicizer® 160[b]	plasticizer	25
Cab-O-Sil® [c]	thickener	3 phr
Lupersol DDM[d]	catalyst	1 phr
6% Nuodex Cobalt[e]	accelerator	0.6 phr

[a]Rohm and Haas Company, Philadelphia, Pennsylvania.
[b]Monsanto Chemical Company, St. Louis, Missouri.
[c]Godfrey L. Cabot, Inc., Boston, Massachusetts.
[d]Wallace and Tiernan, Inc., Buffalo, New York.
[e]Nuodex Products Company, Elizabeth, New Jersey.

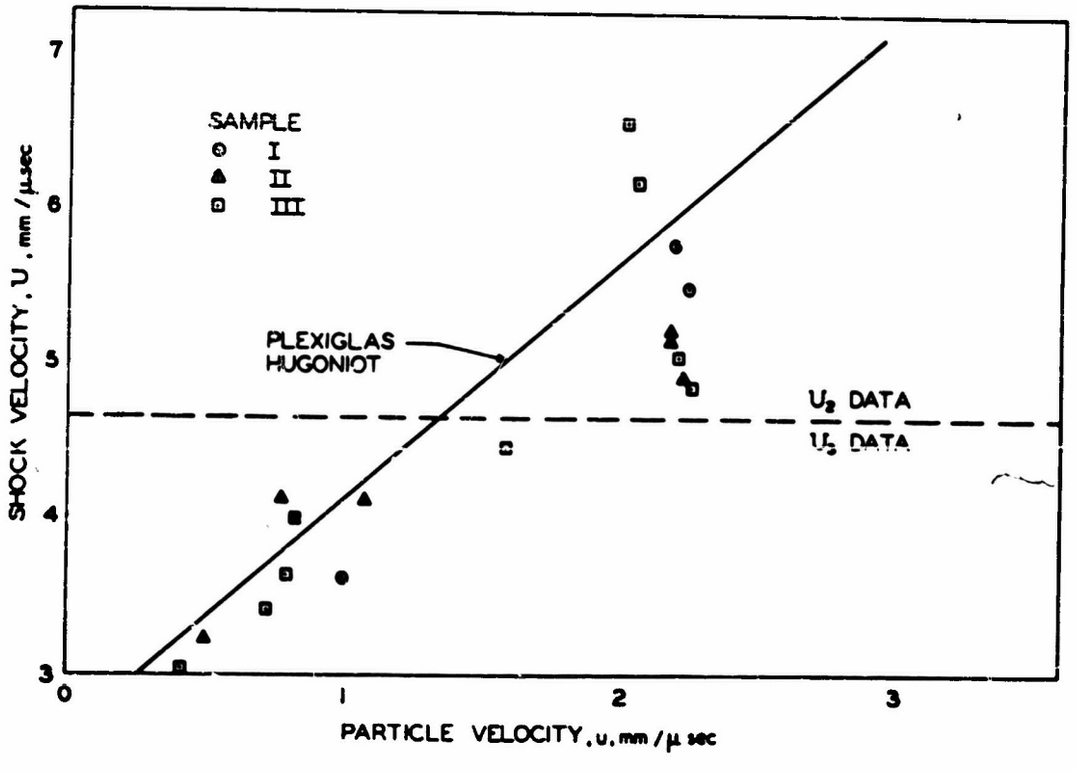

FIG. 1 SHOCK VELOCITY AS A FUNCTION OF MASS VELOCITY.

Measurements on Simulated Propellants

The solids loading in the materials described above is much lower than that encountered with a propellant. Two formulations were selected for experimentation which would more closely simulate conditions found in an actual propellant. A polybutadiene–acrylic acid binder was used in both formulations; both contained aluminum. In one, a dummy oxidizer consisting of potassium chloride was used; the other formulation contained an equal weight of ammonium perchlorate instead of KCl (Table II).

Table II

Propellant Used for Hugoniot Studies

Ingredient	Weight per cent
KCl or NH_4ClO_4 (55μ wt.-median diam.)	62.5
Aluminum (6μ wt.-median diam.)	12.5
PBAA/ERL 2774[a] (89.5/10.5)	25.0

[a]Epoxy resin, Bakelite Division, Union Carbide Corp.

Again the impedance-mismatch method was used to determine particle velocities. A microwave technique ([10]) was used to determine the decay of the shock fronts in the propellant-like formulations and in Plexiglas. The instrumentation used is shown in Fig. 2 and the experimental set-up is given in Fig. 3. Duplicate shots were made with specimens up to 2.5 inches long at 0.5 inch increments interposed between a pentolite booster and a Plexiglas block.

