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THE HARD START PHENOMENA IN HYPERGOLIC ENGINES

VOLUME II. COMBUSTION CHARACTERISTICS OF PROPELLANTS
AND PROPELLANT COMBINATIONS



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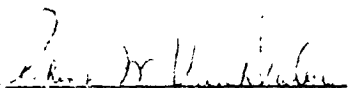
VOLUME II. COMBUSTION CHARACTERISTICS OF PROPELLANTS
AND PROPELLANT COMBINATIONS

By

Yael Miron and H. E. Perlee

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Robert W. Van Dolah
Research Director
Pittsburgh Mining and
Safety Research Center

U.S. Department of the Interior
Bureau of Mines
Pittsburgh, Pennsylvania 15213
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by

Yael Miron¹ and H. E. Perlee²

INTRODUCTION

This volume describes the experimental work of the Bureau of Mines concerning the abnormal hypergolic ignition or "hard-start" phenomenon associated with the RCS engines of the Apollo spacecraft.

Some of the original ideas regarding this phenomenon related it to the combustion characteristics of the individual propellants, hydrazine, monomethylhydrazine, unsymmetrical dimethylhydrazine, and nitrogen tetroxide. In particular, it was suggested that since each of these propellants has an endothermic heat of formation, they could conceivably undergo explosive decomposition. Although the combustion characteristics of these propellants had been extensively studied by other investigators, sufficient information was not available and additional work was required to resolve the specific questions relating to the RCS engines. Thus, this research was conducted to determine if the RCS engine propellants undergo explosive reaction when subjected to the conditions present in the engine at time of ignition.

Only the combustion characteristics believed to be pertinent to the hard-start phenomenon are included in this report. In this volume, we first discuss the explosive combustion characteristics of the propellants and their various combinations; and secondly, we discuss the thermal stability of frozen mixtures of these hydrazine-based fuels with nitrogen tetroxide. As noted elsewhere, it was assumed that the frozen mixtures of the hydrazine fuels and nitrogen tetroxide accumulate in the engine prior to ignition possibly due to leaking valves and then explode on warming, thereby producing an abnormal ignition. In this volume, we also compare the results obtained by the Bureau with results of other organizations.

¹Chemical research engineer.

²Chief, Theoretical Support

Both authors are with the Pittsburgh Mining and Safety Research Center, Bureau of Mines, U.S. Department of the Interior, Pittsburgh, Pa.

Theory

Combustion involving gases or condensed-phase material is either deflagrative or detonative in character. Deflagrative combustion is characterized by the subsonic propagation of the combustion zone (flame) relative to the unburned material. Detonative combustion is characterized by supersonic propagation of the combustion front relative to the unburned material.

Deflagrations are further characterized by a small pressure differential across the combustion zone; that is, the ratio of the pressures across the front is approximately 1. A detonation, on the other hand, exhibits large pressure ratios across the combustion front, typically 20 to 50 for gas mixtures. Since the speed of sound in condensed-phase materials is typically 1,500 m/sec, compared with 300 m/sec for gases, it is apparent that a subsonic combustion zone traveling in the former can be supersonic with respect to the surrounding gas. Consequently, this combustion can produce a pressure field (blast wave) in the surrounding gas that resembles a gaseous detonation. Blast waves have spatial pressure distributions similar to detonation waves except that the pressure decays less rapidly behind the shock front and, with the absence of a combustion zone in the gas phase, its intensity (spike level) decreases rapidly with distance of travel.

Background

Of the propellants studied, that is, hydrazine (N_2H_4), monomethylhydrazine (MMH), unsymmetrical dimethylhydrazine (UDMH), aeroxine-50 (A-50; a 50:50 mixture by weight of N_2H_4 and UDMH), and nitrogen tetroxide (NTO), hydrazine has been most extensively investigated.

An early Bureau of Mines study by Scott, Burns, and Lewis (1)³ revealed that liquid hydrazine did not support a detonation. In a later Bureau of Mines study by Herickes, Damon, and Zabetakis (2), neither liquid hydrazine at 90° C nor liquid UDMH at 53° C exhibited any tendency to detonate when fired with 100 grams of tetryl.

Other investigators have studied the detonability of hydrazine vapors and found that with a low-energy ignition source, such as a weak electrical spark or a hot wire, hydrazine vapors did not detonate in tubes up to 1 meter long and 5 cm in diameter. However, aerodynamic shocks generated by hydrogen and oxygen or by ethylene and oxygen detonations consistently initiated a detonation in hydrazine vapors (3-4).

