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TITLE: The Shock Hugoniot of Liquid Hydrazine in the Pressure Range of 3.1 to 21.4 GPa

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The Shock Hugoniot of Liquid Hydrazine in the Pressure Range of 3.1 to 21.4 GPa

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The shock Hugoniot of liquid hydrazine was determined in the pressure range of 3.1 to 21.4 GPa (31 to 214 kbar) using the impedance matching technique. This technique was similar to that used by Richard Dick, who determined the shock Hugoniots of many liquids such as carbon tetrachloride, benzene, liquid nitrogen, etc. Shock pressures were generated using a plane wave explosive driver system with different explosives and different reference materials against the liquid hydrazine. The velocity of the shock wave in the liquid hydrazine and the free surface velocity of the reference material were measured using different pin contact techniques. The experimental Hugoniot appears smooth and there is no indication of a phase change. The shock Hugoniot of liquid hydrazine was compared against three other liquid Hugoniots: liquid ammonia, water, and carbon tetrachloride and is closest to the Hugoniot for water and in between ammonia and carbon tetrachloride. The hydrazine Hugoniot was also compared to the "Universal" Hugoniot for liquids. The "Universal" Hugoniot for liquids is not a good approximation for the liquid hydrazine Hugoniot in the pressure range studied.

I. Introduction

Hydrazine and hydrazine derivatives have a wide variety of applications which include rocket propellants, explosives, fuel cells, pesticides, pharmaceuticals, and many more [1]. Hydrazine and its derivatives are used in liquid and solid rocket propellants. In the liquid propellant group, hydrazine is used in bipropellant fuels as well as monopropellants. Bipropellant rockets require an oxidizer. Hydrazine as a monopropellant will decompose exothermically in a controlled manner in contact with a catalyst and generate hot gases for thrust or pneumatic power.

NASA has long been concerned about the shock compression of liquid hydrazine because it is the fuel of choice for Space Station Freedom. Because the propellant modules can be subjected to meteorite or space debris impacts during their use, many experiments have been conducted to alleviate concerns about the possibility of shock-compressing liquid hydrazine to a detonation [2]. Although NASA has, to date, been unsuccessful at shock compressing liquid hydrazine to a detonation, the question of whether liquid hydrazine can detonate under a high shock loading remains unanswered. As a fundamental step toward answering this question, the following paper provides the first published shock Hugoniot of liquid hydrazine in the shock pressure range from 3.1 to 21.4 GPa (31 to 214 kbar). Prior to these experiments, it was common to assume that the shock Hugoniot for liquid hydrazine was similar to that of water. This paper also provides additional calculations on the expected decomposition of liquid hydrazine in the above pressure regime.

The method selected to determine the shock Hugoniot of liquid hydrazine is based on proven techniques outlined in the LASL Shock Hugoniot Data [3]. Specifically these experiments used the impedance matching technique patterned after many experiments performed by Dick [4,5,6,7]. The need for understanding the equation of state of many materials under high pressure shock waves was originally driven by the methods established for nuclear weapons research and are directly applicable to the many scenarios encountered in high-velocity space debris impacts. The tremendous impact pressures attained in space can range from meteoroid impacts to space debris piercing shielding.

II. Experimental Technique

The impedance matching technique has been used by many experimenters to construct an unknown shock Hugoniot of a material based on a known reference shock Hugoniot. This graphical technique, developed by Walsh and Christian [8], constructs P-u_p points for the unknown material by shock matching the pressure and particle velocity with a known shock Hugoniot (Figure 1).

