A PHOTOGRAPHIC INVESTIGATION OF THE COLLISION, REACTION, AND IGNITION OF HYPERGOL DROPLETS

by

Robert Bowman Howe, Jr.

Thesis submitted to the Graduate Faculty of the
Virginia Polytechnic Institute
in candidacy for the degree of
MASTER OF SCIENCE
in
MECHANICAL ENGINEERING

August, 1965
Blacksburg, Virginia

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

I. INTRODUCTION

Hypergolic propellants have been used in rocket engines and there is a continuing interest in their future development. The fact that these propellants do not need ignition systems makes them highly advantageous in certain situations. For example, if it is desired to restart a rocket after an inflight shutdown, it is possible, using hypergolic propellants, to simply inject the fuel and oxidizer into the combustion chamber. The weight of an ignition system is thus eliminated.

The ultimate purpose of all injectors in rocket engines is to produce droplets.[1] The droplets begin vaporizing as soon as they enter the combustion chamber. This means fuel can meet oxidizer in four ways:

1. Fuel vapor can mix with oxidizer vapor.
2. Fuel vapor can contact an oxidizer droplet.
3. Oxidizer vapor can contact a fuel droplet.
4. A fuel droplet can contact an oxidizer droplet.

The first three methods of fuel-oxidizer contact have been investigated in some detail. The fourth method has been studied only from the standpoint of liquid-liquid contact of hypergolic propellants. No research has been published of the collision and ignition of a single droplet of hypergolic fuel with a single droplet of its oxidizer.

This investigation was a study of the phenomena occuring when hypergolic propellant droplets collide.

II. REVIEW OF LITERATURE

Introduction

Before reviewing the several articles most pertinent to this investigation, the two prevailing theories of ignition will first be briefly considered. Following the two ignition theory explanations, articles on droplet combustion in vapor atmospheres will be reviewed. These articles are significant to this investigation from the point of view that even though droplets may collide in the liquid phase there are always vapors present. Thus, vapor phase ignition similar to that of droplet-vapor systems may occur. Articles on liquid phase reactions of hypergols are then reviewed with emphasis on the propellant systems: hydrazine/WFNA* and furfuryl alcohol-aniline/WFNA, the systems used in this investigation.

Ignition Theories

The first theory to explain ignition states that when collisions between fuel molecules and oxidizer molecules occur, only those molecules possessing energy in excess of some minimum value, called the activation energy, will react. Since the molecular energy can be increased by raising the temperature, more molecules can be made to react by increasing the temperature of the fuel and/or oxidizer. As the temperature is increased, a point will be reached where the

---

*White Fuming Nitric Acid

exothermic fuel-oxidizer molecular reactions are sufficient to continue raising the temperature upward to the flame temperature without outside heat addition. Ignition is then said to have occurred at that point. This explanation of ignition is known as the thermal theory[2,3]. Unfortunately, the thermal theory does not explain certain combustion phenomena.

A second theory, therefore, has been advanced which states that reactions do not occur by simple molecular collisions. Instead, these first collisions form activated particles known as free radicals or chain carriers. These free radicals then proceed to cause intermediate reactions with the reactant molecules which regenerate more free radicals. At a certain point the chain reactions become sufficiently frequent to propagate rapidly through the entire mixture and ignition can be said to have occurred. This theory is known as the chain reaction theory.[3,4]

Droplet-Vapor Systems

C. A. Gregory and H. F. Calcote[5] made combustion studies of droplet-vapor systems. An experimental technique was developed that allowed the study of the physical and chemical reactions between a single liquid droplet of one reactant and the vapor phase of the other reactant. The investigators stated that in liquid propellant systems of the type considered, the vapor may condense upon the droplet, in which case a liquid-liquid reaction can occur. Basically their apparatus consisted of a drop producer which allowed a drop to fall into a long tube filled with the reactant vapor. A photocell recorded the time delay until light was visible from the reaction. One of the results listed showed that a drop of WFNA falling through hydrazine vapors at 135° C did not ignite in 450 milliseconds, which was the time required to travel the entire length of the reaction tube. It did, however, ignite upon contacting the bottom of the tube.

H. L. Wood[6] studied free falling fuel droplets in the decomposition vapors of WFNA. A high speed camera was employed to observe the ignition process. The parameters affecting ignition delay, defined as the first instant of visible light emission, were observed to be WFNA vapor temperature, initial droplet temperature, and initial droplet diameter. Ignition was accomplished in five consecutive phases: evaporation of fuel vapor from the droplet; mixing of the fuel vapor with the oxidizer vapor; chemical reaction resulting in vapor phase ignition in the trailing wake of the free falling droplet; propagation of a flame front through the mixture of fuel and oxidizer vapor; and ignition of the droplet by the flame front.

Liquid-Liquid Reactions

Stanley V. Gunn[7] described a method to measure the ignition lag of hypergolic combustions. The fuels used were aniline, furfuryl alcohol and mixtures of the two. The oxidizers were red fuming nitric acid and WFNA. The oxidizer was placed in a constant temperature, molded glass reaction dish and the fuel was poured into it from a weir-lipped cup held by a support stand. Ignition lag was defined as the time interval from the instant the fuel hit the oxidizer until the instant light was emitted from the reaction. A timing system was employed using a phototube as the detector. Gunn's results showed that a fuel mixture of 80% furfuryl alcohol-20% aniline was a superior mixture when oxidized with WFNA. The ignition lag for this reaction was 18.0 milliseconds with the propellant temperatures approximately 70°F. The temperature of the propellants had little effect on the reaction time except near the freezing point, where it considerably increased the ignition lag.

One of two methods employed by D. J. Ladanyi and R. D. Miller[8] to measure ignition lag in hypergols consisted of a glass ampule filled with fuel. The ampule was placed in a test tube which also held the oxidizer. When the ampule was crushed with a rod the fuel and oxidizer mixed and reacted. The ignition lag was measured in three ways from the time the ampule was crushed until light and sound were emitted. The data obtained in this modified open-cup apparatus for hydrazine and WFNA as presented in NACA Research Memorandum RM E53D03 follows:[9]

Table 1. Summary of Data Obtained with Modified Open-Cup Apparatus.

Propellant Temp., °F	Fuel Quantity, ml.	Oxidant Quantity, ml.	Ignition Lag	Fuel Oxidant Weight Ratio
68.9	2.0	1.6	57 ms.	0.84
66.2	2.0	1.6	59 ms.	0.84

The second method of determining ignition lag and studying ignition characteristics of hypergols was with a small scale rocket engine utilizing a transparent combustion chamber. The ignition lag was the time interval from first contact of the reactants to the first appearance of flame. Ignition lags ranged from four to nine milliseconds.

M. Barrere and A. Moutet[10] also investigated ignition lag of liquid propellants with a transparent-type rocket engine. The effect of excessive ignition lag was determined to interfere with the operation of the rocket engine. Low amplitude pressure oscillations were created with ignition delays of 16 milliseconds. At an ignition delay of 46 milliseconds, high pressure, with a momentary halt in combustion, resulted. When the ignition delay was 96 milliseconds, the transparent walls of the combustion chamber were shattered.

R. A. Schalla and E. A. Fletcher[11] studied ignition behavior of various amines with nitric acid. Their apparatus consisted of a device which permitted the reactants to be rapidly mixed and injected into a constant-volume bomb in less than one millisecond. The pressure rise as a function of time was recorded to determine the ignition delay. The processes associated with ignition were separated into three well-defined steps: (1) a fast, liquid phase reaction which yields some gaseous products, followed by (2) an induction period, the length of which determines the ignition delay; and then (3) igintion and combustion. The rates of the reactions in step 2 were found to be quite sensitive to the temperature achieved by neutralization, the charge density, and the composition of the reactants in the gas phase. The rates were found to be especially sensitive to the presence of gas phase oxidants. Ignition was completely surpressed by inert gases.

Observation of the time required for ignition under most test conditions does not differentiate between the delay created by the time required to achieve efficient mixing and the delay caused by an actual chemical induction period. M. Kilpatrick and L. Baker[12] used an extremely fast mixing device which allowed them to study chemical induction periods. The apparatus was a pair of simultaneously rapidly driven pistons in cylinders which injected small quantities (less than 3 cc.) of fuel and oxidizer through a T-type mixer.

The following table indicated the ignition delays obtained using pressure rise as the ignition indicator.

Table 2. Transient Pressure and Injection Measurements. Hydrazine - Nitric Acid Reaction

Vol. HNO_3	Vol. N_2H_4	Mole Ratio $HNO_3:N_2H_4$	Max. Press. Rise	Final Press. Rise	Overall Injection Time	Ignition Delay
cc.	cc.		atm.	atm.	msec.	msec.
2.84	0.74	2.87	23.4	2.66	9.2	0.2
1.59	0.74	1.61	31.6	2.21	5.4	0.5
1.11	0.74	1.12	31.7	1.80	4.9	0.9
1.11	1.11	0.75	46.7	3.35	4.7	0.1
0.74	1.11	0.51	43.2	5.57	4.6	0.2
0.74	1.59	0.352	51.3	5.26	6.4	0.4

There was a negligible effect of the initial temperature of the reactants on the ignition delay time.

T. Carpenter[16] experimented with droplet impact of hypergolic propellants in air at room temperature. Using small droplets and a variety of fuels he was unable to obtain ignition with flame. High speed photography revealed that in collisions between WFNA and hydrazine, the droplets immediately shattered due to reaction. When hydrazine drops were allowed to fall into a cup containing several milliliters of WFNA, an orange flame resulted. The temperature of the reaction occurring in the cup was measured and found to be considerably higher than that generated by the impacting droplets. It therefore appeared possible that by raising the temperature of the environment surrounding the impacting droplets, ignition accompanied by flame could be observed. The above idea led to the investigation conducted by the author.

III. THE INVESTIGATION

Object

The purpose of this investigation was to study, by means of high speed photography, the collision and ignition of a single droplet of hypergolic fuel with a single droplet of its oxidizer and to determine the effect of environmental temperature on the reaction.

