

UNITED STATES DEPARTMENT OF THE INTERIOR BUREAU OF MINES Pittsburgh, Pennsylvania

EXPLORATORY STUDY OF HYPERGOLIC IGNITION SPIKE PHENOMENA

Phase II, Part II July 1 to September 30, 1966

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#### INTRODUCTION

During recent test firings of Aerozine-50/nitrogen tetroxide 100-pound thrust engines at environmental pressures of about 0.005 psia, Manned Spacecraft Center (MSC) Personnel observed the formation and accumulation of a residual material on the engine's diffuser bell. Chemical analyses of this material, supplied to the Bureau of Mines by MSC, has subsequently shown it contains water, hydrazine nitrate, and other unidentified compounds. Since these residues apparently contain an appreciable amount of hydrazine nitrate, an explosive material, it has been suggested that these residues could be contributing to the pressure spiking phenomena often observed during ignition of the engines at attitude.

On July 7, 1966, the Bureau of Mines agreed to conduct, as part of its experimental program, an exploratory study of the physical and combustion characteristics of hydrazine nitrate and its water solutions. It is believed this information will permit a more critical evaluation of the potential hazard in the engines. Table 1 lists the suggested experimental studies as outlined and agreed upon at the July 7 conference.

TABLE 1.	-	Suggested	studies	of t	he p	hysical	L and	combustion	charac-
		teristics	of hydr	azine	nit	rate a	nd its	solutions.	,

Physical Properties	Combustion Characteristics
Viscosity Surface tension Vaporization rate Phase diagram	Critical film detonation thickness Shock and impact sensitivity Detonation parameters Thermal stability

This report describes the results of the physical and combustion characteristic study and in addition, the residue chemical analysis. The first section contains the results of the chemical analysis of the engine post shutdown residues received from MSC. The second section discusses the physical characteristics of hydrazine nitrate and its pertinent solutions. The remaining section contains the results of studies conducted at the Bureau and other laboratories concerning the combustion characteristics of these same systems.

#### EXPERIMENTAL STUDIES

#### Materials

The hydrazine nitrate used in these experiments was prepared by the procedure recommended by the Thiokol Corporation in their report RMD 239-Ql (Period June-September 1958, Contract No. as 58-644C). The nitric acid used in this preparation was A.C.S. grade with a purity of 70 percent; the hydrazine was purchased from Olin Mathieson Chemical Corporation with a stated purity of 97.5 percent. The methanol used for recrystallizing the hydrazine nitrate was a Reagent Grade product with a purity of 99.9 percent. Commercial distilled water was used in preparing the various solutions.

#### Residual Analysis

The residues were obtained by MSC personnel following engine shutdown from various locations in the environmental chamber and rocket engine.

The samples received from MSC were divided into two equal portions, one for immediate analysis and the other was reserved for use in case of accidental loss of the first sample. The first sample was freeze-dried at a pressure of about 0.1 psia, thereby separating it into solid and liquid portions. The liquid portions were water clear, and the solid portions, a dark straw color. The liquid portion was analyzed by a gas-liquid chromatograph using a 3-foot column of Carbowax 1540 at a temperature of 113°F. The solid portion was mixed with potassium bromide and pressed into a pellet for infrared analysis. Table 2 shows the results of these analyses conducted on the various samples to date.

## Physical and Thermochemical Characteristics

To understand the role of hydrazine nitrate (HN) in the hard start phenomena, it is pertinent to have available information concerning its physical and thermochemical characteristics. In this regard, several literature searches were conducted for the Bureau by The Chemical Propulsion Information Agency and Defense Documentation Center.