The combustion characteristics of the other propellants have been studied extensively although these studies were primarily concerned with

³Underlined numbers in parentheses refer to items in the list of references at the end of this report.

the flammability and ignitability of the hypergolic combinations (5-10) and, consequently, are of limited interest to this investigation. Although the individual propellants do not detonate easily, they are powerful explosives and under certain conditions (that is, strong initiators) are extremely hazardous. The behavior of the propellants under these conditions was evaluated by Bureau investigators and is described in this volume.

EXPLOSIVE CHARACTERISTICS OF LIQUID PROPELLANTS AND LIQUID PROPELLANT MIXTURES

Discussion

The explosive potential of combustible materials is difficult to determine a priori and various techniques have been developed for measuring it. In one of these, the work performed during the explosive decomposition of a candidate explosive is compared with the work of an equivalent weight of TNT. This technique forms the basis of the ballistic mortar test used by the Bureau of Mines, in which the energy imparted to a projectile when fired from a mortar with TNT is compared to the energy imparted to the same projectile when fired with an equal weight of a candidate explosive. Another method used to measure TNT equivalence involves the comparison of unconfined blast-wave characteristics created by an explosion of equal weights of TNT and candidate materials. A detailed discussion of this procedure and its application to A-50/NTO systems is given in an article by Willoughby and coworkers (11). Although this latter technique generally yields more realistic results, the ballistic mortar test is considerably more convenient and rapid. Early experiments to determine the explosive potential of stoichiometric NTO/fuel liquid mixtures, by blast wave and other techniques, appear to have been mixing-dependent in that the experiments in which the mixing rates were the highest also gave larger TNT equivalences (12-19). Very rapid mixing can be accomplished by an explosion in a confined space such as the ballistic mortar, and this was another reason for selecting the ballistic mortar method.

Although explosive mixing techniques have been used by other investigators (12-19), most experiments were conducted under unconfined conditions using blast-wave techniques and, as a result, large portions of the reactants were explosively separated and failed to react in the time necessary to contribute to the blast wave. The ballistic mortar, on the other hand, not only confines the reactants, but due to the large time constant (large projectile inertia), insures a long contact time between the reactants, and provides for an extensive reaction, thus leading to upper limit values for TNT equivalences. Moreover, the absolute resolution of the ballistic mortar is satisfactory even for samples as small as 5 grams. It is possible, due to the large inertia of the ballistic mortar apparatus, to attribute TNT equivalences to combustibles that do not exhibit blast-wave characteristics. Primarily, the ballistic mortar is useful for a rapid evaluation of the explosive potential of materials

that exhibit fast exothermic reactions. Additional experiments are usually necessary to determine if the combustion reaction proceeds through the material at supersonic speeds.

Experimental Procedures and Results

Two sets of experiments were conducted at the Bureau laboratories using the ballistic mortar test. In the first set, the individual liquid propellants were fired in various atmospheres in the mortar using a No. 8 du Pont⁴ electric detonator; in the second set, the various liquid fuel/liquid NTO combinations were fired in an inert nitrogen atmosphere in the mortar with detonators. In both sets of experiments, the candidate liquids were contained in specially constructed glass vessels (fig. 1). To obtain maximum energy coupling between the exploding detonator and the liquid, the detonator was placed under the liquid surface and at a central position. To avoid contact between the copper-sheathed detonator and the corrosive fuels, the detonator was encapsulated in glass. Special care was taken to insure that the weight of the glass was held within fixed limits. The mortar was calibrated by firing known weights of TNT using the same glass tube configurations and detonators as in the actual experiments.

In the first set of the experiments, 5-gram samples of the individual liquid fuels were tested in atmospheres of nitrogen, air, oxygen, and NTO; results are shown in table 1.

TABLE 1. - TNT equivalents for liquid fuels in various atmospheres

Mortar atmosphere	Detonator type	Liquid fuels (TNT equiv., pct)			
		N ₂ H ₄	A-50	UDMH	MMH
Nitrogen..	No. 8	10	0	0	0
Nitrogen..	J-2	80	-	-	-
Air.....	No. 8	120	0	0	0
Oxygen....	No. 8	110	-	-	0
NTO.....	No. 8	130	10	0	-

¹Each value is the mean result from three consecutive experiments. Zero value implies zero within experimental error.