Preliminary Investigation

In order to determine if it were possible to obtain ignition with flame by impacting single droplets of hypergolic fuel and oxidizer, various experiments were tried. The first consisted of impacting a droplet of WFNA and a droplet of hydrazine directly above a heated chamber. The droplet impacting apparatus was the same as that described later and the heated chamber was a partially covered beaker. The beaker was heated by a Bunsen burner and nitrogen was allowed to flow into it. The nitrogen flowed through copper tubing which was wound in a coil and also heated with a Bunsen burner. It was expected that the drops, after colliding just above the cover and forming one drop, would fall into the heated chamber and ignite. After attempting the experiment several times, it was apparent that the human eye could not follow the action; thus, a 16 mm camera operating at

64 frames per second was used to photograph the event. The film showed the droplets, during the few collisions recorded, would immediately be broken apart by a quick reaction above the hot beaker and, upon reaching the bottom, would flare up in orange flames. Since it did not appear that flame accompanied the initial reaction, the heated chamber was abandoned.

It was decided next to impact the droplets directly over the flame of a Bunsen burner and record the results on film. The droplets were brought together about five inches above the turbulent flame. When the droplets did not collide, the hydrazine did not ignite, in spite of the fact that it is a monopropellant. This was because it passed through the hot volume of gases above the Bunsen flame very rapidly. However, when collision did occur, there was a violent reaction accompanied by orange flame. Because there was a good possibility that the reaction mechanism of the Bunsen flame itself was causing the ignition, the experiment was not considered conclusive.

The last of the preliminary experiments was to impact two droplets over coils of electrically heated nichrome wire. Two concentric coils were used, one on the outside of a one-inch diameter pyrex glass tube and the other on the inside. Air by natural convection passed over the coils and formed a hot volume directly above the vertically mounted tube.

In this hot volume a droplet of WFNA and a droplet of 20 percent aniline and 80 percent furfuryl alcohol by weight were impacted. One drop was formed which fell a short distance and ignited with flame. It was felt that this ignition accompanied by flame justified a continuation of the investigation using, however, considerably different equipment.

Final Investigation

Description of Apparatus

The apparatus employed in this investigation consisted of three major components:

1. The droplet impacting assembly
2. The nitrogen heater and receptacle
3. The photographic equipment

Figure 1 illustrates schematically the arrangement of the apparatus.

1. Droplet Impacting Assembly

The droplet impacting assembly was designed to throw two drops at each other in such a manner that they collided without being in contact with any solid surface. The assembly consisted of two pendulum rods which were separated by a spacer connected to a solenoid. On the end of each pendulum rod was a polyethylene tip from which was suspended a liquid

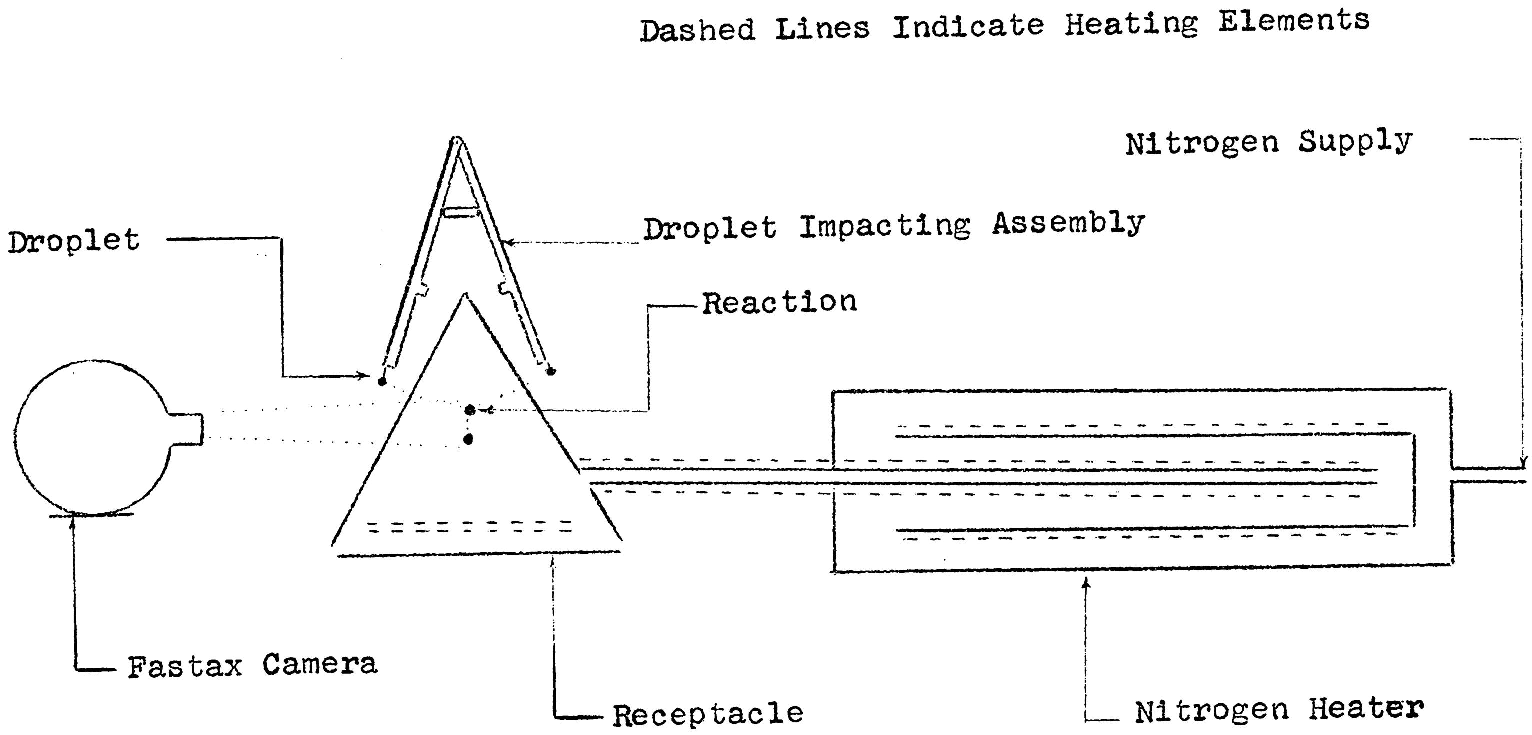
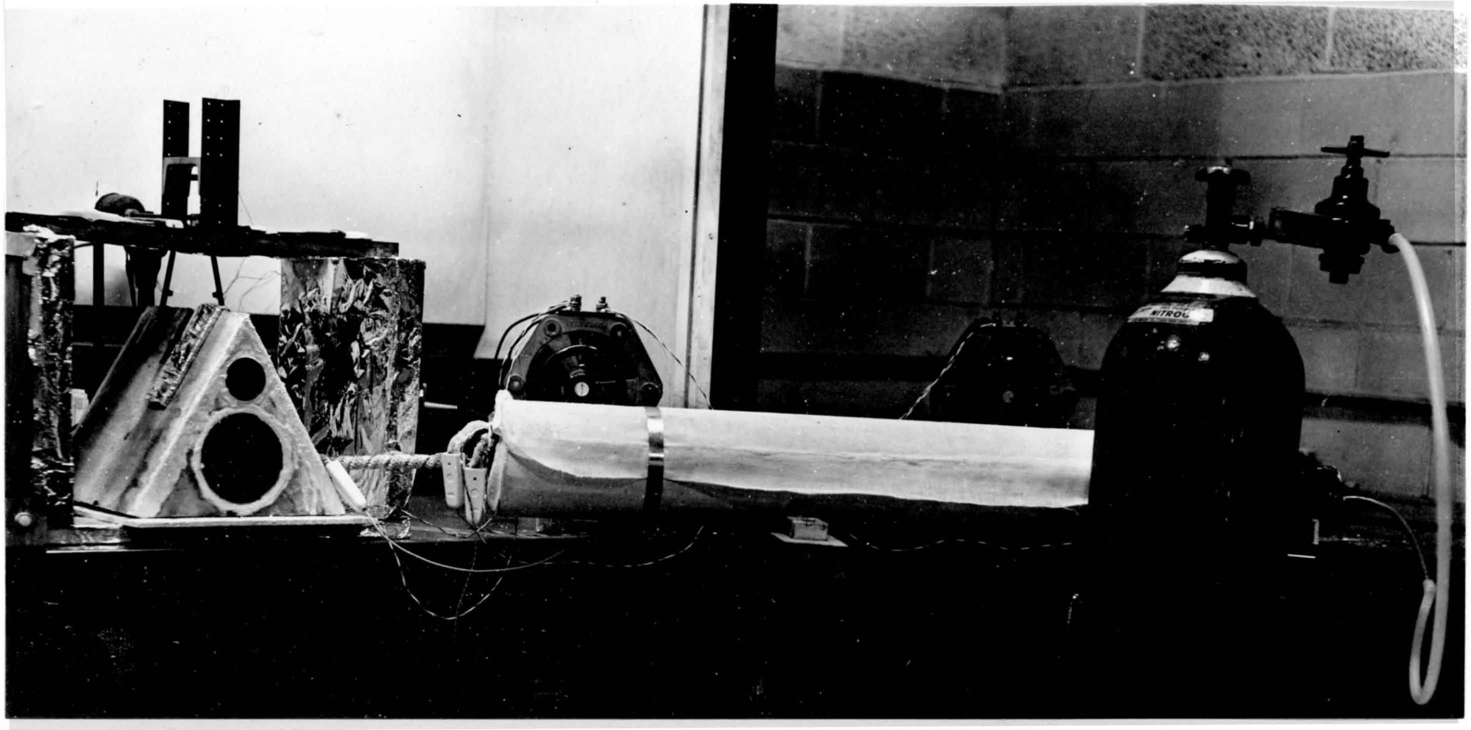


Figure 1. Schematic of Apparatus.