The oscilloscope was triggered by the ionization probe near the base of the pentolite charge to record the detonation front in the pentolite, the decay of the shock front through the specimen and into the Plexiglas. Each cycle of the recorded signal on the oscillogram represents a displacement of the shock front by a half wavelength of the microwaves in the sample. The wavelength in the samples was found by determining the dielectric

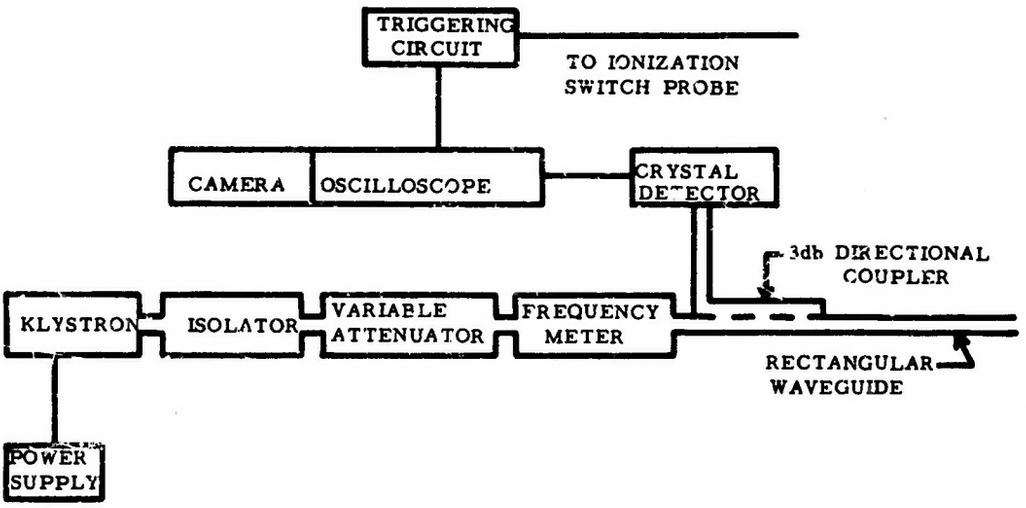

FIG. 2 INSTRUMENTATION.

constant of the propellant (relative to vacuum) in a slotted waveguide (4.46 at 20 GHz for the KCl formulation, 4.97 at 20 GHz for the NH_4ClO_4 formulation) and calculating [11] the wavelength for the dominant hybrid mode in a 2-inch-diameter rod of the sample [9]. The wavelength in the Plexiglas was calculated in the same way, using a dielectric constant [12] of 2.65[12]. In a typical oscillogram (Fig. 4) the detonation front in the explosive (a), the shock front in the sample (b), and the shock front in Plexiglas (c) can be seen.

The shock front in both the specimen and the Plexiglas is partially transparent to microwaves and reflections behind this front, moving at a lower velocity, produce a large, low-frequency signal at the beginning of (b) and (c). A 180-ohm load was used at the oscilloscope to keep attenuation of the high-frequency signal from the shock front less than attenuation of the low-frequency signal behind the front.