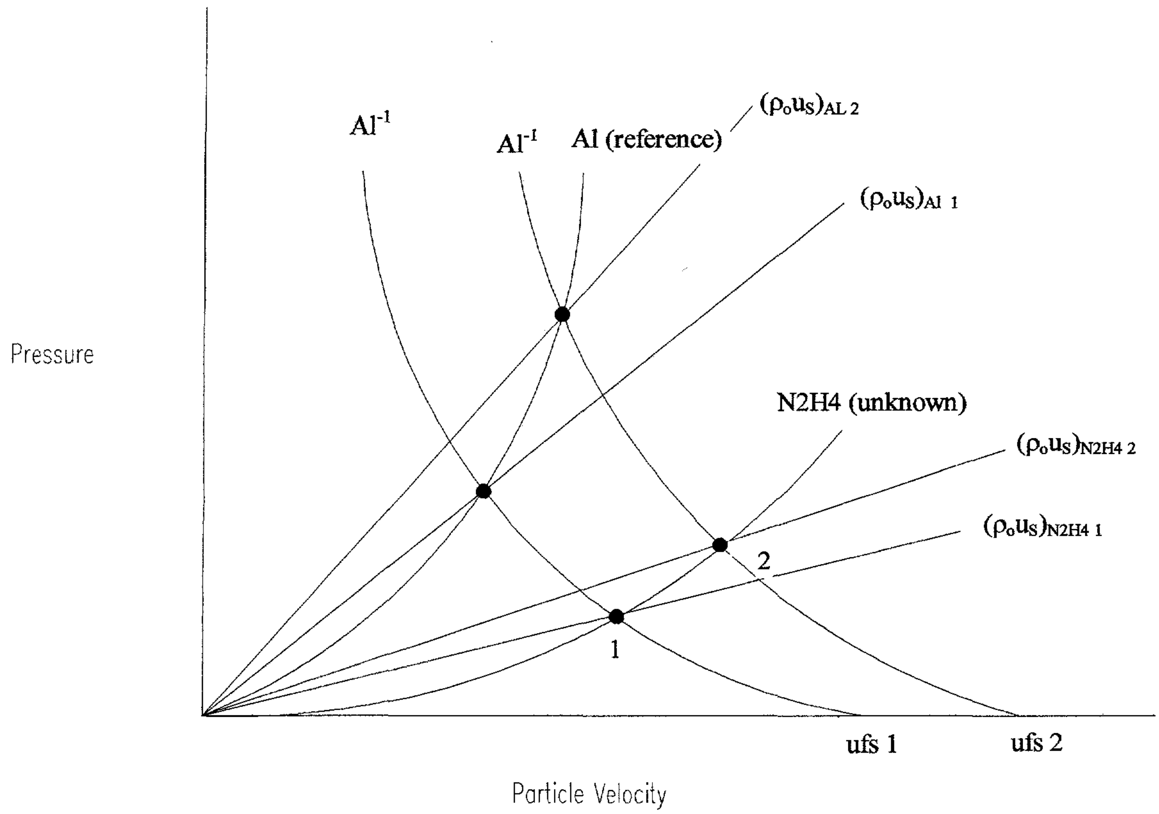

Figure 1. Impedance matching technique.

Figure 1 is a graphical representation in the pressure-particle velocity plane of an aluminum base plate sharing an interface with a liquid of lower shock impedance for which the Hugoniot is sought. By measuring the shock velocity, u_S, or in this case the free surface velocity, u_{fs}, and knowing the initial density, ρ_o, of the aluminum (reference), one can draw the Rayleigh line with the slope $(\rho_o u_S)_{Al\,1}$. At the Al/liquid interface, a rarefaction is reflected back into the aluminum and a shock is transmitted in the liquid with the constraint that P and u_p must both be continuous across the interface. By measuring the shock velocity, u_S, in the liquid (unknown) and knowing the initial density, ρ_o, one can draw the Rayleigh line with slope $(\rho_o us)_{N2H4\,1}$. The intersection of the Rayleigh line and the rarefaction release wave shown as point 1 determines the pressure and particle velocity in the unknown Hugoniot. By repeating this procedure for different Rayleigh lines, produced by different combinations of explosive drivers with different reference materials, one can determine other points such as point 2 of the unknown shock Hugoniot. An algebraic solution is given with all the measured variables for these experiments included. The resulting solution for the particle velocity is of the form:

$$\alpha u_p^2 + \beta u_p + \gamma = 0 \qquad (1)$$

where

$$\alpha = -(\rho_{oAl} s_{Al})$$

$$\beta = 2(\rho_{oAl} s_{Al} u_{fs}) + (\rho_o u_S)_{N2H4} + \rho_{oAl} c_{oAl}$$

$$\gamma = -u_{fs}\rho_{oAl} c_{oAl} - \rho_{oAl} s_{Al} u_{fs}^2$$

In these experiments, it was decided to measure the free surface velocity instead of the shock velocity in the reference materials for several reasons. The first was a practical design reason based on the difficulty of machining a number of 0.036-inch flat-bottom holes in the reference plate and then accurately measuring the depths, positioning the pins, and trying to verify that they did not move. It was much simpler to design a block to contain and restrain a number of pins which were backed off a known location from the free surface. The second reason for measuring the free surface instead of the shock velocity is that there is less error in this measurement. The free surface velocity is defined as follows:

$$u_{fs} = u_p + u_r \approx 2u_p \qquad (2)$$

For most metals, the assumption that $u_{fs} \approx 2u_p$ is probably satisfactory but is only approximate because the release wave is actually adiabatic while the reflected Hugoniot is not. The error introduced is normally less than one percent and a full discussion can be found in the work of Walsh and Christian. At the instant the shock arrives at the free surface, the material is moving in the same direction as the shock with a particle velocity, u_p. Since the surface is free to expand outward, the release wave starts to propagate back into the aluminum and the pressure of the compressed material is reduced by this rarefaction. Upon a complete pressure release, the compressional energy shows up as an additional particle velocity, u_r, added to u_p.

III. Experimental Results and Disscussion

The Hugoniot data for liquid hydrazine are listed in Table 1. A comparison of the calculated and measured free surface velocities is presented in Table 2. The derived pressure, specific volume and temperatures for theses experiments is presented in Table 3.

Table 1. Liquid hydrazine shock wave data.

Test	Date	Test Description	Us (km/s)	Up (km/s)	P (kbar)	U_{fs} (km/s)
BE95-079	07/18/95	P81/ 2" Baratol/ 1/2"Al	4.44	1.384	61.5	1.788
BE95-092	08/03/95	P81/ 2" Baratol/ 1/2"Al	4.44	1.297	57.6	1.654
BE95-117	09/22/95	P81/ 4" Comp-B/ 1/2" Al	6.09	2.321	143	3.465
BE95-123	10/24/95	P81/ 4" 9501/ 1/2" lexan	6.76	3.122	213.6	5.825
BE95-124	10/24/95	P81/ 4" 9501/ 1/2" Al	6.27	2.84	179.4	3.809
BE95-125	10/25/95	P81/ 2" TNT/ 1/2" Al	5.29	2.264	100	2.849
BE95-126	10/25/95	P81/ 2"Baratol/ 1/2" Cu	3.72	.8206	30.8	.9056

Table 2 Comparison of free surface velocity data

Test	Test Description	U_{fs}^{a} (km/s)	U_{fs}^{b} (km/s)	U_{fs}^{c} (km/s)
BE95-079	P81/ 2" Baratol/ 1/2"Al	1.76	1.788	1.67,1.70,1.69
BE95-092	P81/ 2" Baratol/ 1/2"Al	1.76	1.654	1.67, 1.70,1.69
BE95-117	P81/ 4" Comp-B/ 1/2" Al	3.12	3.465	3.03, 3.04(2")
BE95-123	P81/ 4" 9501/ 1/2" lexan	5.27	5.825	5.60
BE95-124	P81/ 4" 9501/ 1/2"Al	3.72	3.809	--------
BE95-125	P81/ 2" TNT/ 1/2" Al	2.50	2.849	2.54, 2.43
BE95-126	P81/ 2" Baratol/ 1/2" Cu	1.04	.9056	

[a] Calculated values from SIN.
[b] Measured values from this work.
[c] Measured values from Los Alamos provided by J.J. Dick.