Table 3 contains a list of the known physical and thermochemical properties of HN. As shown in the table, there exists two crystalline forms of HN, and  $\alpha$  and the  $\beta$ . The  $\beta$  form melts at 158°F with no apparent decomposition or sublimation. Robinson and McCronel/ found that the resulting melt supercools readily and usually crystallizes as the  $\alpha$ form. However, on seeding the  $\alpha$  form with  $\beta$  crystals, it reverts to the  $\beta$  form at a rate which decreases with decreasing temperature. Due to the unstable nature of the  $\alpha$  form, it has not been possible to determine from the MSC residue samples whether this or the  $\beta$  form is actually generated in these engines. Furthermore, these authors found no indication of any additional thermal (phase) changes in the crystalline

Hydrazine Nitrate >90 Hydrazine Nitrate >90 (Possible ammonium nitrate)	93.0 7.5 0.5	Water Hydrazine UDMH	100/0 <del>2</del> / 29/71	Residue taken 7-22-66 after 1000 pulses, origin unknown Precup (after block 74) <u>3</u> /	8/3 8/19	19 24
Hydrazine Nitrate >90			100/0 <del>1</del> /	Injector face following run No. 59-22	21/2	9
Hydrazine Nitrate >90			100/0 <mark>7</mark> /	Rocket combustion chamber	7/12	4
Not enough residue recovered for reli able analysis	80 o v	Water Hydrazine Unknown	7/93	Cooling shroud	1/12	ကဲ
Hydrazine Nitrate >90	е 0 г	Water Hydrazine Unknown	58/42	Environmental chamber wall	21/L	ci
Hydrazine Nitrate >90			/ <u>t</u> 0/001	Rocket nozzle	6/6	0
Residue Composition (Infrared Analysis) Weight Percent	Composition by GLC2/) Mole Percent	Distillate ( (Analyzed Constituent	Residue/Distillate Weight Ratio	Origin of MSC Sample	Date Received	ple

GLC-Gas-liquid partition chromatography

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MSC test run designation

Sample received as solid

m

TABLE 2. - Results of chemical analysis of Manned Spacecraft Center residues.

# TABLE 3. - Physical and thermal chemical properties of hydrazine nitrate.

Formula weight	95.06
Density (X-ray)	95.35 lb/ft <sup>3</sup>
Melting point $\alpha$ form $\beta$ form	159°F 144°F
Heat of formation	+107,000 Btu/mole
Heat of solution	-15,700 Btu/mole
Heat of decomposition	-15,900 Btu/1b
Combustion temperature	4,350°F

structure of HN between  $-94^{\circ}F$  and the melting point; the system is therefore probably monotonic. These results are in accord with results of similar work conducted at the Bureau, using a differential scanning calorimeter<sup>2</sup>.

Moisture absorption experiments were conducted on HN by Medard<sup>2/</sup> using various Regnault mixtures (sulfuric acid of ll° Be, 21° Be, and 31° Be) to obtain various water vapor pressure environments. Figure 1, reproduced from Medard's report, shows the results of these experiments. The figure shows that at 60°F HN will absorb moisture from an environment at 90 percent relative humidity at a rate of 0.01 pounds of water per pound of HN per day.

Medard also examined the weight loss of anhydrous HN during intermittent heating to 230°F for a period of 315 hours (apparently the author attributes this weight loss to thermal degradation). He found this loss to be linearly dependent with time, and amounted to a loss of about 0.005 weight percent per hour. Kissinger<sup>47</sup>, in similar work, found that the HN decomposition at 280°F is "barely noticeable by the standard vacuum stability technique." He also reported that it can be stored under 95 percent ethyl alcohol at a maximum temperature of 86°F for as long as four months without any "apparent ill effects." Shidlovskii, Semishin, and Simutin<sup>57</sup> in their work observed "an intense thermal decomposition of HN at 392-428°F and a flash at 518°F." This latter observation seems to be in accordance with the Bureau's results where impure HN was found to decompose explosively at a temperature of about 518°F<sup>2</sup>.