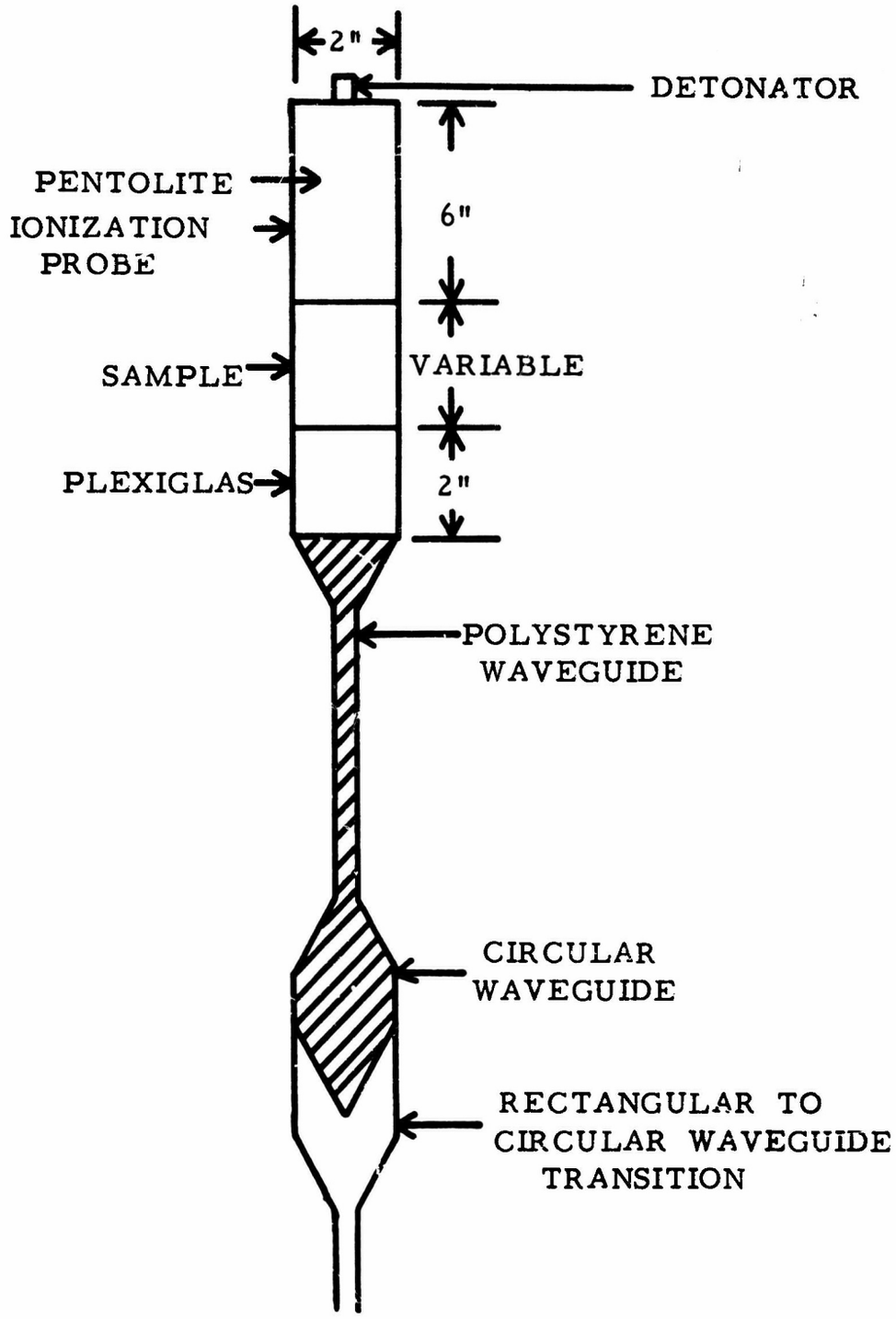

FIG. 3 EXPERIMENTAL SET-UP.

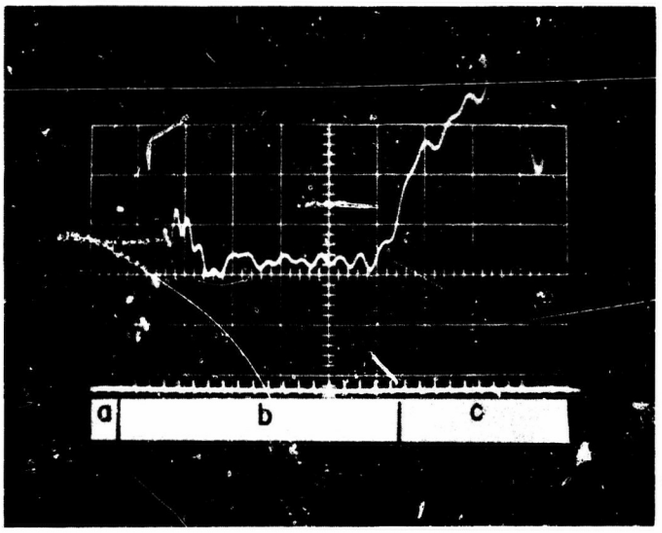

FIG. 4 TYPICAL OSCILLOGRAM.

Data Reduction Three velocities were of interest: the velocity in the sample at the pentolite–specimen interface, and the velocities in both the sample and the Plexiglas at the sample–Plexiglas interface. To determine these velocities the displacement–time data in the sample obtained from the oscillograms were fitted to curves of the form $t = A + Bs + Cs^2 + \ldots$ and $t = e^{A + Bs + Cs^2 + \ldots}$, where t is time and s is displacement. Equations of degrees from 1 to 5 were used, depending on the number of experimental points and the degree of curvature of the data. The best curve fit was selected by comparing the velocity–distance curves obtained by differentiation of displacement–time equation with velocities determined graphically from the slopes of the experimental displacement–time curves. The velocity–distance curve with the best fit was then used to extrapolate linearly to the interfaces of interest. Velocity–distance curves of the decaying shock front determined in this manner are shown in Figs. 5 and 6 for the two propellant-like formulations.