Table 3 Derived pressure, specific volume and temperatures on the liquid hydrazine Hugoniot

Test	ρ_o (Mg/m^3)	P (GPa)	ν (m^3/Mg)	T* (K)
BE95-079	1.0006	6.15	0.6883	420
BE95-092	0.99873	5.76	0.7079	409
BE95-117	1.0175	14.3	0.6189	762
BE95-123	1.0014	21.36	0.5382	1160
BE95-124	1.0070	17.94	0.5470	945
BE95-125	-------	10	0.5720	565
BE95-126	1.0080	3.08	0.7794	338

* The temperatures were calculated using the SEQS code.

An examination of the u_S-u_p plot reveals that the data can be represented as a straight line fit.

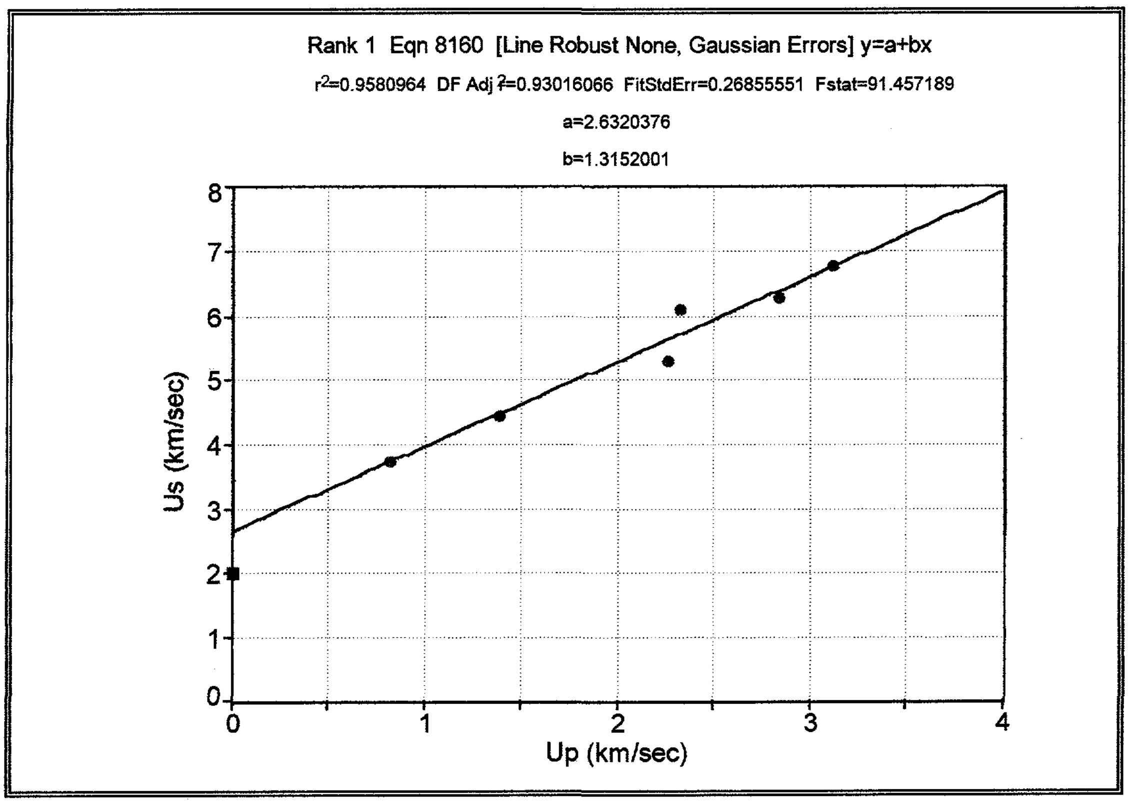

Figure 2. The us-up plot for liquid hydrazine.