The solubility of HN in water and in hydrazine has been studied by a number of investigators; among these Corcoran, Kruse, Skolnik, and Lieber / conducted the most extensive study. Their results for the three component system HN-water-hydrazine are shown in figure 2. The concentration triangular grid has not been included in the figure to avoid obscuring the pertinent features of the phase diagram structure. The figure shows the isothermal contours for the liquidous surfaces of the ternary system and also shows that the system has four invariant points: two ternary eutectics, a ternary peritectic, and the eutectic of the quasi-binary system hydrazine hydrate (hydrazine nitrate-l-hydrazinate). Figures 3 and 4 show the liquidous lines for the HN-water and HN-hydrazine binary systems drawn from the results shown in figure 2. Figure 4 indicates the formation of the compound hydrazine nitrate-l-hydrazine  $(N_{p}H_{g}NO_{3} \cdot N_{p}H_{4})$  which melts at 37.4°F and the eutectic composed of 47.5 weight percent HN which melts at -50.8°F. The data used to prepare these curves can be found in the author's original papers. It is interesting to note (figure 3) that HN does not form a hydrate, although several authors reported that HN exhibits hydroscopic characteristics. It is also interesting that, although water solvates with hydrazine (figure 1) and hydrazine hydrates with HN (figure 4), water does not hydrate with HN.

Another binary system of interest in this investigation was HN and ammonium nitrate, materials that were reported by various investigators to be products of the reaction between hydrazine and nitrogen tetroxide  $\overline{7,8,9}'$ . Barlot and Marsaule<sup>10</sup>/ examined the phase relationship for this system; their results are shown in figure 5. The figure shows the liquidous line as a function of the percent ammonium nitrate. Kissinger<sup>4</sup>/ also studied this system and found that the solidification temperature of this mixture appeared to decrease approximately linearly at a rate of 44°F per weight percent of ammonium nitrate at the freezing point of HN. This appears to be a lower rate than Barlot and Marsaule's results (figure 4) indicate; they find a value closer to 35°F per weight percent. Kissinger reports that the eutectic occurs at 67 weight percent hydrazine nitrate and freezes at 116°F; this appears to agree with the results of Barlot and Marsaule.

The density of HN-hydrazine and HN-water solutions has also been reported. Vango and Krasinsky $\frac{11}{}$  measured the density of hydrazine solutions of HN containing a fractional percent of aniline. Their measurements were made using a  $1.54 \text{ in}^3$  (25 cm<sup>3</sup>) volume pycnometer with a calibrated stem for observing the change in the liquid volume with temperature. These authors used two solution concentrations, 82.04 and 69.74 weight percent HN. Figure 6 shows a replot of these results; for comparison, the temperature dependence of pure hydrazine, taken from the work of Walden and Hilgert  $\frac{12}{2}$ , and of water, taken from Lange's Handbook of Chemistry, are also shown in the figure. Except for water, which shows a nonlinear behavior, these solution densities exhibit a linear dependence on the temperature. The dependency of these solution densities on the HN concentration at 75°F is shown in figure 7. Again, it appears that a linear relationship between the density and the HNconcentration satisfactorily represent the data. Theoretically, the solution density of nonionic materials should be a linear function of the concentration (molality), whereas for strongly ionic 1:1 salts, the density is a more complex function of the salt concentration containing two terms: one term is linear in concentration, and the other a three halves power of the concentration  $\frac{13}{}$ . That our results appear to be a linear function of the concentration is in accord with the fact that HN is a salt of a weak base and a strong acid, and therefore, it exhibits more nonionic character than ionic.

Since viscosities for the HN-hydrazine solutions had already been determined by Vango and Krasinsky<sup>11</sup>/, the Bureau confined its investigation of viscosity to HN-water solutions. Vango and Krasinsky used a Cannon-Zhukov viscosimeter, modified slightly to prevent evaporation or moisture pick-up. The Bureau's experiments with HN-water solutions were conducted with a Cannon-Fenske viscometer. The kinematic viscosity of these solutions are shown in figure 8, where the log to the base 10 of the kinematic viscosity is plotted as a function of the reciprocal of the absolute temperature. The figure shows that the data for the HN-water solutions seems to fit a linear relation, with respect to the reciprocal of

the absolute temperature. Theoretically there is no reason for this to be true, except possibly in very dilute solutions 1/3. As in the case of solution densities, this inconsistency is also due to the fact that HN is a weak electrolyte and therefore its properties in solution approach that of a nonelectrolyte.