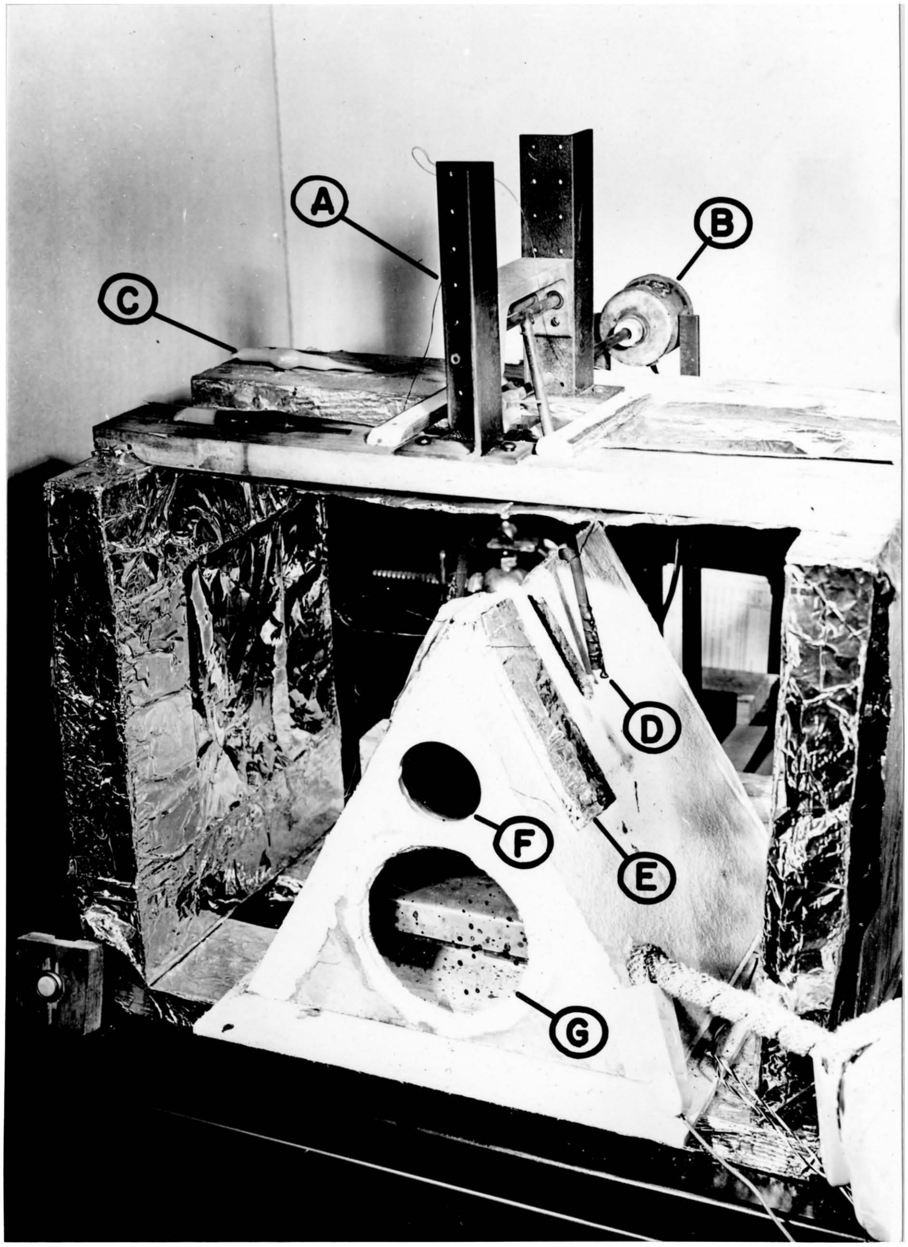
Droplet Impacting Assembly Variacs Valve

Receptacle Nitrogen Heater Nitrogen Bottle

Figure 2. Assembly of Apparatus.

drop. When the solenoid was activated, the spacer was withdrawn and the pendulum rods would swing together. A short perpendicular extension on each rod caused the pendulums to stop abruptly while the drops were 7/8 inch apart. The liquid drops would continue to move toward each other and pull free of the polyethylene tip. They would then follow a trajectory until they collided.

The pendulum rods were T-shaped and made of $\frac{1}{4}$-inch round steel stock. The length was eight inches and the top of the T was four inches. Each pendulum had a 3/16-inch extension placed $5\frac{1}{4}$ inches down from its top which acted as a stop. The ends of the four-inch cross member of the pendulum were inserted in needle bearings. These needle bearings were mounted in the flange of a four-inch aluminum channel. This channel was suspended between two support L's. (See Figure 3.) This allowed the pendulum rods to swing freely beneath the aluminum channel. A plexiglass spacer mounted on the end of a rod connected to a solenoid was placed between the pendulum arms. The rod was supported by one of the two L's and this held the spacer in the correct position. The solenoid was mounted on a separate stand to prevent its shaking the drops from the pendulums when activated.



A. Support L
B. Solenoid
C. Polyethylene syringe
D. Pendulum rod and tip
E. Slide
F. Observation window
G. Light Window

Figure 3. Droplet Impacting Assembly and Receptacle.

2. Nitrogen Heater and Receptacle

The nitrogen heater and receptacle were designed to raise the temperature of nitrogen to about 400° C. and maintain that temperature in a receptacle where the droplets would be brought together. The nitrogen heater was a three-pass concentric heat exchanger. The outside diameter of the heat exchanger was three inches and this was encircled by a layer of insulation one inch thick. The entire length was $3\frac{1}{2}$ feet. Nitrogen was piped into the right end of the heat exchanger at a very slow rate from a pressurized bottle. It flowed to the left along the periphery of the three-inch diameter pipe. Upon reaching the left end, it entered the second pipe and flowed to the right. The second pipe was $1\frac{1}{2}$ inches in diameter and wrapped with heating tape. After flowing through this pipe the nitrogen entered $\frac{1}{4}$-inch diameter copper tubing which was wrapped with heating tape. This tubing led the nitrogen to the left through the entire length of the heat exchanger and out into the receptacle. The heating tape was connected to a 110-volt variac and the maximum power delivered to the heat exchanger was 900 watts. The receptacle was built of $\frac{1}{4}$-inch asbestos sheet and made in the shape of a triangular prism with 10-inch sides. (See Figure 3.) Four 8 x 2 x $\frac{1}{2}$ inch space heaters, each delivering 250 watts, were placed at the bottom of the receptacle to maintain the nitrogen atmosphere at a high temperature. An aluminum sheet was placed $\frac{1}{2}$ inch above the heaters to prevent radiant heat reaching the drops. Slots were cut in the top of the receptacle to allow the pendulum rods of the droplet impacting assembly to enter. An asbestos slide wrapped in aluminum foil covered these slots until just prior to the time the droplets were allowed to come together. The aluminum foil reduced radiation from the hot slide to the droplets. Two circular holes were cut in the front face of the receptacle and pyrex glass was mounted in them. The $3\frac{1}{2}$-inch diameter hole allowed light to enter and the two-inch diameter hole was used for observation and photography.

3. The Photographic Equipment

The photographic equipment used for taking high speed motion pictures of the collision and reaction of the droplets was a Wollensack 16mm Fastax Camera with a timing control unit. The camera speed was controlled by the voltage and ranged, during the investigation, from 1200 frames per second to 3400 frames per second. The timing was accomplished with a Goose Control Unit, Model J-515, made by Industrial Timer Corporation. By means of this timer it was possible to start the camera operation using a remote push button and, at a preset fraction of a second later, a switch closed, activating the solenoid. The Goose Control Unit also operated an argon lamp that flashed 120 times per second within the camera.

This exposed streaks along one edge of the film which could be used to measure the time lapse between frames. A spotlight was directed through the $3\frac{1}{2}$-inch window on the projected point of collision of droplets in the receptacle. It provided sufficient light to expose the 16mm Tri-X film.

Procedure

Three series of tests were conducted in order to determine the effect of environmental temperature on the collision of hypergolic fuel droplets. The first series was conducted at an impact velocity of 35 cm/sec using hydrazine as the fuel and WFNA as the oxidizer. The second series, using the same fuel and oxidizer, was conducted at an impact velocity of 122 cm/sec. The third series was conducted at an impact velocity of 35 cm/sec using 80% furfuryl alcohol and 20% aniline as the fuel and WFNA as the oxidizer. The tests were run with the temperature varying from 50°C to 430°C.

To start a given series of droplet collision and reaction studies, the heat exchanger tape and receptacle heaters were first connected to a 110 volt supply. Nitrogen was then allowed to flow slowly through the heat exchanger and into the receptacle for about fifteen minutes to displace the oxygen in the system and to bring the heat exchanger to