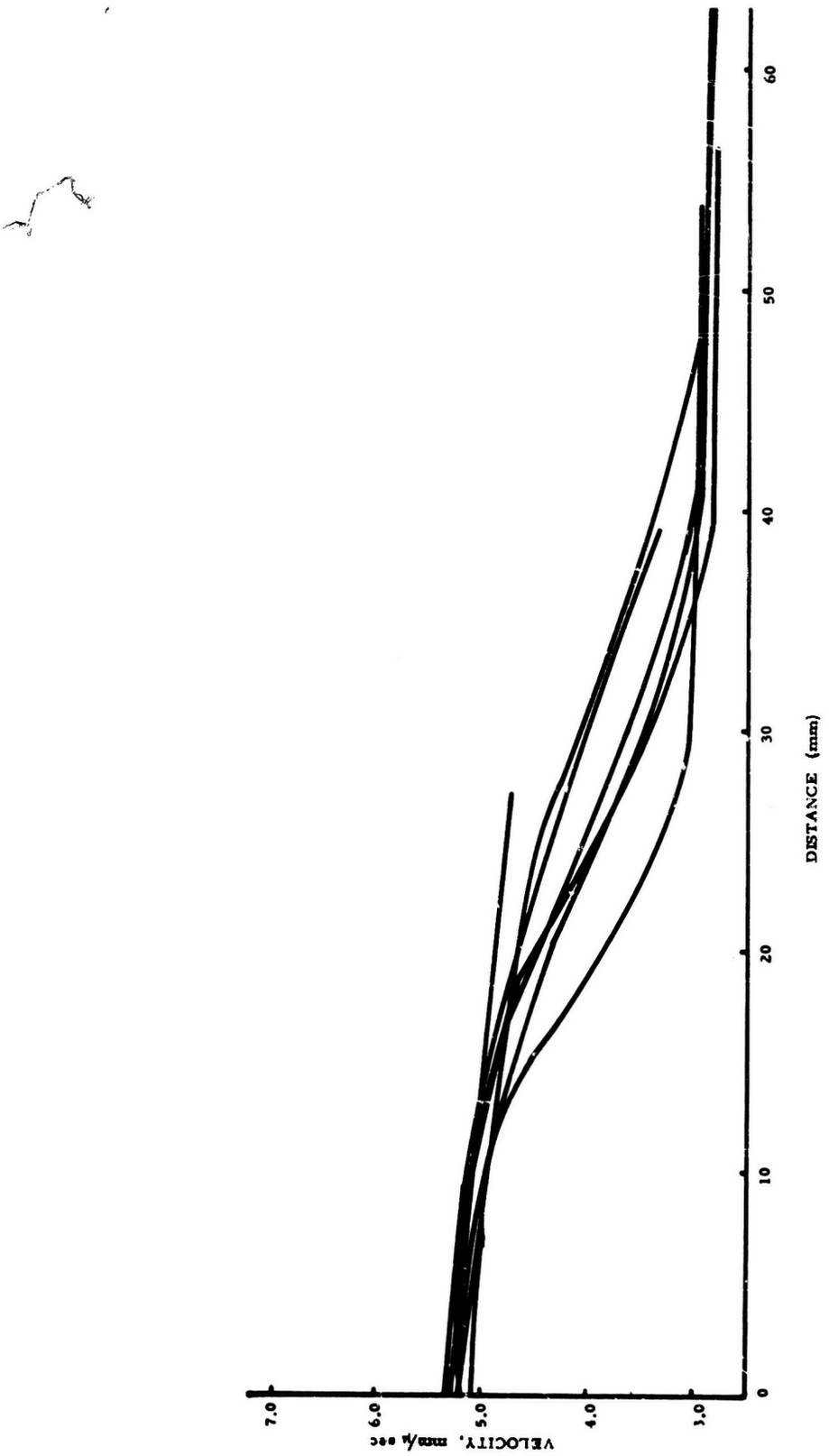

FIG. 5 SHOCK VELOCITY–DISTANCE CURVES FOR KCl-CONTAINING PROPELLANT.