A least squares fit to the u_S-u_p data shown in Figure 2 yields the following equation:

$$u_S = 2.632 + 1.315 u_p \qquad (3)$$

Interval: 0.8206 - 3.122 (km/sec)

The extrapolated linear fit to a zero particle velocity results in a shock velocity higher than the sound speed in liquid hydrazine. The sound velocity of hydrazine is shown as a square in Figure 2. This phenomenon has been observed by Ramsay [9] in the study of Us-Up data for some 17 liquids and Dick [4] in the study of the Us-Up data for the liquids he studied. Liquids do not typically approach the sound speed in a linear fashion but in more of a parabolic fashion, as observed by Woolfolk, Cowperthwaite, and Shaw [10].

The shock Hugoniot of liquid hydrazine in a P-V plot was compared to that of ammonia, water, and carbon tetrachloride as shown in Figure 3.

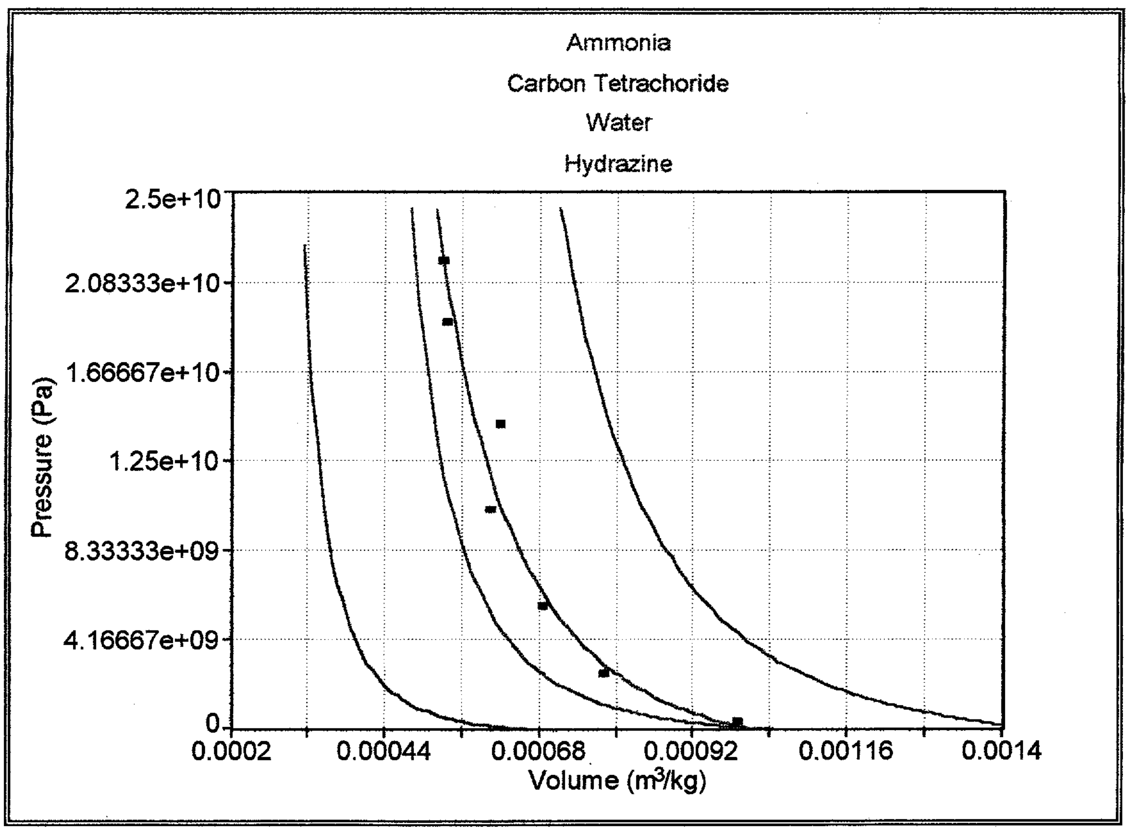

Figure 3. P-V plot for liquid hydrazine compared to ammonia, water and carbon tetrachloride.