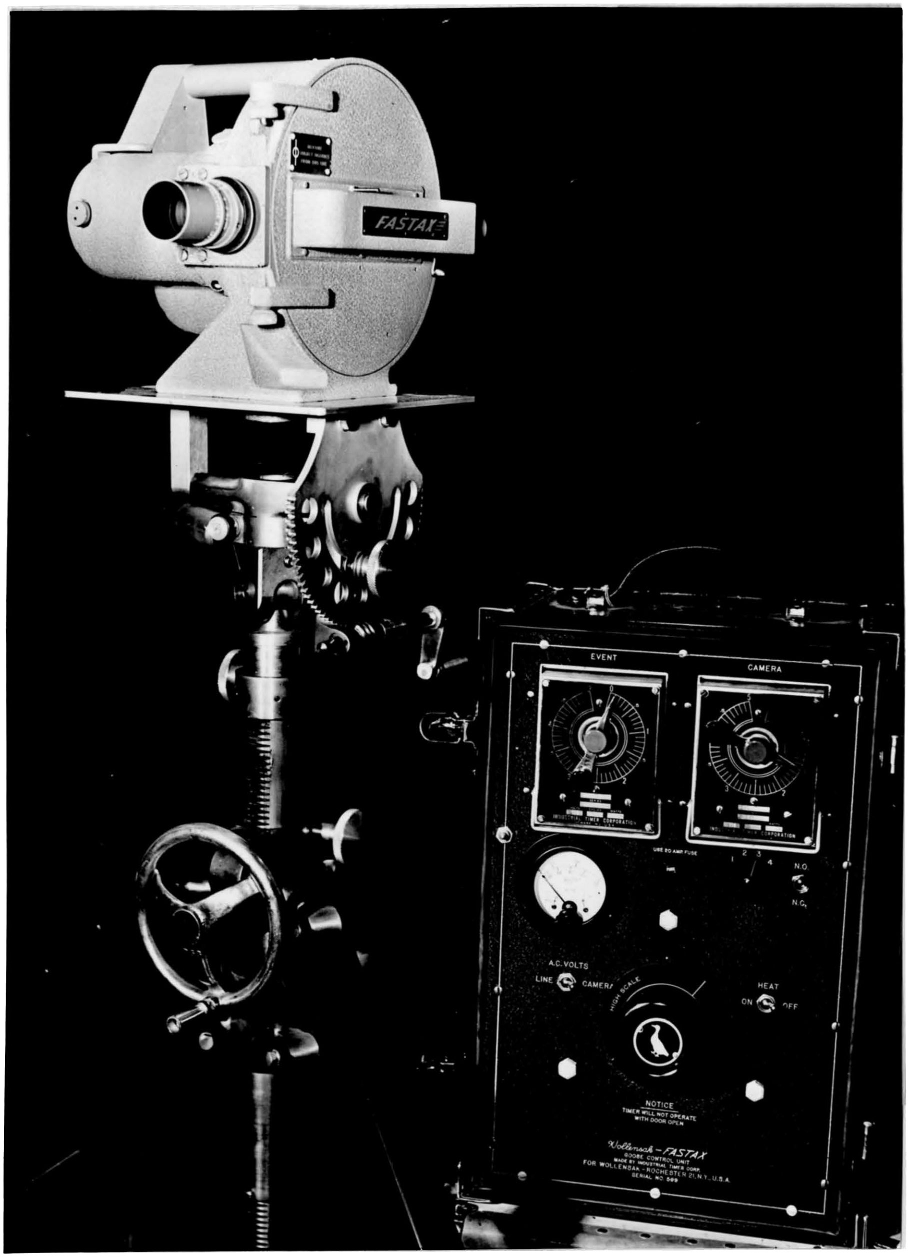


Figure 4. Fastax Camera, Tripod, and Timing Unit.

equilibrium. During this period the temperature within the receptacle was raised to the starting point of the series. The Fastax telephoto lens was focused and the camera loaded with film. Film lengths varied from 12 feet to 33 feet, depending on the speed at which the camera was run. The voltage was set on the Goose Control Unit to obtain the camera speed desired and the timer was set so that the event occurred directly after the camera was started. The delay ranged from 0.1 to 0.6 second, allowing the camera to come up to the correct speed before the droplets collided. Droplets of WFNA and the fuel were suspended from the polyethylene tips on the pendulum rods. The droplets were placed on the tips using polyethylene syringes. The temperature in the receptacle was monitored with a chromel-alumel thermocouple located near the position of the droplet impact. When the desired temperature was approached the spotlight was turned on, the slide on the top of the receptacle was removed, and simultaneously the remote push-button was depressed. This started the camera and subsequently activated the solenoid allowing the pendulum arms to swing into the receptacle through the roof slots. The two droplets, after leaving the pendulum, collided and were photographed through the observation window. As soon as the film was exhausted the camera automatically stopped. The pendulum arms were then swung out of the receptacle and the slide replaced.

Results

The results of the investigation are presented in two forms. The first includes four tables showing the pertinent data obtained in each of the three series of the investigation. The second is a sequence of pictures enlarged from the 16 mm movie film of four selected runs.

For the purpose of the study the reaction delay time is defined as the time lapse from the first contact of the droplets to the first visible sign of physical reaction. Where there are two such reactions in the same run, the time lapse from the first contact of the droplets to the initial reaction is called the first reaction delay time and the time lapse from the first contact of the droplets to the second reaction is called the secondary reaction delay time. Ignition delay time is the time lapse from first contact of the droplets until the first appearance of flame. Error refers to the time lapse between two frames on the film at the slowest camera speed for the series. The temperature of the suspended droplets was in all cases 41°C.

Table 3. Series 1-A. Hydrazine and WFNA

Average Droplet Diameter 3.3 mm Impact Velocity 35 cm/sec

Run No.	Temp., °C	Camera Speed, frames per second	First Reaction Delay Time, milliseconds	Secondary Reaction Delay Time, milliseconds
1	231	1200	1.7	6.7
2	252	1260	3.2	10.3
3	275	1200	2.5	9.2
4	300	no collision		
5	325	no collision		
6	350	1260	1.6	5.6
7	375	1260	0.8	4.8
8	400	1320	0.8	--

Error 0.8 millisecond

Table 4. Series 1-B. Hydrazine and WFNA

Average Droplet Diameter 3.3 mm Impact Velocity 35 cm/sec

Run No.	Temp., °C	Camera Speed, frames/sec	First Reaction Delay Time, milliseconds	Secondary Reaction Delay Time, milliseconds
1	200	1320	4.5	--
2	225	1260	4.8	--
3	300	1320	3.0	--
4	325	1260	--	6.4
5	375	1320	1.5	--
6	400	1320	0.8	--
7	425	1680	1.2	4.8

Error 0.8 millisecond

Table 5. Series 2. Hydrazine and WFNA

Average Droplet Diameter 3.1 mm   Impact Velocity 122 cm/sec

Run No.	Temp., °C	Camera Speed, frames/sec.	Reaction Delay Time, milliseconds
1	52	2280	2.2
2	100	2280	1.8
3	150	2340	1.7
4	200	2460	1.6
5	250	2340	2.6
6	300	2220	2.3
7	350	2160	2.3
8	400	2280	1.3
9	430	2280	2.2

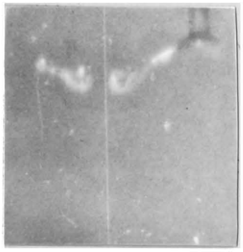
Error 0.5 millisecond

Table 6. Series 3. Alcohol - Aniline and WFNA

Average Droplet Diameter 3.3 mm   Impact Velocity 35 cm/sec

Run No.	Temp., °C	Camera Speed, frames/sec	Ignition Delay Time, milliseconds	
1	50	2400	*	
2	100	2280	*	
3	150	2400	*	
4	200	2160	40.2	
5	250	2400	39.5	
6	300	2280	36.9	
7	350	2400	36.7	
8	400	2520	49.6	
9	415	2400	25.4	Error 0.5 millisecond

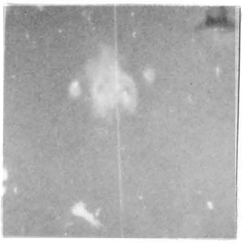
*Ignition did not occur during entire time droplet was under observation, 67 milliseconds.



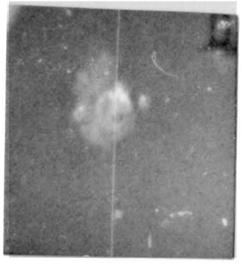
1. Before Impact

2. I (Impact)

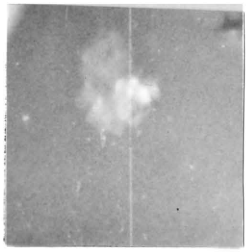
3. I + 3.2 ms.



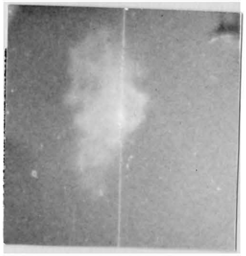
4. I + 4.8 ms.



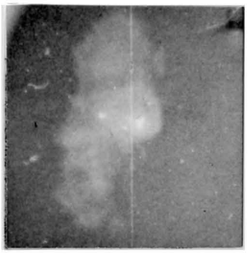
5. I + 7.1 ms.



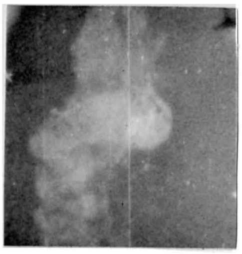
6. I + 9.5 ms.



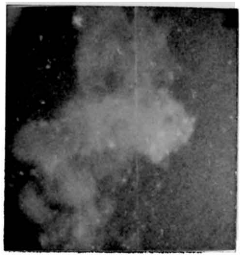
7. I + 11.1 ms.



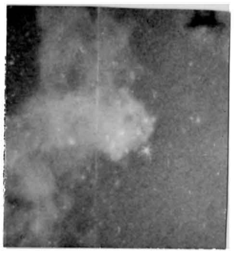
8. I + 12.7 ms.



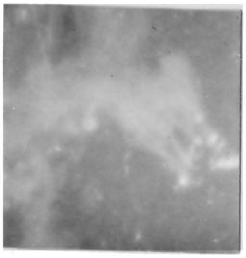
9. I + 15.0 ms.



10. I + 18.2 ms.



11. I + 23.0 ms.

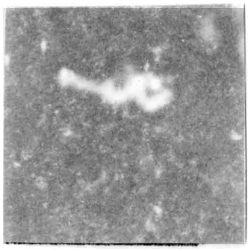


12. I + 37.2 ms.

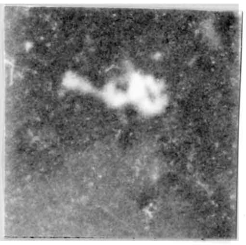
Figure 5. Collision and Reaction of Hydrazine and WFNA Droplets at 250°C and an Impact Velocity of 35 centimeters per second.

1. Before Impact

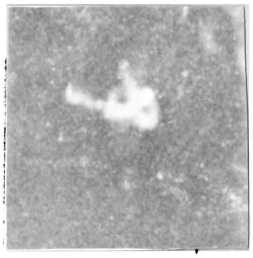
2. I (Impact)



3. I + 2.5 ms.

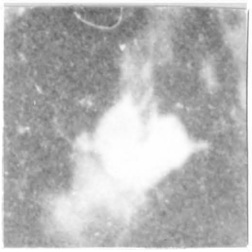


4. I + 4.2 ms.

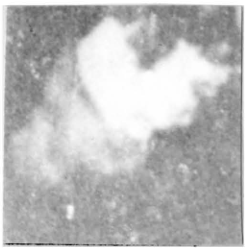


5. I + 5.8 ms.

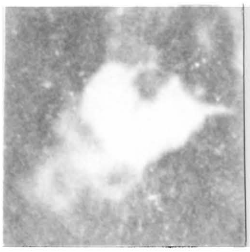
6. I + 6.7 ms.