⁴Reference to specific brands, equipment, or trade names in this report is made to facilitate understanding and does not imply endorsement by the Bureau of Mines.



FIGURE 1. - Sample Tubes used for Determining Explosive Potential
of (a) Individual Liquids, and (b) Mixtures.

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From the results in table 1, it can be seen that none of the liquid fuels exhibit explosive reactions when fired in a nitrogen atmosphere with a No. 8 detonator, which contains a total TNT equivalent weight of explosive of approximately 0.83 gram. However, with a more potent detonator, the J-2 (army special) containing a larger TNT equivalent charge of approximately 1.3 grams, the hydrazine apparently underwent an explosive reaction with an energy release equivalent to about 80 pct TNT. Although the J-2 detonator represents an unrealistically large ignition source not likely to be found in the RCS engines, it was used to determine the energy conditions necessary to induce an explosion with hydrazine fuel. This value, then, could be used as an upper limit for evaluating various energy sources within the RCS engines. When the hydrazine-type fuels were fired in air, oxygen, and NTO atmospheres, only hydrazine showed a measurable exothermic reaction and an average TNT equivalent value of 120. However, compared with the mass of fuel used in each test, only small amounts of the air, oxygen, or NTO were present inside the mortar for the test. Thus, the oxidant/fuel (O/F) ratio was small. Water and powdered TNT were included in these tests although not listed in table 1. They provide and illustrate results for an inert and an explosive in an inert nitrogen atmosphere. Compared to a value of 100 pct for TNT, a value of 6 pct was obtained for the water; obviously this represents the extent of experimental uncertainty in using the ballistic mortar. Liquid NTO was also fired, without a fuel, to evaluate its contribution to the reaction even when present in small quantity. Water and the liquid NTO were also fired in a nitrogen atmosphere with an army special J-2 detonator (which imparts more energy than the No. 8 du Pont detonator). Even with the stronger detonator, the TNT equivalent of the liquid NTO was measured to be 13 pct, a small contribution when compared with TNT equivalences of 100 pct or more for the N_2H_4 fuel/oxidant combination. This value of 13 pct for NTO, these authors believe, is still indicative of no reaction.

Table 2 shows the calculated percentage of fuel consumed in these reactions, assuming that the fuel and oxidant reacted stoichiometrically, and the resultant percent TNT equivalences for these assumed reactions. For the fuel/oxygen reaction a TNT equivalence of 100 pct was used in the calculations, a reasonably good assumption; TNT equivalence value, given in table 3, was used for the fuel/NTO reaction calculations. The table shows that about 1, 5, and 10 pct of the liquid fuel samples reacted with the air, oxygen, and NTO, respectively, and that the corresponding calculated TNT equivalence values are about 0, 4, and 30 pct for the air, oxygen, and NTO, respectively. Comparing these results with those of table 1, it can be seen that the experimental TNT equivalent values for hydrazine with small amounts of oxidants greatly exceed the calculated values, indicating that there is considerable reaction exclusive of the oxidation and due to the fuel itself. Furthermore, because the TNT