These shock Hugoniots were drawn based on the following P-V relationship:

$$P(\nu) = \frac{c^2(\nu_0 - \nu_1)}{[\nu_0 - s(\nu_0 - \nu_I)]^2} \tag{4}$$

The values of c and s for the above figure were taken to be as follows:

Ammonia	$u_S = 2.579 + 1.365u_p$	M.I Kovel, LLNL [11]
Water	$u_S = 1.5 + 1.5u_p$	Rice&Walsh, LANL [12]
Hydrazine	$u_S = 2.632 + 1.315u_p$	This work
Carbon Tetrachloride	$u_S = 1.074 + 1.594u_p$	R.D. Dick, LANL [4]

Using the Rankine-Hugoniot relationships, an alternate form can be derived as follows:

$$P = \frac{c^2\rho_0\left(1 - \frac{\nu_1}{\nu_0}\right)}{\left(1 - s\left(1 - \frac{\nu_1}{\nu_0}\right)\right)^2} \tag{5}$$

Based on this equation, there is an asymptote at $\left(1 - s\left(1 - \frac{\nu_1}{\nu_0}\right)\right)^2 = 0$.

Solving and rearranging this equation leads to the following result:

$$\frac{\nu_0}{\nu_1} = \frac{s}{s-1} \tag{6}$$

Therefore equation (4) leads to the result that there is a limit to the shock compression based on

$\frac{s-1}{s}\nu_0 < \nu \le \nu_0$. So compression limits for the liquids listed are as follows: ammonia,

$0.27v_0 < v \le v_0$; water, $0.33v_0 < v \le v_0$; hydrazine, $0.24v_0 < v \le v_0$; and carbon tetrachloride, $0.37v_0 < v \le v_0$. Based on the P-V plots the hydrazine Hugoniot appears to be between that of ammonia and water and is very close to the same compressibility as water.

Woolfolk, Cowperthwaithe, and Shaw [9] have proposed the following equation, known as the "Universal" Liquid Hugoniot, for pressures up to 20 kbars:

$$\frac{u_S}{C_0} = 1.37 - 0.37e^{-2\frac{U_P}{C_0}} + 1.62\frac{u_P}{C_0} \qquad (7)$$

This equation was plotted in the Us-Up plane and then straight-line-fitted to an equation of the form $u_S = 2.077 + 1.94u_p$. This was done to provide some Hugoniot constants that would allow a comparison in the P-u_p plane. Figure 4 shows the results of comparing the "Universal" Liquid Hugoniot with hydrazine and water.