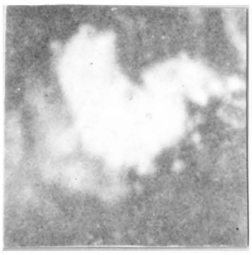
7. I + 7.5 ms.



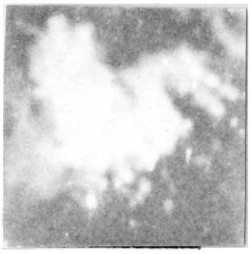
8. I + 9.2 ms.



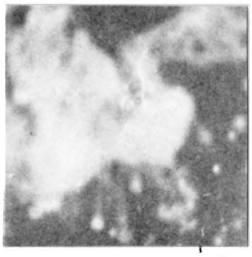
9. I + 11.6 ms.



10. I + 15.0 ms.



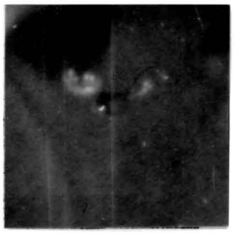
11. I + 23.3 ms.

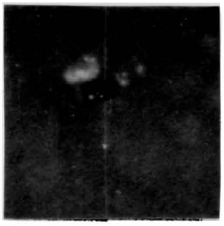


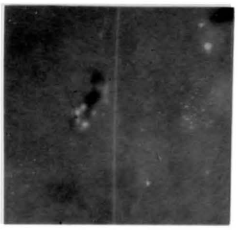
12. I + 31.6 ms.

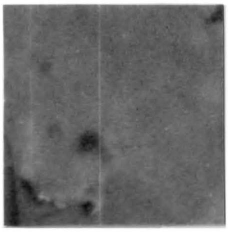
Figure 6. Collision and Reaction of Hydrazine and WFNA Droplets at 325°C and an Impact Velocity of 35 centimeters per second.

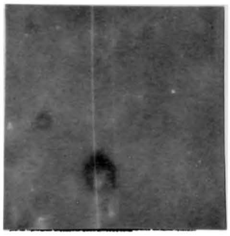

1. Before Impact

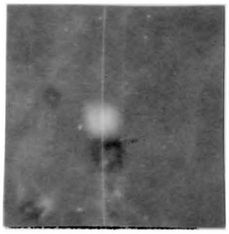

2. I (Impact)

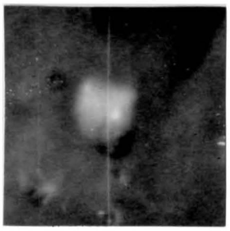

3. I + 4.6 ms.

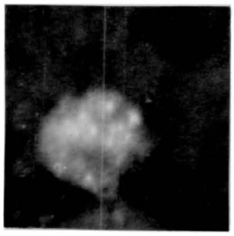

4. I + 15.3 ms.

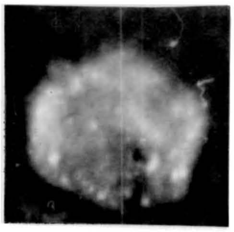

5. I + 31.7 ms.

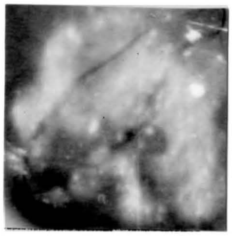

6. I + 40.3 ms.


7. I + 40.7 ms.


8. I + 41.2


9. I + 42.1 ms.


10. I + 45.4 ms.


11. I + 48.6 ms.

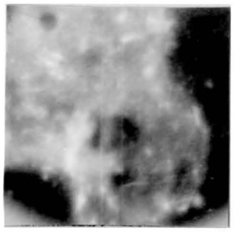
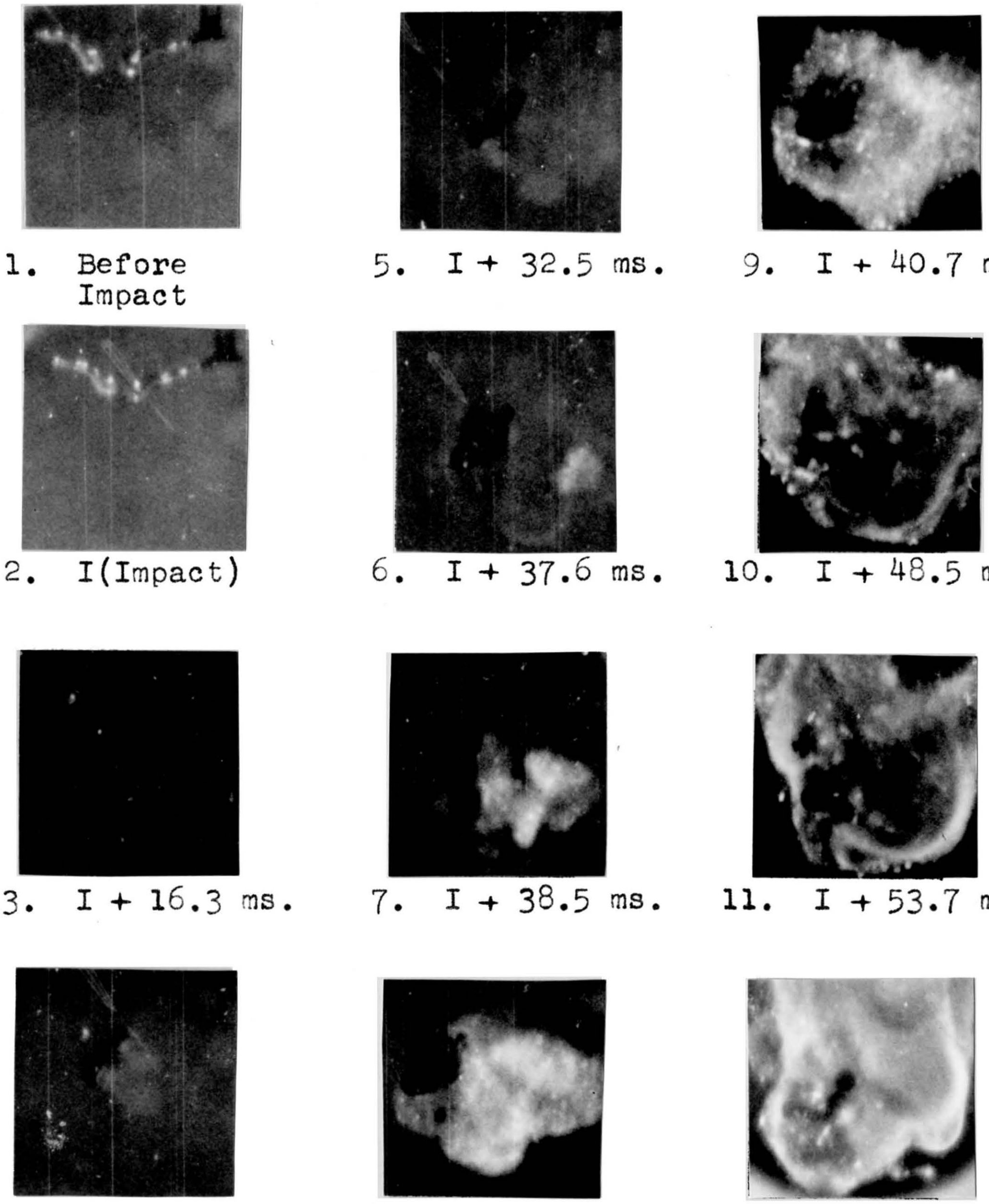

12. I + 54.6 ms.

Figure 7. Collision and Ignition of Furfuryl Alcohol-Aniline with WFNA Droplets at 200°C and an Impact Velocity of 35 centimeters per second.



1. Before Impact
2. I(Impact)
3. I + 16.3 ms.
4. I + 24.6 ms.
5. I + 32.5 ms.
6. I + 37.6 ms.
7. I + 38.5 ms.
8. I + 39.3 ms.
9. I + 40.7 ms.
10. I + 48.5 ms.
11. I + 53.7 ms.
12. I + 64.0 ms.

Figure 8. Collision and Ignition of Furfuryl Alcohol-Aniline with WFNA Droplets at 250°C and an Impact Velocity of 35 centimeters per second.

IV. DISCUSSION

Introduction

Of the many ways in which propellant droplets can react during a collision, four ways appear most probable. First, as one droplet approaches another, each surrounded by its own vapors, the vapors will be the initial point of contact. If the vapor mixing and reaction is faster than the time it takes for the droplet surfaces to come into contact, the vapor reaction may well be strong enough to prevent the two droplets from ever contacting in the liquid phase. However, should the approach velocity of the droplets be sufficiently high, contact of the two droplets will occur in the liquid phase because the vapors do not have time to react; or, if they do have time to react, the momentum of the droplets will carry them through the vapor phase reactions. The droplets might then form an interface. A third possibility is that the two droplets will combine into one larger droplet and become a more or less homogeneous mixture. The liquid phase reaction and ignition could then take place throughout the droplet. Finally, the droplets may form one droplet with insignificant liquid phase reactions. The vapors evolved from the droplet would be premixed and reaction and ignition could occur in the premixed vapors.

Hydrazine System

In analyzing the collisions of WFNA with hydrazine at an impact velocity of 35 centimeters per second, it appears that an initial vapor phase reaction does take place, followed in some cases by a second more violent reaction. The first reaction appears to occur immediately after the droplets first touch in the liquid phase. The reaction is mild compared to any secondary reaction that might occur. In many cases no secondary reactions do occur and the droplets become separated, almost appearing to bounce off each other. Even with a secondary, more violent reaction, in all cases but one, the droplets were not shattered or vaporized, but merely separated into two or three falling liquid spheres. The falling droplets were presumed to contain only hydrazine or WFNA since no further reaction took place. White smoke, generated by the reaction, made it difficult to tell exactly what occurred after collision; but it appeared that an interface or at least a very limited amount of mixing took place as the droplets started to flatten out against each other. The reaction delay time was sufficiently short, so that the droplets barely started to change shape due to the collision when they were blown apart. In no instance did ignition (as defined by the emission of visible light) occur.