The Bureau's initial surface tension measurements on HN-water solutions used a DuNuoy tensiometer. However, these experiments were more difficult than had been anticipated since it was found that the surface tension of freshly prepared HN solutions changes gradually with time, and even after standing several days in covered containers, the phenomenon does not subside. Apparently the act of measurement disturbed the surface state of the solution and as a result, the surface tension was lowered by each succeeding measurement. By careful preparation and filtration of these solutions, it was possible to obtain fairly consistent results. The values obtained by this method at a temperature of 75°F are given in figure 9. The figure shows a fairly linear dependence of the surface tension on the HN concentration.

In view of the difficulties encountered with this technique, it was decided to use another technique for measuring the temperature dependence of the surface tension. The bubble technique  $\frac{14}{}$  was selected since a fresh surface is formed with each bubble. Hopefully this would eliminate the drift problem. In principle this method consists of measuring the pressure required to form a small bubble under the surface of the solution. The bubble pressure is proportional to the sum of the hydrostatic pressure and the ratio of the surface tension to the bubble radius. A complete description of this technique can be found in reference 14. The apparatus was calibrated with liquids having known surface tension. A silicone oil bath was used to obtain temperatures up to 400°F. The surface tensions of molten HN, water, and hydrazine were measured and the results are shown in figure 10. It is assumed that the surface tension of the various HN-water and HN-hydrazine solutions are intermediate between these curves. Above 260°F the molten HN begins to decompose noticeably as evidenced by the continuous formation of bubbles on the walls of the vessel. At 350°F the decomposition increased to the extent that the liquid had the appearance of freshly poured carbonated water. The rising bubbles were so numerous that the liquid was almost opaque. As a result of the decomposition above 260°F, the surface tension measurements became noticeably erratic. The results for hydrazine (figure 10) show an abnormally large rate of decrease in the surface tension with increasing temperature although the reason for such a rapid drop is not immediately apparent.

The remaining study of the physical properties of these solutions concerned their rate of vaporization. From the literature it is apparent that the rate of vaporization of condensed phase substance is currently a controversial subject. Investigators cannot agree as to whether or not the accommodation coefficient is an artifact. A number of investigators believe that contaminated liquids or improper experimental conditions account for the use of accommodation coefficients. They maintain that all

liquids have accommodation coefficients of unity. If one assumes this to be the case and neglects bubble formation, then the calculation of evaporation rates is a matter of measuring the vapor pressure of pure liquids. No work appears to have been conducted on measuring the vaporization rates of solutions. The lack of such work may be attributed to the added complication of the concentration gradient at the liquid surface resulting from the loss of the more volatile constituent. This complication, in conjunction with thermal gradient due to the latent heat of vaporization, makes the vaporization process for solutions highly transient. Thus it appears thay any experimental study becomes a major undertaking. Figure 11 shows the temperature dependence of the vapor pressure of various hydrazine-HN solutions obtained by Vango and Krasinsky.

## Combustion Characteristics

HN has been of considerable interest in explosives research for many years, primarily because having no carbon content, it represents a truly smokeless explosive, its ultimate explosion products being only nitrogen and water. Many attempts have been made to use HN as an artillery projectile propellant. As a result, a considerable amount of information pertaining to its explosive characteristics has accumulated. Unfortunately all the investigations conducted to date, including those in this report, have been confined to its  $\beta$  crystalline form. As a result, no information is available concerning the  $\alpha$  form. However like lead azide, which also has two crystalline forms, the two forms of HN probably have different explosive characteristics.

One of the more interesting combustion characteristics of HN is its relatively low combustion temperature;  $4350^{\circ}F_{--}^{--}6'$ . Its thermal stability has been studied by numerous investigators including the Bureau and there seems to be general agreement that the pure material decomposes explosively at about 570°F. Shidlovoskii and Semishin<sup>5</sup>/ found that glass tubes containing molten HN were unable to support stable burning; apparently the combustion transited to a detonation. Moran, Burnett, and Smith<sup>1</sup>/<sub>2</sub>/ conducted tests on HN-hydrazine mixtures. They found that, only after the liquid portions of the samples had either mostly burned or vaporized off and the vessel temperature rose to about 570°F, did an explosive reaction occur.