equivalence values for the hydrazine when fired in the air, oxygen, and NTO are statistically the same, the concentration or type of oxidant apparently has little effect on the result of the reaction. It would appear that the oxidant catalyzes the reaction, since small amounts seem to have a pronounced effect on the reaction, while increasing the oxidant concentration has no noticeable influence. The TNT equivalence for liquid hydrazine, measured to be 120 \pm 10 pct whether fired in the presence of small amounts of air, oxygen, or NTO, has been corrected for the contribution of the detonator. It appears, from the calculations presented in table 2, that A-50, UDMH, and MMH, although somewhat weaker than N_2H_4 , should also show some reaction when tested experimentally. But these are only theoretical calculations, presuming that certain reactions take place. Experimentally, only hydrazine was found to be a monopropellant, and although A-50 contains 50 pct by weight of hydrazine, it is apparently diluted by the UDMH to a point where it does not react explosively or as a monopropellant. This value, obtained for hydrazine, compares favorably with the value of 135 pct reported by Scott, Burns, and Lewis (1) who used 10-gram charges of N_2H_4 contained in small glass bottles, and initiated by a J-2 detonator. There is no reference to the type of atmosphere in the mortar; it is presumed that the tests were done at atmospheric conditions. It has been shown that the TNT values for the MMH, UDMH, or A-50 fired in air, oxygen, or NTO are not significantly different than TNT values obtained when the No. 8 detonator is fired alone. Therefore, it must be concluded that no exothermic reaction occurs when these fuels are fired with a No. 8 detonator in the oxidant atmospheres. Moreover, as noted in table 2, it was shown that with the exception of the NTO atmosphere where a TNT equivalence of approximately 30 pct was calculated, the oxidation reaction for the other oxidants was lower than the detection limit of the ballistic mortar (about 10 pct TNT). Since there was some speculation that NTO might undergo exothermic reaction and give similar results, both water and liquid NTO were fired in a nitrogen atmosphere in the mortar. As explained earlier, the water and NTO values were not significantly different to indicate an exothermic reaction for NTO; whatever the difference between the two values, it is probably due to differences in the physical and thermochemical properties of water and NTO. From this then, it can be concluded that the value of 30 pct TNT equivalence calculated for the fuel/NTO atmosphere is not due to the NTO, but to an oxidation reaction. In the experiments, the TNT equivalence values for MMH, UDMH, and A-50 were measured to be below the detection limit of 10 pct TNT equivalence values rather than closer to the 30 pct calculated value. Unlike hydrazine, the substituted fuels are not monopropellants and traces of oxidant are not enough to set them off.

TABLE 2. - Computed TNT equivalents and percent fuel consumed

Fuel	Oxidant					
	Air		O ₂		N ₂ O	
	Fuel consumed, pct	TNT equiv., pct	Fuel consumed, pct	TNT equiv., pct	Fuel consumed, pct	TNT equiv., pct
N ₂ H ₄	1.5	0	7.4	6	14.8	30
A-50	1.0	0	5.1	4	12.1	30
UDMH	0.7	0	3.5	2	7.0	30
MMH	.9	0	4.3	3	8.6	28

TABLE 3. - Maximum TNT equivalents of liquid N₂O/fuel mixtures as a function of the concentric arrangement of the liquids

Fuel	Propellant adjacent to detonator	
	Oxidizer	Fuel
	Maximum TNT equiv., pct	Maximum TNT equiv., pct
N ₂ H ₄	165	158
MMH	149	101
UDMH	162	101
A-50	168	85

In the second set of experiments, some thought was given to the possibility that the explosibility might depend on the coaxial arrangement of the fuel and N₂O; since the fuel and liquid N₂O were contained in separate compartments, it was possible to check for this effect. Analysis of the results showed: (1) that the various fuel/N₂O combinations had significantly different TNT equivalences, and (2) that placing the oxidant next to the detonator gave significantly higher TNT equivalences. The first result was not unexpected. The second result indicates that the TNT equivalence depends on the concentric arrangement of the fuel and N₂O and requires a more detailed study. According to calculations by Willoughby and his coworkers (11), N₂H₄/N₂O and A-50/N₂O should have approximately the same TNT equivalence of 125 pct, a value significantly lower than the corresponding value obtained by the Bureau. The value for A-50/N₂O (168 pct) is considerably higher than values reported by other investigators (12-19) given in table 4. The only value close to the Bureau value is that of 90 pct TNT equivalence obtained in the Deep Hole experiment (18). These results are not surprising; as explained earlier, the ballistic mortar values are expected to be highest due to the rapid mixing and initial confinement in the mortar. The other investigators whose results are quoted obtained the TNT equivalence values under simulated spill or rocket fallback conditions, where confinement is minimal. The experiments in the ballistic mortar with liquid fuel/liquid N₂O combinations show that these combinations constitute powerful explosives, obviously capable of doing considerable damage to rocket engines. The question remains as to the quantity of these materials that the R/S engines can safely accommodate. This subject is discussed in volume IV.