At the high impact velocity the WFNA and hydrazine droplets appeared to penetrate directly into each other. While it was not possible to tell if an interface actually existed, it can be stated that complete mixing did not occur. This can be determined from two observations. First, the reaction delay time was extremely short (approximately two milliseconds); and second, the shattered tiny droplets showering away from the reaction underwent no further reaction. At no time was ignition observed to have taken place.

The temperature of the environment in which the droplet collision took place affected the reaction delay time at the low impact velocities. Reaction was obtained from 430°C down to room temperature and, in general, there was a decrease in reaction delay time with an increase in environmental temperature. Figure 9, a plot of each run in Series 1, illustrates this graphically. In order to determine if there was any significance to the trend, the reaction delay time was plotted as a function of the inverse absolute environmental temperature on semi-logarithm paper. Figures 12 and 13 show the results as a straight line with positive slope in both cases. Activation energy can be calculated from the chemical induction period. Since the activation energy of most reactant systems is constant, it can be determined from any two points on the line in Figure 12 or 13 by using the equation[17]

$$E = \frac{R \log (t_1/t_2)}{(1/T_1 - 1/T_2)}$$

where E = overall activation energy
R = universal gas constant
t = reaction delay time
T = absolute temperature

The overall activation energy for the reaction system in Series 1 was computed to be 5.16 kcal/gm-mole depending upon whether the first or secondary reaction delay time was used. At the higher impact velocity of 122 centimeters per second, there was no noticeable effect caused by environmental temperature as shown in Figure 10. Thus, the calculated activation energy for the reaction system was zero. Since all the molecules possess more than zero energy, it is only necessary to bring the fuel and oxidizer molecules together to obtain the reaction. This is essentially the definition of a hypergol. The activation energies have been calculated from the time delay between droplet contact and reaction, not ignition (characterized by flame). At higher temperatures such ignition may occur and yield an entirely different activation energy. The reaction delay time, which varied with a change in environmental temperature in Series 1, may then be better explained as a result of the temperature affecting the physical, rather than the chemical, induction period. At the higher temperatures more rapid evaporation may cause faster mixing along the interface, reducing the physical induction period. In Series 2 the higher impact velocity caused mechanical mixing to dominate the physical induction period, and therefore environmental temperature had an insignificant effect.

Alcohol-Aniline System

The collision of the mixture of aniline and furfuryl alcohol with WFNA gave a significantly different reaction than was obtained with hydrazine. In every case, after impact the alcohol-aniline formed one droplet with the WFNA. A high rate of vaporization then occurred, often accompanied by droplet break-up. The vapors ultimately ignited (as indicated by the appearance of flame) if the temperature was over 200°C. The increase in vaporization shortly after droplet collision can be explained by the internal heating of the droplet caused by liquid phase reactions. Apparently the liquid phase reactions were often strong enough to break the droplet apart, although not violently. It is significant that in no case did a flame start directly from the liquid reaction. Figure 7, Plates 7 and 8, show the closest point of flame origin to a droplet. The plates show a marked resemblance to the photographs of Wood[6] showing fuel droplets igniting in a hot oxidizing atmosphere. Ignition of droplet-vapor systems were stated to occur in the mixed turbulent vapor phase wake of the droplet. It therefore can be stated that the ignition of colliding droplets of furfuryl alcohol and aniline with WFNA occurs in the vapor phase.

Ignition delay time for the alcohol-aniline with WFNA system at the impact velocity of 35 centimeters per second decreased with an increase in environmental temperature as shown in Figure 11. No ignition was obtained below 200°C. The overall activation energy determined from the slope in Figure 14 was 498 cal/gm-mole. Mullins[17] measured overall activation energies for high temperature ignition delays of furfuryl alcohol with air and aniline with air. He obtained 47.9 kcal/gm-mole and 48.0 kcal/gm-mole respectively. Once again it is postulated that the physical delay time (evaporation, mixing, heat transport, etc.), as well as a different reaction system, result in different activation energies.

Experimental Accuracy

In utilizing motion picture photography to take data, there is automatically a loss of accuracy due to the finite time between frames on the film. The error which may be introduced is entirely dependent on camera speed and was listed for the investigation on each page of the results. In all cases it was less than 0.8 milliseconds.

A grosser error was caused by the difficulty in determining in which frame of a particular sequence the collision or reaction actually first occurred. At the low impact velocities there were from two to four frames in which it was possible to say collision initially occurred. There were often two frames in which reaction appeared to be starting. At the low impact velocities the error was less than 3 milliseconds and at the high impact velocities, less than 1 millisecond.

Scattering of data was to be expected during the investigation, since collisions could not be precisely controlled. While one collision might experience a dead-center impact, the next might experience only a glancing touch. This quite naturally affected mixing and therefore reaction and ignition delays.

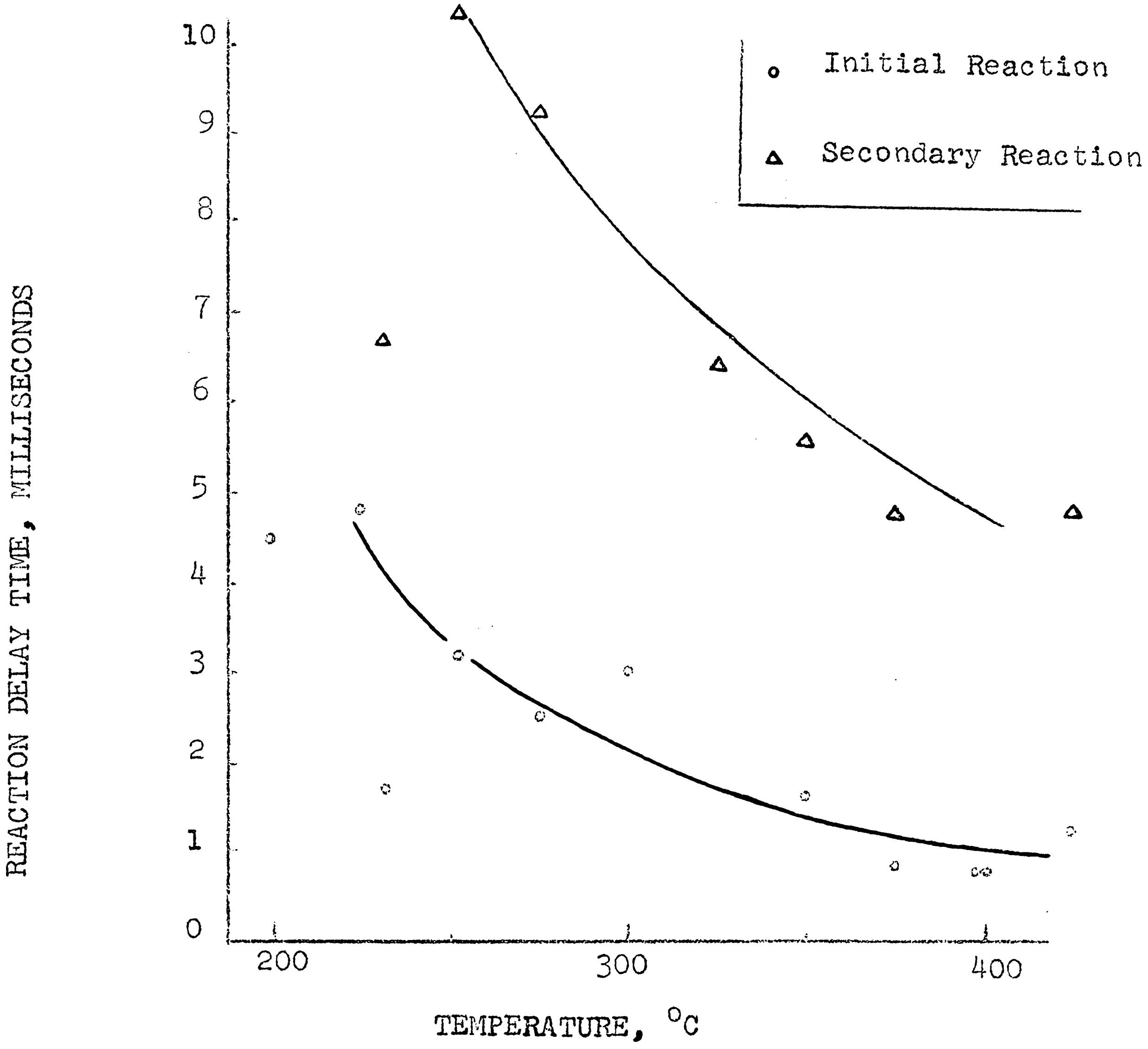


Figure 9. Effect of Temperature on the Reaction Delay Time of WFNA and Hydrazine Droplets at an Impact Velocity of 35 centimeters per second.