One of the first detonation characteristics of HN studied was its gap-sensitivity. In this test, a gap consisting of various thicknesses of an inert shock attenuation material is placed between an explosive booster of fixed (standard) size and the candidate material. The maximum gap through which the fixed charge can initiate the candidate material 50 percent of the time is its gap or card value. Originally the standard charge used in these measurements on HN was 100 grams of tetryl and the cards consisted of Acrawax B cast to the desired thicknesses. In their experiments Eyster, Smith, and Walton<sup>14</sup>, using pressed HN (density 100 lb/ft<sup>3</sup>) found a gap value of 2.51 inches (of wax). This can be compared with corresponding values of 1.68 inches for TNT and 2.01 inches for tetryl, both considered to be "safe explosives" for handling purposes. In later work, Medard found the drop weight sensitivity of HN to be 14 to 18 foot-pound.

The detonation velocity of HN has been measured by Medard<sup>3/</sup> and Price, Liddiard, and Drosd<sup>19/</sup>. Medard, using 6.7 inch diameter by 21.18 inch long pressed charges of hydrazine nitrate, found that its detonation velocity exhibited a maximum at a density of 81.2 lb/ft<sup>3</sup>. However, Price, Liddiard, and Drosd established that such maxima are likely to occur for explosives for which the critical diameter increases with density. The critical diameter is the minimum charge diameter at which propagation of a stable detonation is possible. The results of both these investigations are shown in figure 12. From these results the authors concluded that HN exhibits a critical diameter which increases with increasing packing density. Price, Liddiard, and Drosd found that the infinite charge diameter detonation velocity for HN can be expressed as V = 283.2 w - 328 ft/sec, where w is the explosive density in lb/ft<sup>3</sup>. Michel, Harms, Koepche, Mueller, Jacobson, Syolund, and Christians<sup>10</sup> calculated a Chapman-Jouguet detonation velocity of 19,150 ft/sec for an explosive density of 62 lb/ft<sup>3</sup> (1 gm/cc), whereas the above relation would predict a value of 17,350 ft/sec, 10 percent lower than the theoretical value.

Although the work of previous investigators has established values for the sensitivity and detonation velocities of bulk HN, it remained to determine if this material will support a detonation in the form of a thin film as found in these engines. In view of this, the Bureau conducted experiments to determine the thin film detonation characteristics<sup>21</sup> of HN and its water and hydrazine solutions. These experiments were performed at a temperature of 75°F (above the melting point of HN) in the apparatus shown in figure 13. The apparatus developed at the Bureau consists of an open plastic tray inclined at a slight angle so that the contained candidate liquid forms a wedge whose thickness varies from one quarter inch to zero. A collapsible probe22, extending the length of the wedge, was used to record the rate of propagation of the detonation front. This probe consists of a thin metal tube through which is extended a bare resistance wire separated from the tube by a spiral of insulating thread. As a detonation propagates along the tube, it collapses and shorts the resistance wire and the resulting change in the resistance is recorded on an oscilloscope. A resistive pressure gauge, 2 located on one tray wall opposite the initiating explosive, provides a qualitative indication of the presence of a detonation. The explosive initiating charge consists of a 50-gram tetryl pellet formed from two, 1 X 5/8-inch diameter by 1/2-inch thick tetryl pellets. The charge was separated from the tray wall by a plastic spacer which provides for the transmission of an attenuated shock into the liquid wedge. These experiments were conducted on HN, HN-water and HNhydrazine solutions. Figure 14 shows two oscilloscope records of the