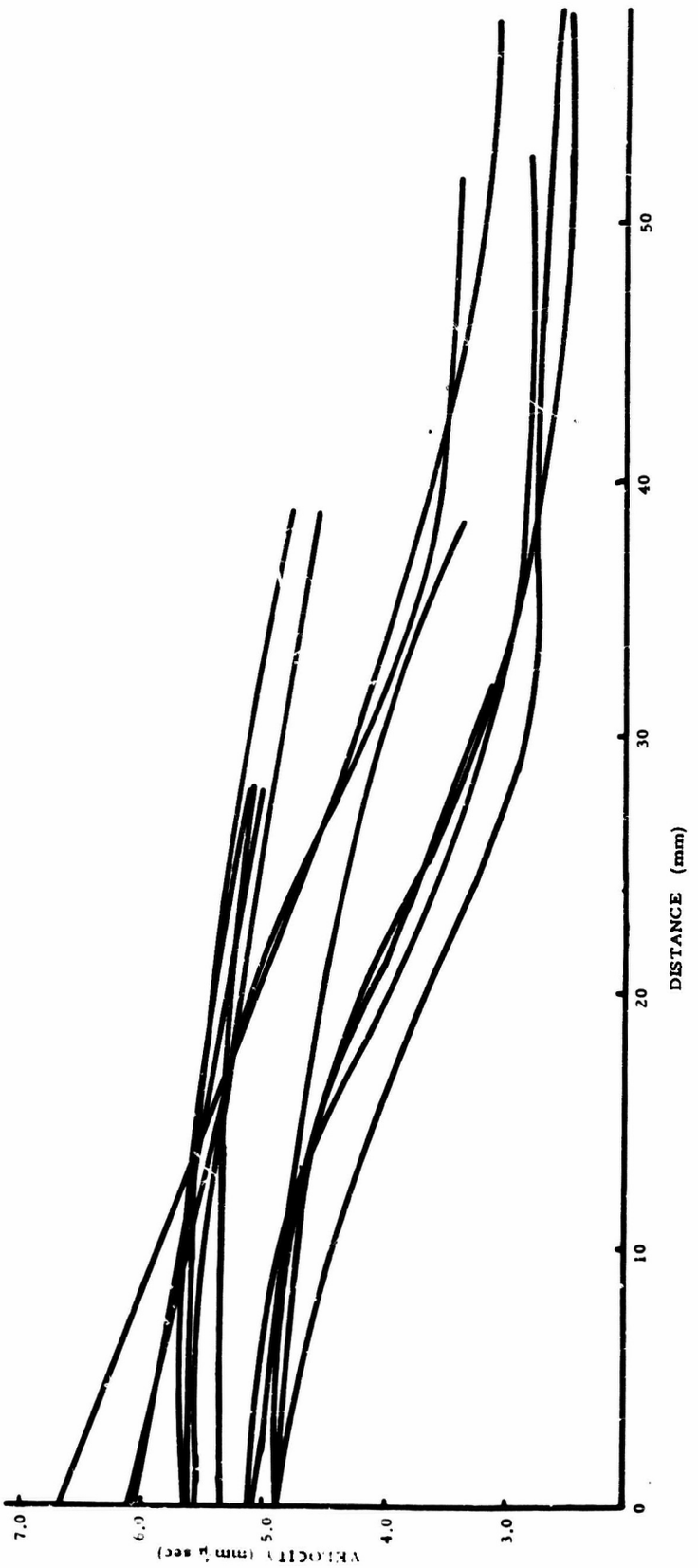

FIG. 6 SHOCK VELOCITY–DISTANCE CURVES FOR NH_4ClO_4-CONTAINING PROPELLANT.

The velocities used to determine the shock Hugoniots are given in Tables III and IV. Since the longer specimens yielded velocities at intermediate distances as well as at the sample–Plexiglas interface, the velocities were averaged over all the values obtained at a given distance in the sample. However, this averaging method could be used only for the data of the KCl formulation; the scatter of the data for individual samples of the NH_4ClO_4 samples was so great that only the measurement at the terminal face of each sample was used.

The Plexiglas particle velocity at the interface was determined from Fig. 7([7]). The particle velocities in the sample were then calculated using Eq. 5. Pressures and specific volumes in the samples were calculated with Eqs. 2 and 3 (Tables V and VI; Figs. 8, 9, and 10). The respective densities were: Plexiglas, 1.18 gm/cm^3; the KCl-containing formulation, 1.593 gm/cm^3; the NH_4ClO_4-containing propellant, 1.583 gm/cm^3; pentolite donor, 1.56 gm/cm^3. The first row of numbers given in the tables was obtained at the donor–receptor interface and donor–Plexiglas interface. Calculation of the particle velocity, therefore, required use of the impedance-mismatch equation twice: first, to determine the particle velocity in the donor, and then, to determine the velocity in the specimen. The detonation velocity in 50/50 pentolite at this density is 7.21 mm/μsec.([13]).