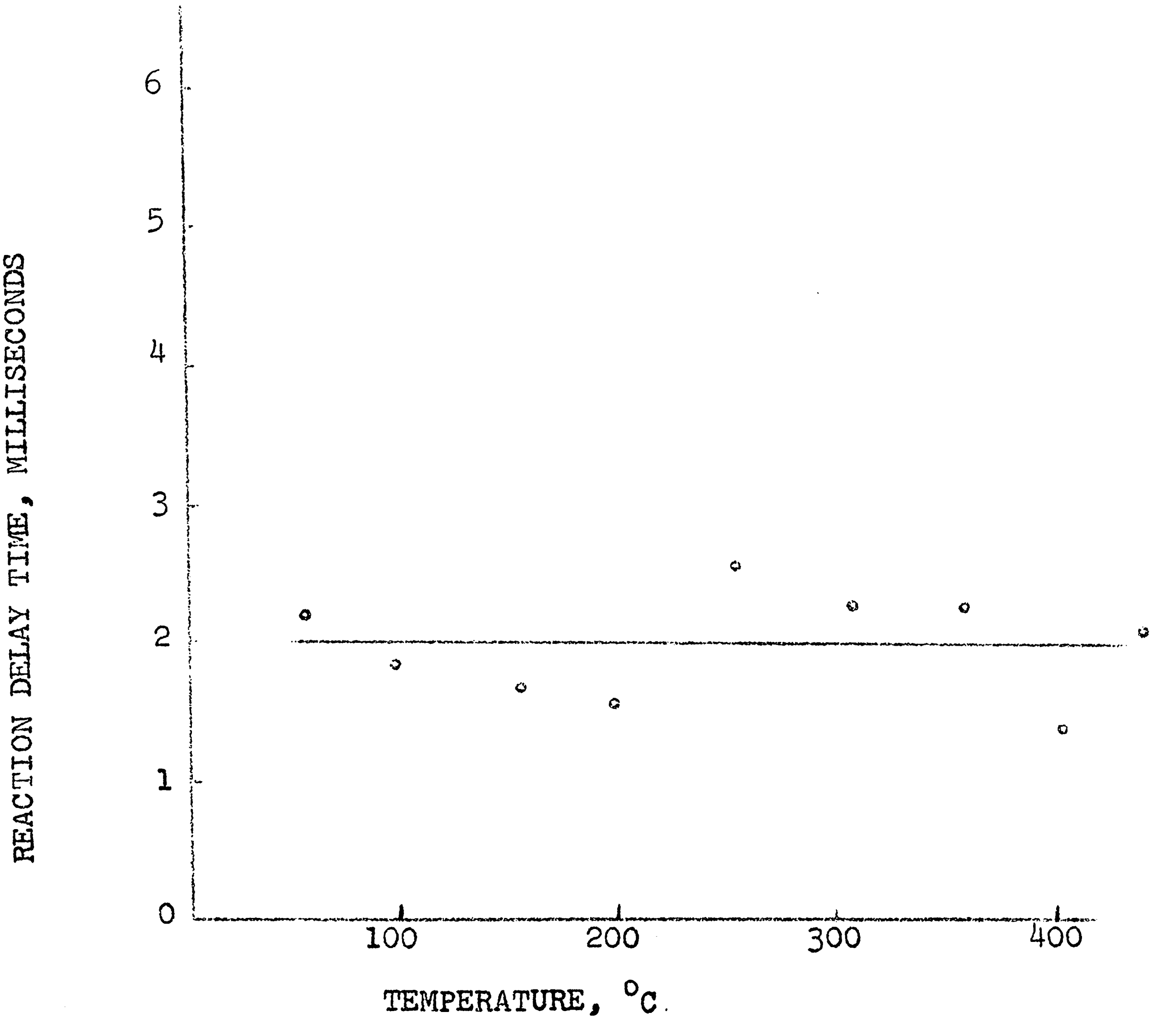


Figure 10. Effect of Temperature on the Reaction Delay Time of WFNA and Hydrazine Droplets at an Impact Velocity of 122 centimeters per second.

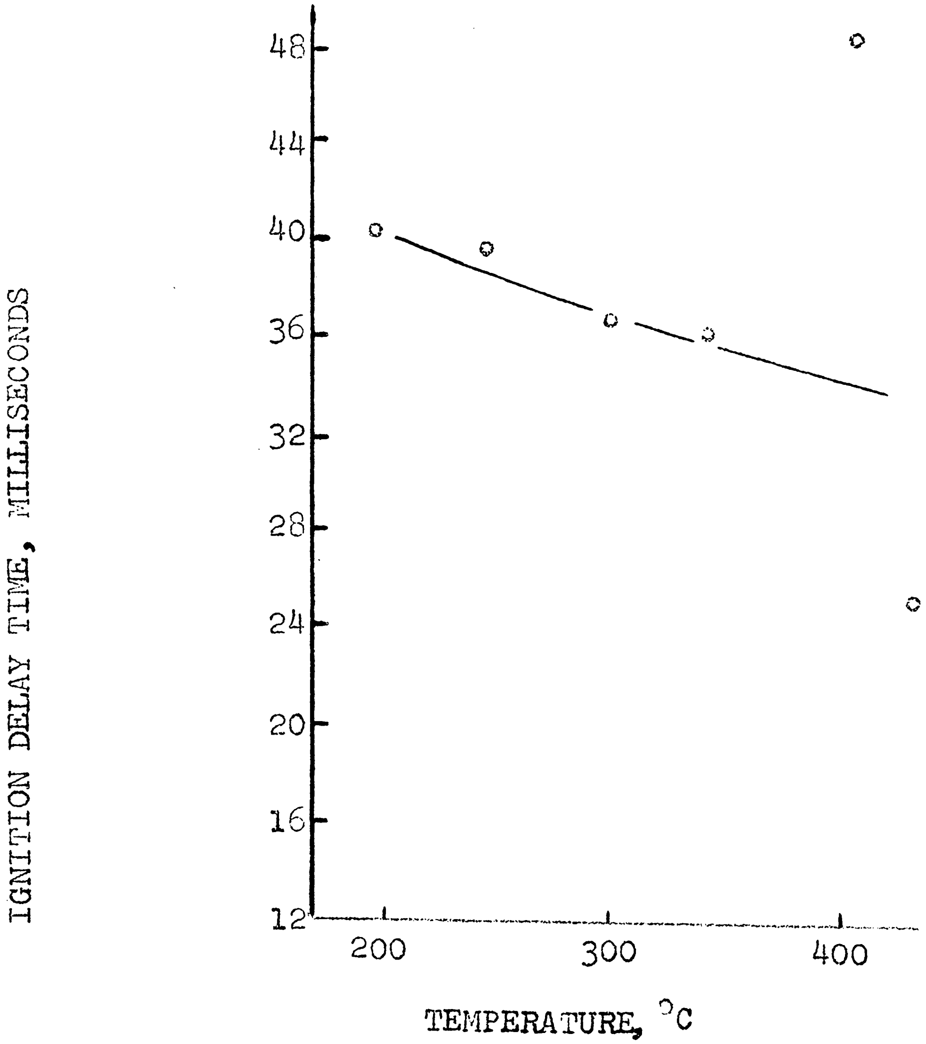


Figure 11. Effect of Temperature on the Ignition Delay of Alcohol-Aniline and WFNA Droplets at an Impact Velocity of 35 centimeters per second.

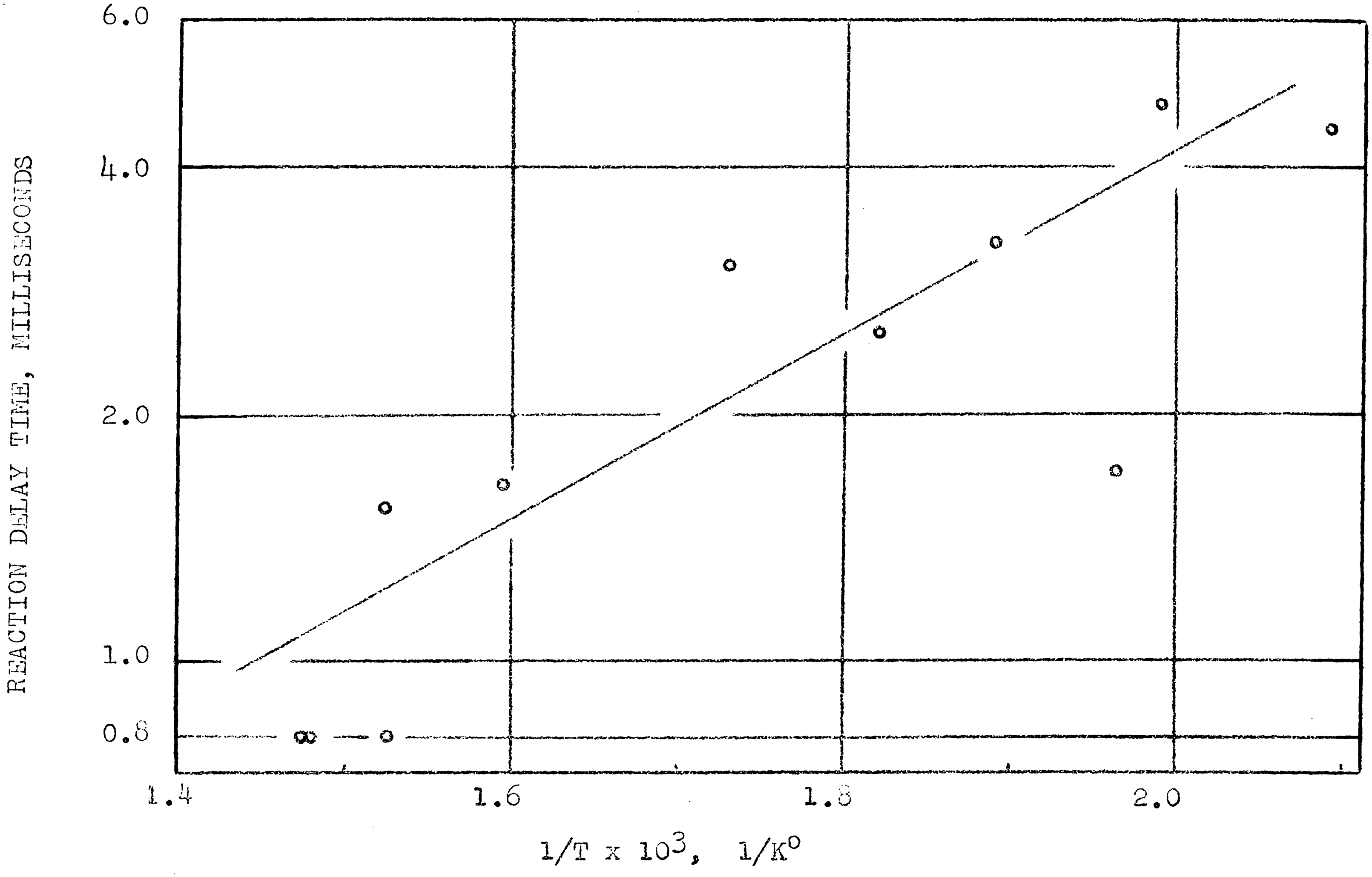


Figure 12. The Effect of the Reciprocal Environmental Temperature on the First Reaction Delay Time of Hydrazine and WFNA Droplets.