changing resistance of the collapsible probe (lower trace) and the resistor transducer (upper trace) for a positive and negative result. The top oscillogram in figure 14 is typical of a positive result showing two detonation regions, a high velocity and a low velocity. The high velocity detonation, conceived first, transits to a low velocity detonation when the film thickness reaches a critical value. The low velocity detonation then continues to its point of extinction at its critical film thickness. The upper trace in figure 14a is the output of the resistive transducer showing a strong shock striking it at the same time the low order detonation reaches the far end of the tray. Figure 14b shows the probe signal for a negative result (no propagation) for the 65 percent HN-water solution. In this experiment the explosive shock was initially sufficiently intense in the liquid wedge nearest the charge to collapse the probe; however as the trace shows, this shock decayed rapidly. Table 4 summerizes the results of the complement of thin film experiments. Using the velocity data, shown in the table, it can be seen that if a film of HN-hydrazine covering the walls of these RCS engines detonates, it requires approximately 4 microseconds to travel the length of the combustion chamber. The thin film detonation velocity for pure hydrazine nitrate shows reasonable agreement with the results of other investigators as indicated in figure 12.

Furthermore, from the table it can be seen that HN-water solutions, having 65 or less weight percent HN, do not support a stable detonation in thin films, whereas HN-hydrazine solutions having as little as 40 weight percent HN still detonate. The table also shows that molten HN, HN-water solutions having HN concentrations greater than 80 weight percent, and HN-hydrazine solutions having HN concentrations greater than 80 weight percent, exhibit stable detonation in films thinner than 0.01 inch.

# REMARKS AND CONCLUSIONS

The experiments discussed in the previous sections complete the suggested studies originally agreed to by the Bureau and MSC, (table l). Using the results of the physical characteristics study of hydrazine nitrate solutions, one can estimate such items as the thickness and flow of the residue films in these engines during the various periods of engine operation, the maximum amount of residue that accumulates in these engines during any pulse sequence, and when the residues have the proper hydrazine nitrate content to constitute a detonable mixture. The density, viscosity, surface tension, and vapor pressure dependence of these solutions on the temperature and hydrazine nitrate concentration is sufficiently reliable to permit their extrapolation to temperatures or HN concentrations beyond the region of investigation.

Hydrazine nitrate, pressed to near its crystalline density (104 lb/ft<sup>3</sup>) has a shock sensitivity greater than that of TNT or tetryl. As with all solid explosives, its infinite diameter detonation velocity increases linearly with packing density. Thin film detonation studies of molten HN and HN-water and HN-hydrazine solutions have shown that the

# TABLE 4. - Detonation velocities and critical film thicknesses (cft) for both low velocity and high velocity detonations for HN-water and HN-hydrazine solutions.

Liquid Solution		Detonation Velocity				
		High Ord	ler	Low	Low Order	
Composition	HN Concentration Weight Percent	Velocity ft/sec	eft <u>in</u>	Velocity ft/sec	cft in	
HN	100	27,900	0.05	4,600	<u>&lt;</u> 0.01 <sup>⊥/</sup>	
HN/H <sub>2</sub> O	85 75 65	24,900 NOT OBS	0.12 SERVED NO PRO	7,900 6,900 PAGATION	<u>≺</u> 0.01 0.13	
$\mathrm{HN/N_{2}H_{4}}$	80 60 40 20	28,200 26,900 25,600	0.03 0.03 0.10 NO PRO	5,900 NOT 7,200 PAGATION	<0.01 OBSERVED 0.03	

1/ 0.01 inch represents the limit of resolution of the apparatus.

molten HN, and either solutions having an HN concentration greater than 80 weight percent, are capable of supporting a stable low velocity detonation in films at least as thin as 0.01 inch. Furthermore, HN-water and HN-hydrazine solutions containing less than 65 and 20 weight percent HN respectively do not support stable detonations in films thinner than 0.25 inch. From these results it appears that neither of the two liquid residue samples (No. 12 and 24) taken from MSC engines, (table 2) contained sufficient hydrazine nitrate at the time of analysis to constitute a detonable inixture. However, these samples were removed from engines that did not spike -- a fact which may attest to its nondetonable nature. Although the solid residue samples, shown in table 2, contained more than 90 weight percent HN, certainly detonable material, one cannot be sure that this material existed in the solid state at the time of engine restart. Furthermore, to do any structural damage to these engines, it is necessary to accumulate at least 1 gram of this material in the chamber--a much larger quanity than has been removed from the MSC engines to date.