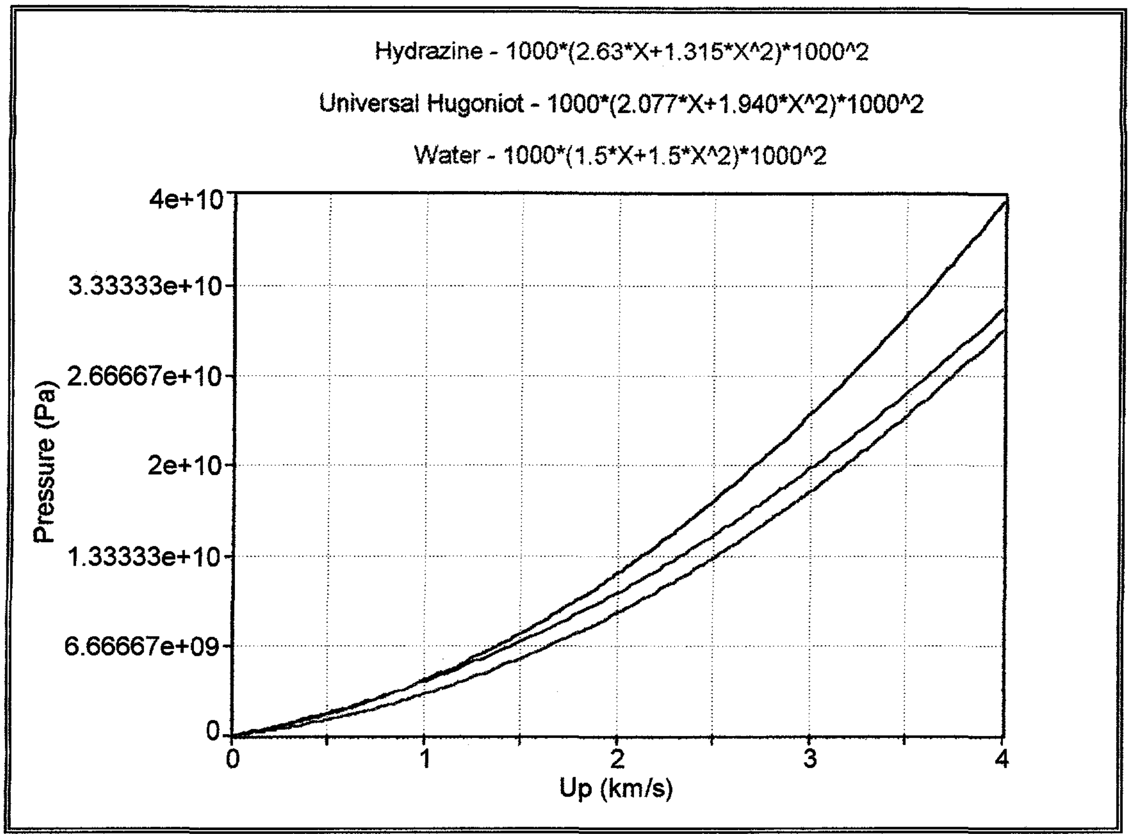

Figure 4. P-u_p plot for liquid hydrazine compared to the "Universal" Liquid Hugoniot and Water.

Figure 4 shows that the "Universal" liquid Hugoniot does not compare very well with the hydrazine Hugoniot. Perhaps this is because the experiments performed were between the pressures of 31 to 214 kbars, which is out of the range where this equation was fitted. If the experiments were performed at lower pressures, it would be reasonable to expect that the "Universal" liquid Hugoniot may be a good approximation. The water Hugnoiot, however, seems to be a reasonable approximation to the hydrazine Hugoniot, which has been a standard assumption for a number of years.

IV. Conclusions

The major thrust of this paper was to determine a shock Hugoniot for liquid hydrazine so that the shock response of this monopropellant under high pressures could be better understood. The shock Hugoniot of any material is the starting point for all high- pressure physics of that material. The response of this monopropellant is further complicated because it is an exothermic material and so, theoretically, at some given shock pressure, will produce a reaction of some magnitude. To limit the scope of this paper, it was decided early on to focus on a small pressure region of interest, in this case up to 250 kbar. To that end the following conclusions were derived:

1) Liquid hydrazine exhibits a linear relationship in the u_S-u_p plane. The linear extrapolation of the least squares fit gives a bulk sound velocity about 32% higher than the measured sound velocity in hydrazine. Previous studies of u_S-u_p data of other liquids have shown similar results.

2) No evidence of phase changes was found in the pressure regions study. There was also no method in this experiment to detect whether there was any chemical reaction of the hydrazine.

3) A reliable electrical shorting pin was designed to provide quality shock velocity data. This was accomplished through several iterations of pin designs to overcome all the problems encountered during testing.

4) The "Universal" liquid Hugoniot for hydrazine is not a good approximation in the pressure region studied, but the water Hugoniot appears to be adequate.

This paper would not be complete without some recommendations for future experiments with liquid hydrazine or any other material using the impedance matching technique with a shorting pin technology. The following recommendations are provided to the interested reader who wishes to pursue to shock response of liquid hydrazine further:

1) In the early days of characterizing shock Hugoniots for materials a tremedous amount of data was gathered by several different experiments. This paper only provided a small number of data points in a particular pressure region. To augment the information gathered, more information should be collected to fill in the pressure regions below 30 kbars and above 200 kbars.

2) To provide a complete equation of state, future experiments should provide information off the Hugoniot. This thesis provided no information on Gruneisen gamma. Typically these have been performed as double-shock experiments.

3) An expansion isentrope should be pursued. Typically these have been calibrated by cylinder expansion tests.

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