TABLE 4. -- TNT equivalent of the NIO/A-50 system obtained by various investigators using various mixing techniques

Type of mixing	Mixing device	O/F	Total propellant weight, lb	TNT equivalence, pct ¹	Reference No.
Ruptured diaphragm	Explosively driven ram.....	1.9:1	200	0.15 (2-3)	(13)
	Linear charge... ..	2:1	300	.01 (5)	(12)
	Drop.....	2:1	300	.5 (3-4)	(12)
	Linear charge double diaphragm.....	2:1	32,700	.6 (3-4)	(14)
	Explosive rupture of multiple concentric glass tube configuration.....	2.4:1	-	47 37 33	(19)
	Explosive ruptures of multiple plexiglass concentric tube configurations ²	2.4:1	128	³ 49	(19)
Liquid spill	Small scale.....	1.2-2.0 0.7-4.0 2.0	2.5-6.0 2.5 90-300	.25 (3-4) .18 (3-4) .02 (4-5)	(15) (16-17)
	Destruct ⁴	1.9	200	.32 (2)	
	Model missile.....	2.0	300	.03 (3-4)	(15)
	do.....	2.0	300	.15 (3-4)	
	do.....	1.9	50	⁵ .45 (3-4)	(15)
	do.....	2.0	300	⁶ .40 (3-4)	
	Large scale.....	4.3 1.6	1,600 1,300	No explosion .14 (3-4)	(15)
	Impact	Dropped, flat-wall target..	1.9:1 1.9:1 1.9:1	200 200 1,000	7 (1.5) 14 (1.5) 22 (1.5)
Dropped, shallow hole.....		1.9:1	200	53 (1.5)	(18)
Dropped, deep hole.....		1.9:1	200	62 (1.5)	(18)
do.....		1.9:1	200	90 (1.5)	
do.....		1.9:1	1,000	42 (1.5)	
do.....		1.9:1	340	33 (1.5)	(18)

¹Values in parentheses indicate error factor.

²Maximum value of four trials for 0.6 msec delay between two charges in reference.

³These experiments were conducted by first firing an explosive charge to mix the propellants and then a number of milliseconds later firing another charge to initiate the mixture.

⁴Use N₂H₄ rather than A-50.

⁵Average of three trials.

⁶Average of two trials.