In conclusion it can be said that there is sufficient evidence to indicate that hydrazine nitrate is a major constituent of these engine residues and that its combustion characteristics classify it as a potential contributor to the ignition spike phenomena.

#### REFERENCES

- 1. Robinson, R. J., and W. C. McCrone. Hydrazine Nitrate (1) Analytical Chemistry, Volume 30, 1958, pp. 1014-1015.
- 2. Christos, Theodore, Yael Miron, Harry James, and Henry E. Perlee. Exploratory Study of Hypergolic Ignition Spike Phenomena, Bureau of Mines Quarterly Report, Phase II, January 1 to March 31, 1966, 64 pp.
- 3. Medard, L. Explosive Properties of Hydrazine Nitrate, Memorial des Poudres, Volume 34, 1952, pp. 147-157.
- 4. Kissinger, L. W. The Preparation and Properties of Hydrazine Nitrate, Naval Ordnance Laboratory Memorandum 10,359, July 7, 1949, p. 4.
- 5. Shidlovskii, A., V. I. Semishin, and V. I. Simutin. Thermal Decomposition of Combustion of Hydrazine Nitrate, Zhural Prikladnoy Khimii, Volume 33, No. 6, 1960, pp. 1411-1413.
- 6. Corcoran, J. M., W. H. Kruse, S. Skolnik, and F. Lieber. Thermal Analysis of the System Hydrazine-Nitrate-Water-Hydrazine, U. S. Naval Ordnance Test Station, NAVORD Report 2087, January 1954, 13 pp.
- 7. Skinner, G. B., W. H. Hedley, and A. D. Snyder. Mechanism and Chemical Inhibition of the Hydrazine-Nitrogen Tetroxide Reaction, ASD-TDR-62-1041, December 1962, 29 pp.
- Perlee, H. E., A. C. Imhof, and M. G. Zabetakis. Flammability Characteristics of Hydrazine-Unsymmetrical Dimethylhydrazine-Nitrogen Tetroxide-Air-Water Mixtures, Explosives Research Laboratory Report No. 3844, (Sponsored by Bell Aerosystems Company) December 12, 1961, 14 pp.
- 9. Nadig, E. W., and B. P. Breen. Liquid Phase Kinetics for the Hypergolic Nitrogen Tetroxide Hydrazine System, 3rd Combustion Conference Abstract, CPIA Publication No. 118, September 1966, pp. 188-189.
- Barlot J., and S. Marsaule. Studies of Binary Systems: Hydrazine Nitrate and Alkaline Salts, Compt. Rend., Volume 226, 1948, pp. 1981-1983.
- 11. Vango, S. P., and J. B. Krasinsky. Density, Vapor Pressure and Viscosity of Solutions of Hydrazine Mononitrate in Hydrazine, Jet Propulsion Laboratory, Technical Memorandum DO. 33-103, October 15, 1962, 12 pp.
- 12. Walden, P., and H. Hilgert. Water-Free Hydrazine as Ionizing Medium for Electrolyte and Nonelectrolytes. I. The Behavior of Typical Electrolytes and Semielectrolytes. Futschrift fur Physikalische Chemic, Volume 165A, 1933, pp. 241-271.