In each of Figs. 8, 9, and 10 the large scatter of the data on the NH_4ClO_4-containing formulation is evident. The curves for the KCl formulation were drawn in by inspection to the data in Figs. 8 and 9. The curves for Plexiglas were included for comparison in Figs. 8 and 10, and for aluminum in Fig. 10.

Table III

Velocity–Distance Data for KCl-Containing Formulation

Distance (mm)	Velocity in Sample (mm/μsec)	Velocity in Plexiglas (mm/μsec)
0	5.29	5.91
15.1	4.93	5.44
32.2	3.75	4.31
43.7	3.11	3.95
56.8	2.86	3.08
73.5	2.86	3.22

Table IV

Velocity–Distance Data for NH_4ClO_4-Containing Formulation

Distance (mm)	Velocity in Sample (mm/μsec)	Velocity in Plexiglas (mm/μsec)
0	5.91	5.82
12.8	5.33	5.87
26.8	5.16	4.14
26.9	5.11	4.65
38.5	4.80	4.37
38.7	4.56	4.58
64.2	3.04	3.00

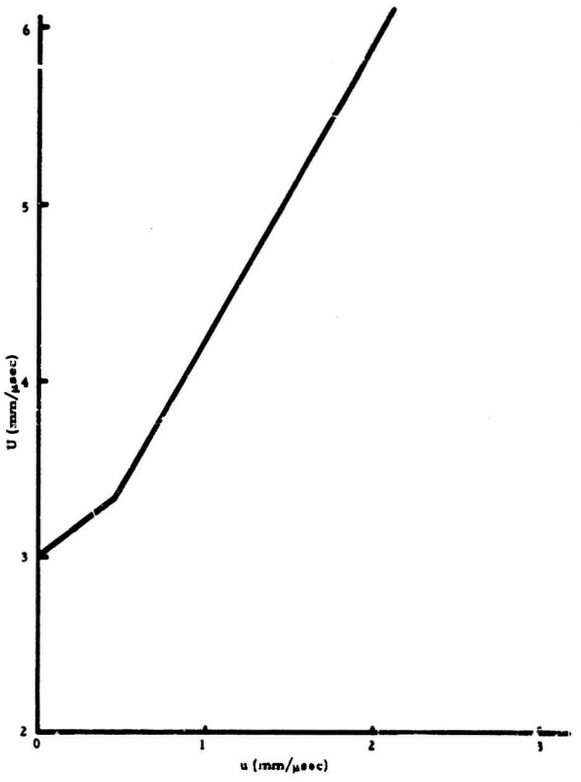

FIG. 7 SHOCK VELOCITY-PARTICLE VELOCITY RELATIONSHIP FOR PLEXIGLAS [from reference (4)].

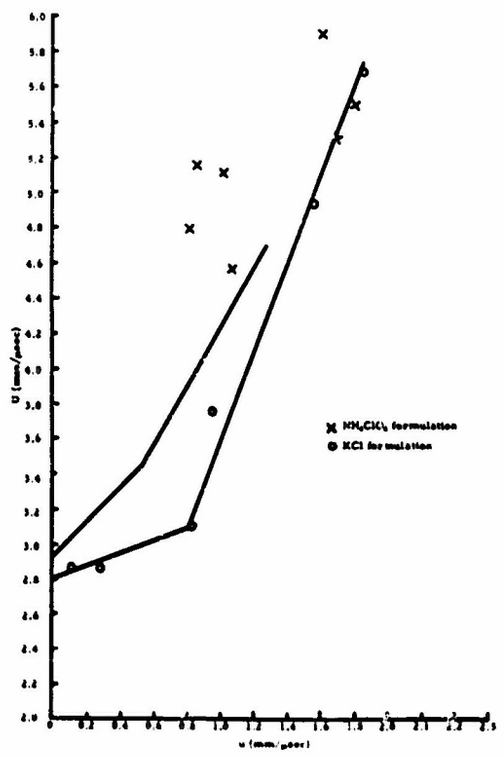

FIG. 8 PARTICLE VELOCITY-SHOCK VELOCITY DATA.