EXPLOSIVE CHARACTERISTICS OF FROZEN PROPELLANT MIXTURES

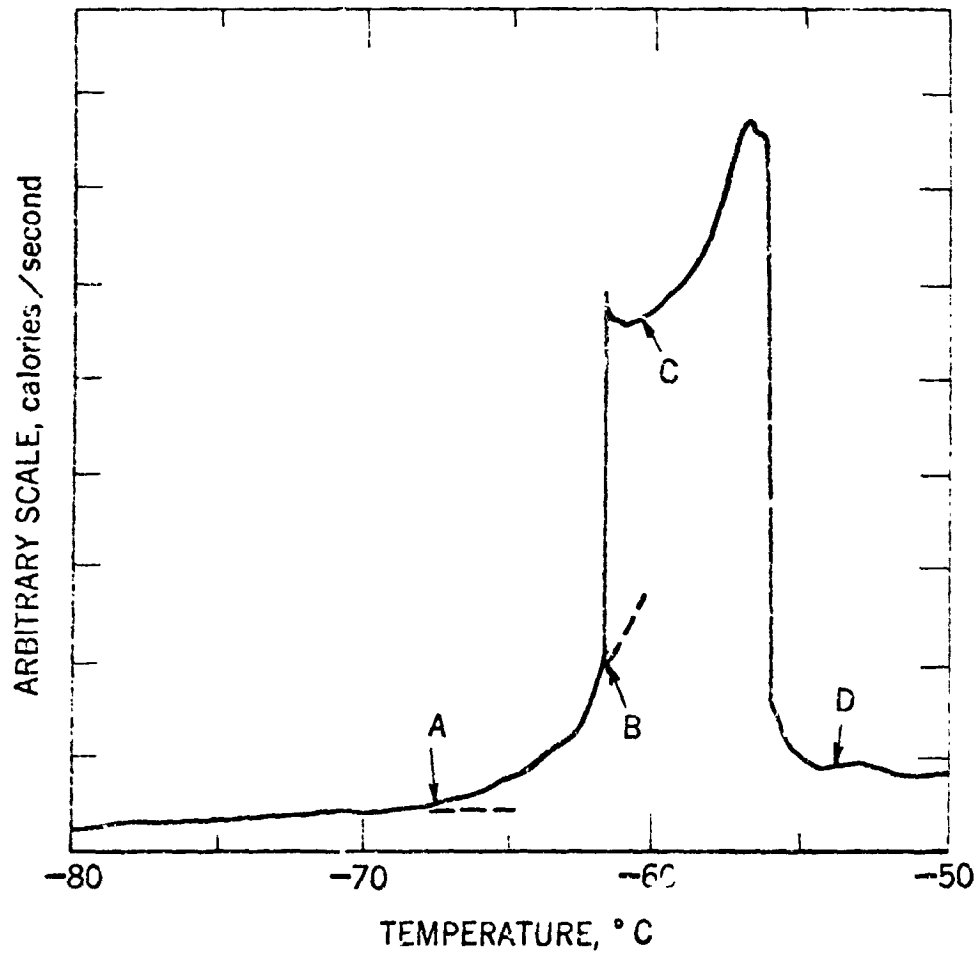
DSC Studies

Two types of experiments were conducted to determine the explosive characteristics of frozen propellant mixtures. One was a study of the thermal reactions that occur when frozen mixtures of fuel and NTO are permitted to warm gradually from liquid nitrogen temperatures (-190°C) to ambient conditions, and the second was to measure the potential explosiveness of such mixtures.

The thermal analysis was conducted with a differential scanning calorimeter (DSC),⁵ equipped with dewar attachment for low temperature studies. The propellants, frozen separately in the form of fine powders, were transferred to the DSC cups, maintained at liquid nitrogen temperatures, and were carefully mixed with a cooled spatula. Total sample weight was approximately 20 to 40 mg. For the test, the DSC temperature programmer was set for the desired constant rate of temperature increase. Results were obtained in the form of thermograms. The lowest temperature that DSC was able to record was -100°C ; reactions below that temperature could not be observed. No endothermic reactions were observed to precede the expected exothermic reaction. A typical thermogram for a frozen propellant/NTO mixture is shown in figure 2. Point A in the figure marks the first indication of a slow exothermic thermal reaction; a fast exothermic reaction occurs at point B, corresponding to a vertical rise in the trace. At B the thermal reaction rate exceeds the response of the DSC, thus making it impossible to obtain rate data, although the area under the curve is directly proportional to the energy released in the reaction. In some of the experiments with the A-50/NTO mixtures, an audible report occurred during the fast exothermic reaction, suggesting that the reaction was explosive in nature. Following this fast reaction the trace falls slightly and then rises again slowly to a broad peak before returning to the baseline. The thermal event giving rise to this second peak is unknown. When the DSC was opened at point C, a yellow liquid residue was observed in the sample cups; when it was opened at point D there was no visible liquid residue.

The frozen mixtures of $\text{N}_2\text{H}_4/\text{NTO}$, MMH/NTO , UDMH/NTO , and $\text{A-50}/\text{NTO}$, all exhibit similar thermal traces, although the relative heights and widths of the two peaks differ.

⁵Perkin-Elmer, Model DSC-1.



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FIGURE 2. - Thermogram for a Frozen A-50/NTO Mixture
for a Heating Rate of 5° F/min.

Table 5 lists the results of the thermal experiments for the various fuel/NTO mixtures showing the temperature at which the fast exothermic reaction occurs.

TABLE 5. - Temperature of rapid exothermic reaction for various fuel/NTO mixtures

Fuel	Fuel melting point, ° C ¹	Average temperature of fast reaction, ° C
N ₂ H ₄	+1.5	-55 ±1
MMH.....	-52.3	-61 ±6
UDMH.....	-57.2	-60 ±6
A-50.....	-6 to -8	-60 ±3

¹NTO has a melting point of -11.2° C.

As was mentioned earlier, the DSC used by the Bureau was limited in its range of test temperatures, with the lowest temperature being -100° C. In a similar study using thin frozen layers of propellants deposited in a specially constructed differential thermal analyzer (DTA), Weiss (20) found that the N₂H₄/NTO mixture underwent an exothermic reaction at about -57.7° C, in good agreement with the Bureau's value of -55 ±1° C. Weiss (20) also observed two peaks with his apparatus; he attributed the second peak to equipment malfunction. In conjunction with the DTA studies, Weiss (20) followed the course of the reaction by means of infrared spectroscopy. He found that absorption peaks in this frozen mixture at liquid nitrogen temperature corresponded to that of unreacted NTO and N₂H₄. On warming the mixture to -133° C, the reactant peaks diminished in size and additional peaks appeared. At about -57.7° C, an exothermic reaction occurred and hydrazine nitrate absorption peaks were found in the product spectrum. A close examination and comparison with available infrared spectra showed Weiss's product infrared spectrum to be almost identical to that for a solution of hydrazine nitrate in hydrazine prepared by the Bureau.