- 13. Harned, H. S., and B. B. Owen. The Physical Chemistry of Electrolyte Solutions, Reinhold Publishing Company, 1950, pp. 250-267.
- 14. Partington, J. R. An Advanced Treatise of Physical Chemistry; Volume 2, The Properties of Liquids, Longmans, Green and Company, 1951, p. 185.
- 15. Burrows, G. Evaporation at Low Pressures, Journal of Applied Chemistry, July 7, 1957, pp. 375-384.
- 16. Michel, R. E., G. G. Harms, J. M. Koepche, R. W. Mueller, W. O. Jacobson, J. R. Syolund, and N. G. Christians. Detonation Reaction Control (Small Impulse Engine), Air Force Flight Dynamic Laboratory, Wright-Patterson Air Force Base, Technical Documentary Report No. FDL-TDR-64-63, March 1964, 90 pp.
- 17. Moran, H. E., J. C. Burnett, and E. I. Smith, Jr. Explosion Hazards of Mixed Hydrazine Fuel, Naval Research Laboratory Memorandum Report 1615, May 1965, 13 pp.
- Eyster, E. H., L. C. Smith, and S. R. Walton. The Sensitivity of High Explosives to Pure Shocks, Naval Ordnance Laboratory Memorandum 10,336, July 14, 1949, p. 39.
- Price, D., T. P. Liddiard, Jr., and R. D. Drosd. The Detonation Behavior of Hydrazine Nitrate, U. S. Naval Ordnance Laboratory, NOLTR-66-31, April 15, 1966, 15 pp.
- 20. Cited by C. L. Mader in Los Alamos, Report No. LA-2900, February 19, 1963.
- 21. Ribovich, J. A Wedge Technique for Evaluation of Detonation Hazards of Liquid Explosives, Paper Presented at the Conference on Prevention of and Protection Against Accidental Explosions of Munitions, Fuels and other Hazardous Mixtures, New York, N. Y., October 10-13, 1966.
- 22. Gibson, F. C., M. L. Bowser, C. R. Summers, and F. H. Scott. An Electrical Method for the Continuous Measurement of Propagation Velocities in Explosives and Propellants, Bureau of Mines Report of Investigation, RI 6207, 1963, 8 pp.
- 23. Watson, R. A Gauge for Determining Shock Pressures, submitted for publication in Review of Scientific Instruments.





Figure 1: Weight of moisture absorbed by HN over various Regnault mixtures as a function of time at  $60^{\circ}$ F. The quantities in parenthesis are equivalent relative humidities in percent.



Figure 2: Three component liquidous isotherms for the ternary system HNhydrazine-water. The concentration triangular grid, used to construct this figure, although not shown, is linear in the weight percent of each constituent. The temperatures shown in the figure are in degrees centigrade.



temperature, °C

TEMPERATURE °F

Figure 3: Liquidous line for the binary system HN-water.



HYDRAZINE NITRATE CONCENTRATION, weight percent

Figure 4: Liquidous line for the binary system HN-hydrazine.



------ benomination, worker beroom

Figure 5: Liquidous line for the binary system HN-ammonium nitrate.



Figure 6: Density of hydrazine nitrate-hydrazine solutions, for two concentrations of HN, plotted as a linear function of the absolute temperature.

![](_page_22_Figure_0.jpeg)

HYDRAZINE NITRATE CONCENTRATION, weight percent

Figure 7: Density of HN-hydrazine and HN-water solutions as a function of the HN concentration at 75°F.

![](_page_23_Figure_0.jpeg)

Figure 8: Kinematic viscosity of various HN-hydrazine and HN-water solutions as a function of the reciprocal of the absolute temperautre.

![](_page_24_Figure_0.jpeg)

HYDRAZINE NITRATE CONCENTRATION, weight percent

Figure 9: Surface tension of HN-water solution at 75°F as a function of the HN concentration.

![](_page_25_Figure_0.jpeg)

AJ/AT E-OIX 'NOISNEL EDVEROS

Surface tension of HN, hydrazine, and water as a function of temperature as measured by the bubble technique. Figure 10:

![](_page_26_Figure_0.jpeg)

TEMPERATURE °R

Figure 11:

Vapor pressure for water, hydrazine, and two HN-hydrazine solutions as a function of the reciprocal of the absolute temperature.

![](_page_27_Figure_0.jpeg)

Figure 12: Detonation velocity of pressed HN as a function of the packing density for various charge diameters.

![](_page_28_Picture_0.jpeg)

FIGURE 13. - Apparatus used in determining critical film thicknesses for stable detonation

![](_page_29_Figure_0.jpeg)

![](_page_29_Figure_1.jpeg)

FIGURE 14. - Typical oscillogram of the pressure transducer and collapsible probe signals for (a) propagation of a stable detonation and (b) no propagation