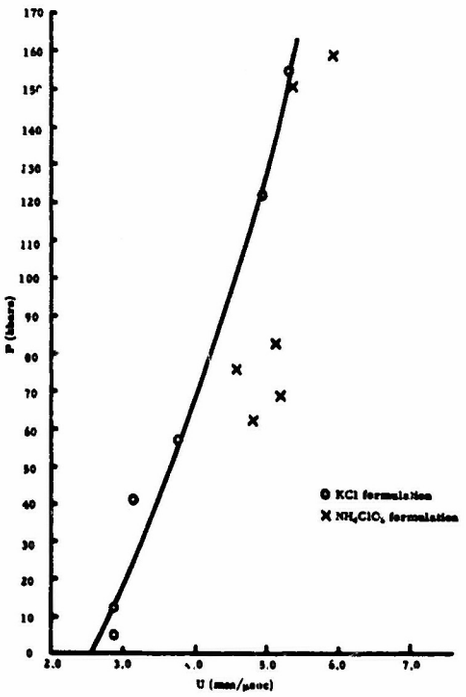

FIG. 9 PRESSURE-SHOCK VELOCITY DATA FOR SIMULATED PROPELLANT.

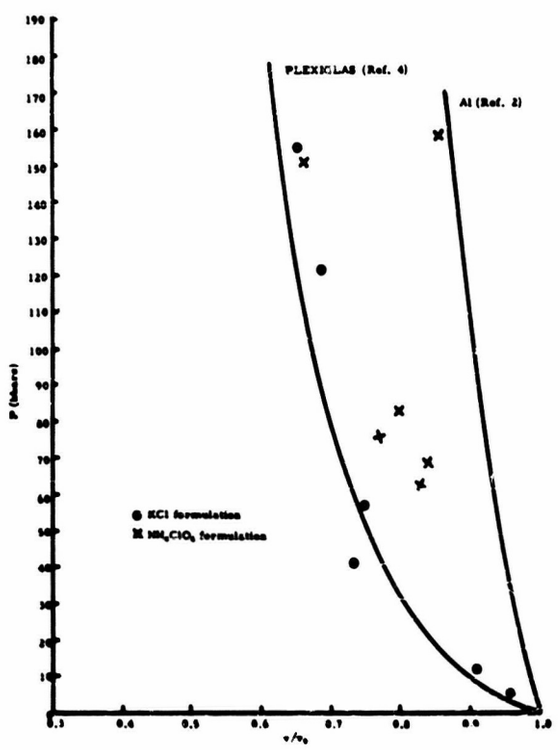

FIG. 10 PRESSURE-COMPRESSION FOR SIMULATED PROPELLANTS.

Table V

Hydrodynamic and Thermodynamic Data for KCl-Containing Formulations

Shock Velocity in Plexiglas (mm/μsec)	Particle Velocity in Plexiglas (mm/μsec)	Shock Velocity in Sample (mm/μsec)	Particle Velocity in Sample (mm/μsec)	Preasure in Sample (Kbars)	Specific Volume Ratio, τ/τ_0 in Sample
5.91	1.99	5.29	1.84	155	0.652
5.44	1.71	4.93	1.55	122	0.685
4.31	1.03	3.75	0.95	57	0.746
3.95	0.84	3.11	0.82	41	0.734
3.08	0.11	2.86	0.10	5	0.962
3.22	0.29	2.86	0.27	12	0.908

Table VI

Hydrodynamic and Thermodynamic Data for NH_4ClO_4-Containing Formulation

Shock Velocity in Plexiglas (mm/μsec)	Particle Velocity in Plexiglas (mm/μsec)	Shock Velocity in Sample (mm/μsec)	Particle Velocity in Sample (mm/μsec)	Preasure in Sample (Kbars)	Specific Volume Ratio τ/τ_0 in Sample
5.82	1.94	5.91	1.70	159	0.856
5.87	1.97	5.33	1.79	151	0.664
4.14	1.07	5.16	0.85	69	0.836
4.65	1.22	5.11	1.02	83	0.799
4.37	0.97	4.80	0.81	62	0.830
4.58	1.20	4.56	1.05	76	0.769
3.00	0	3.04	0	0	1

DISCUSSION

The results of previous experiments to determine the Hugoniot of a poly(methyl methacrylate) base with 20% aluminum had shown that, at these low loadings, the aluminum did not affect the particle-velocity–shock-velocity relation. The polymeric base alone completely determined this relationship.

The present studies on more highly loaded materials (75% dispersed solids) show a somewhat different behavior. Since these materials are close in solids loading to actual propellants, their behavior may be used to approximate that of compositions in actual use.