Weiss (20) also noted the presence of NH₂ and NH absorption bonds as well as peaks indicative of ammonium and azide ions.

Weiss (20) has suggested that the propellants react at about -130° C to form a product that is not stable above approximately -70° C. Possibly, this product might be nitrosyl azide, as subsequently suggested in volume III of this report. This seems a reasonable conclusion in view of the fact that all three fuels (N₂H₄, UDMH, AND MMH) undergo this very fast reaction at about the same temperature, suggesting that the unstable, low-temperature species is a common product of these fuels.

The doublet exotherm may arise from a two-step process involving crystalline rearrangement as the second step. Otherwise, a violent evolution of gases that will change the ambient atmosphere in the sample vicinity so markedly that the reaction rate is temporarily reduced, causing the first peak. With dissipation of gaseous products reaction rate again increases, forming the second peak (21).

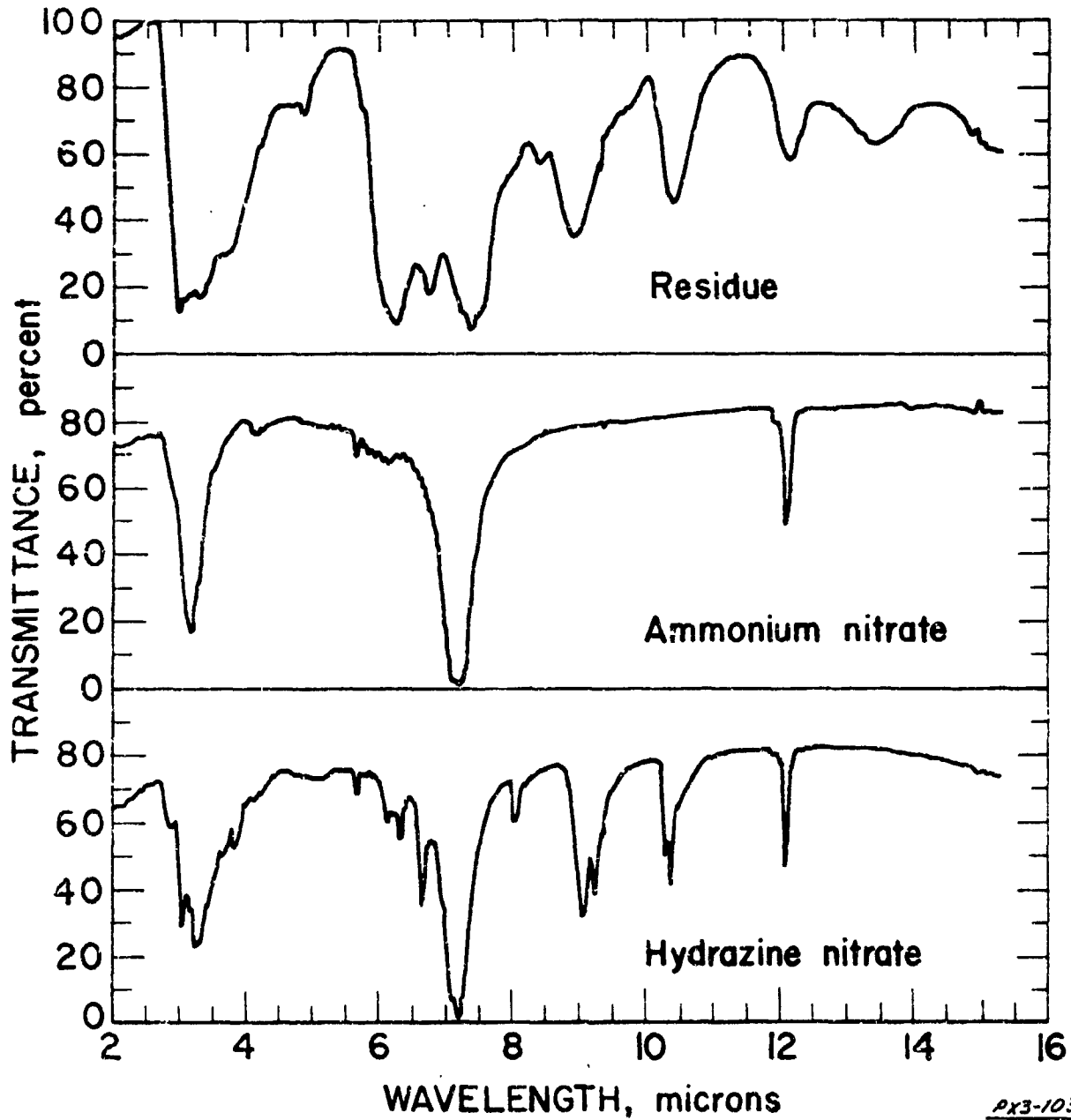
Large Scale Frozen Mixtures--Potential Explosiveness

In these experiments, 1 to 60 grams of frozen fuel/NTO mixtures similar to those used in the DSC experiments were mixed under liquid nitrogen in uncovered, wide-mouthed glass jars. The jars were placed in a dry ice bath (-78.5°C) until the liquid nitrogen evaporated and then they were removed from the dry ice and placed on a table top in a bombproof to warm. Eventually, as the temperature of the sample rose, a violent reaction occurred accompanied by considerable fire and spewing of burning debris. No attempt was made to monitor the rate of these reactions, but only to observe whether or not they proceeded at an explosive rate.

In these experiments, the reaction was observed in all cases to occur while the mixture appeared to be frozen. Although the reaction was violent, the container, whether glass or metal, remained undamaged. When a screwtop cover was fitted on the glass containers the resulting reaction broke the vessel, but the size of the glass fragments indicated that the reaction was not excessively violent--certainly not detonation-like. In two instances, using 50-gram A-50/NTO mixtures and an uncovered glass beaker, the reaction resulted in a loud report and broke the glass container into a powder. The extent of the damage to the surrounding area and to the container indicated that this reaction was indeed detonation-like. In these experiments the mixtures were loosely packed and it is believed that increasing the packing density will significantly increase the probability of a detonation-like reaction.

Comparison of an infrared spectrum of the yellow residue remaining after these reactions with the spectrum of hydrazine nitrate (with both spectra shown in fig. 3), indicates that the residue contains an appreciable percentage of hydrazine nitrate.

These studies have demonstrated that frozen fuel/NTO mixtures exhibit fast exothermic reactions at approximately -60°C and that under appropriate conditions, can reach explosive magnitudes. Although considerably more work is required to clarify the exact nature of the unstable species and the nature of the thermal reactions, it is nevertheless evident that the presence of frozen mixtures in the RCS engine should be avoided.



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FIGURE 3. - Infrared Spectra of Residue from N_2H_4/NTO Reaction, Ammonium Nitrate, and Hydrazine Nitrate.

CONCLUSIONS

Although N_2H_4 vapor exhibits monopropellant burning characteristics, neither the liquid form nor hydrazine's two derivatives, MMH and UDMH, appear to exhibit explosive reactions through a monopropellant decomposition process. However, in the presence of small amounts of oxidant (air, oxygen, or NTO), N_2H_4 when suitably dispersed and initiated (that is by an explosive device) is capable of exhibiting an explosive reaction releasing energy equivalent to approximately 150 pct that of TNT, as shown by Bureau tests and by the investigations of other researchers.

Explosive mixing of liquid N_2H_4 , MMH, UDMH, and A-50 with liquid NTO results in an explosive reaction yielding TNT equivalences as high as 165, 149, 162 and 168 pct, respectively. These values for N_2H_4 and A-50 are considerably larger than the theoretically predicted value of 125 pct (11) and the experimental values previously reported by other investigators using blast-wave techniques (12-19), as expected. Frozen mixtures of each of the four fuels (N_2H_4 , MMH, UDMH, and A-50) in combination with NTO react violently and rapidly at $-55^\circ C$ for N_2H_4 /NTO and at $-60^\circ C$ for MMH/NTO, UDMH/NTO, and A-50/NTO. Although hydrazine nitrate (HN) was often recovered as a product of these reactions, it does not appear to be the chemical species responsible for the reaction, since it has been found to explosively decompose at approximately $304^\circ C$.

From the results of these tests, it is evident that the accumulation of either unreacted liquid propellants or frozen propellants inside the combustion chamber of the RCS engine is to be avoided because under certain specific conditions they might detonate. The frozen mixtures, without any external initiation, react violently each and every time, upon reaching a certain temperature, and at times even detonate.

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