Examination of Fig. 8 shows that a propellant in which an inert material (KCl) is used to simulate the oxidizer has a significantly different particle-velocity–shock-velocity relation than straight polymeric material (Plexiglas). However, when these data are converted through Eqs. 2 and 3 to pressure–compression values, the relationship for the composition with the high solids loading is very similar to that of Plexiglas (Fig. 10). At higher pressures the simulated propellant is less compressible than the polymer, as is to be expected from the compressibilities of the salt and aluminum contained in the propellant-like prototype composition. The Hugoniot of this material is quite different from that of aluminum, which is shown in Fig. 10 as an example of a relatively incompressible material. Thus the compressibility appears to be most strongly a function of the continuous polymeric phase.

Experiments to determine the Hugoniot of a composition containing NH_4ClO_4 gave results in which the points scattered widely. This series of experiments was carried out to determine whether a "sub-detonation" reaction behind the shock front contributed energy to the forward motion of the decaying front. This would result in a less rapid decay of the front as it moves through the material and should change the Hugoniot characteristics since the particle velocity determined would include that of the reaction products behind the front. Despite the scatter of the data for the ammonium perchlorate-containing formulation it is evident from Figs. 8, 9, and 10 that this composition has a Hugoniot relation quite different from that of the KCl-containing formulation. Since ammonium perchlorate and potassium chloride are not very different in density and would be expected to have similar compressibilities, the difference in Hugoniots must be explained by a contribution of the reacting ammonium perchlorate.

In a re-examination of the experimental technique it was considered that a possible explanation for the scatter of the data might lie in the unevenness of the surfaces of the samples. This results

from shrinkage of the samples on cure. Thus the Plexiglas surface and the sample surface are not always flush. This also applies to the donor-sample interface. Preparation of samples in the form of rectangular solids is planned in the hope that this will give more regular surfaces. Both the inert and active compositions will be repeated in this new geometry.

CONCLUSIONS

1. The shock response of solids-filled elastomeric polymers is the same as that of the continuous phase alone, at loadings as high as 75 wt. % of solids.

2. Ammonium perchlorate decomposes exothermally under shock, even in nondetonable propellants.

3. Because of AP decomposition, truly non-reactive shock Hugoniots cannot be obtained with live-oxidizer formulations, at least not at shock strengths above 10 kbar.

SYMBOLS LIST

e	Specific internal energy
P	Pressure
τ	Specific volume
ρ	Density
u	Particle velocity
U	Shock velocity
U_{FS}	Free-surface velocity

Subscripts:

0	Unshocked state
1	Shocked, but unreacted state
f	Receiving or refracting medium
i	Incident medium

REFERENCES

1. M. W. Evans and C. M. Ablow, Chem. Rev. 61, 129 (1961).
2. J. M. Walsh and M. H. Rice, J. Chem. Phys. 26, 815 (1957).
3. J. M. Walsh and R. H. Christian, Phys. Rev. 97, 1544 (1955).
4. Rohm and Haas Company Quarterly Report on A.R.P.A. Projects, P-64-26, January 28, 1965, p. 83.
5. M. H. Rice, J. Chem. Phys. 26, 824 (1957).
6. T. P. Liddiard, Jr., Preprints of the Fourth Symposium on Detonation, Oct. 12-15, 1965, at U. S. Naval Ordnance Laboratory, White Oak, Silver Spring, Maryland, p. B-47.
7. N. L. Coleburn, AIAA (Am. Inst. Aeron. and Astronaut.) J., 4, 521 (1966).
8. J. B. Ramsay and A. Popolato, Preprints of the Fourth Symposium on Detonation, Oct. 12-15, 1965, at U. S. Naval Ordnance Laboratory, White Oak, Silver Spring, Maryland, p. B-10.
9. Rohm and Haas Company Quarterly Report on A.R.P.A. Projects, P-64-26, January 28, 1965, p. 66.
10. E. G. Johnson, AIAA J. 3, 2109 (1965).
11. W. M. Elsasser, J. Appl. Phys. 20, 1193 (1949).
12. C. G. Montgomery (ed.), Techniques of Microwave Measurements (1st ed.) McGraw-Hill Book Company, Inc., New York, 1947, p. 666.
13. Arthur D. Little Inc., Final Report to Picatinny Arsenal, Physical and Explosive Properties of Compounds and Mixtures, Vol. IV, Contract DA-19-020-501-ORD-(P)-57, Project TA3-5002, 31 December 1961.

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13. ABSTRACT

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Microwave interferometry						
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Non-reactive shock Hugoniot						
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