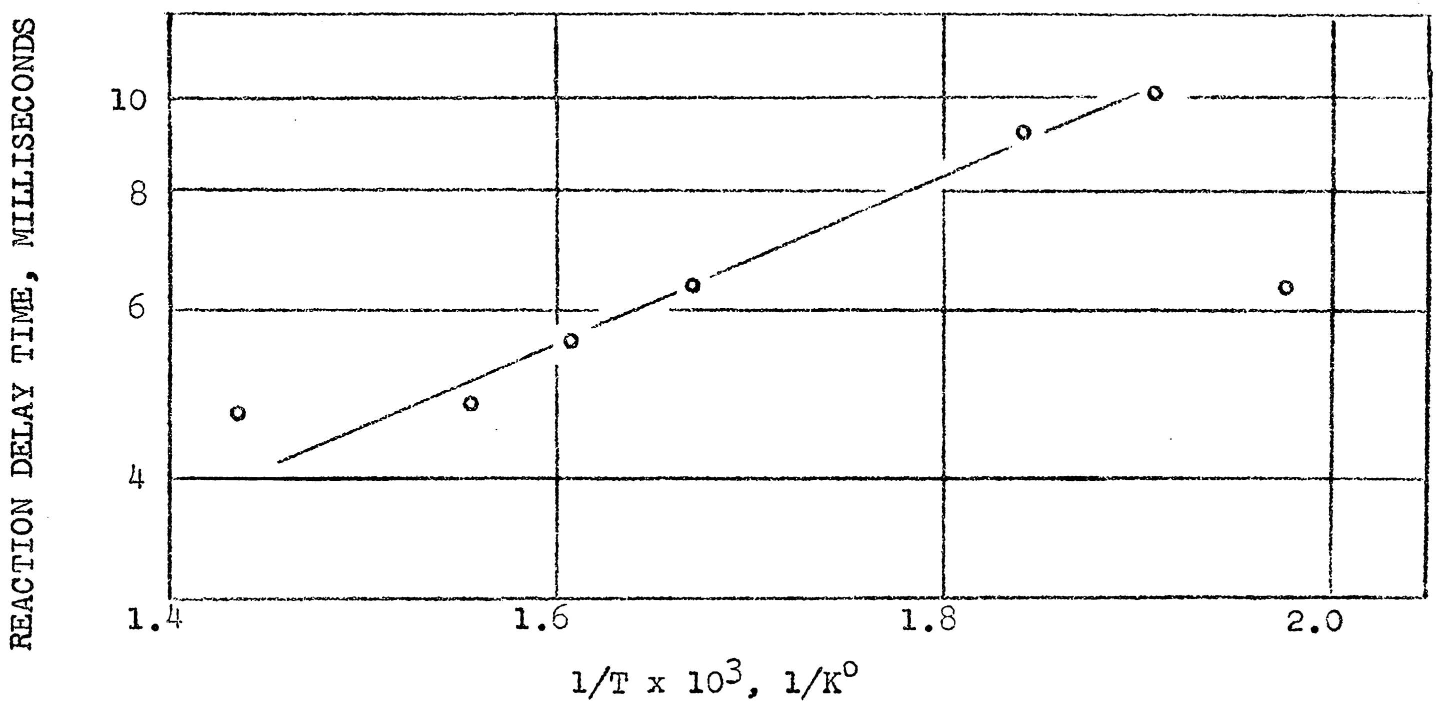


Figure 13. The Effect of the Reciprocal Environmental Temperature on the Secondary Reaction Delay Time of Hydrazine and WFNA Droplets.

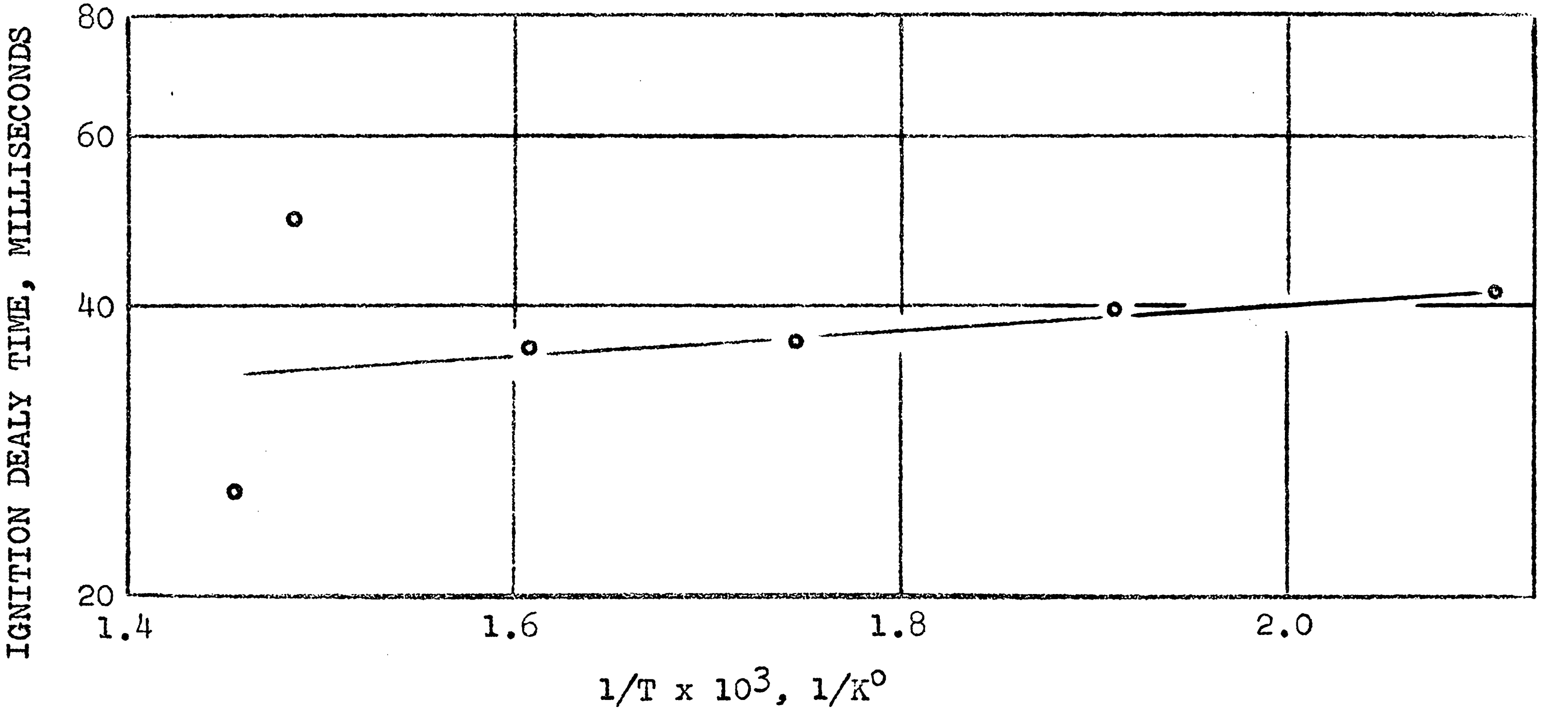


Figure 14. The Effect of the Reciprocal Environmental Temperature on the Ignition Delay Time of Alcohol-Aniline and WFNA Droplets.

V. CONCLUSIONS

1. The collision of a hydrazine droplet with a WFNA droplet at impact velocities of 35 centimeters per second is characterized by slight deformation of the droplets followed by reaction which blows the two droplets apart.

2. The collision of a hydrazine droplet with a WFNA droplet at impact velocities of 122 centimeters per second is characterized by partial penetration of one droplet into the other followed by violent reaction which shatters and scatters the unmixed portion of the droplets.

3. Ignition, as defined by the emission of visible light, did not occur in the collision of hydrazine droplets with WFNA droplets in environmental temperatures up to 430°C.

4. The collision of a furfuryl alcohol-aniline (80%-20% by weight) droplet with a WFNA droplet at an impact velocity of 35 centimeters per second was characterized by the formation of one droplet, then rapid vaporization, often accompanied by droplet breakup, and finally ignition of vapors when the environmental temperature was over 200°C.

VI. RECOMMENDATIONS

Several avenues of approach are open to future investigations into droplet collision and ignition:

1. The investigation of the effect of pressure on the droplet reactions.
2. The investigation of the effect of impact velocity on the droplet reaction.
3. The investigation of the effect of droplet size on the droplet reaction.
4. The investigation of droplet reactions with divers hypergolic propellants.

VII. ACKNOWLEDGMENTS

The author wishes to express his appreciation to the members of his thesis committee, Dr. H. L. Wood, Chairman, Professor C. H. Long, and Professor D. S. Cassell, for their guidance, assistance, and helpful suggestions during the course of the investigation.

The United States Army and the Transportation Corps made possible this work by the assignment of the author to Virginia Polytechnic Institute.

To his wife, appreciation is expressed for encouragement and assistance.

VIII. BIBLIOGRAPHY

Literature Cited

1. Somogyi, D. and Feiler, C. E., "Mixture Ratio Distribution in the Drops of Spray Produced by Impinging Liquid Streams," Jour. A.R.S., February 1960, p. 185.

2. Mullins, B. P., Spontaneous Ignition of Liquid Fuels, AGARDograph; Butterworth's Scientific Publications, London, 1955, pp. 5-13.

3. Obert, E. F., Concepts of Thermodynamics, McGraw-Hill Book Company, New York, 1960, pp. 462-466.

4. Semenov, N. N., Some Problems in Chemical Kinetics and Reactivity, Vol. 2, Princeton University Press, New Jersey, 1959, pp. 87-89.

5. Gregory, C. A. and Calcote, H. F., "Combustion Studies of Droplet-Vapor Systems," Fourth Symposium(International)on Combustion; The Williams and Wilkins Co., Baltimore, 1953, pp. 830-837.

6. Wood, H. L., "A Photographic Investigation of the Ignition of Fuel Droplets in the Decomposition Vapors of White Fuming Nitric Acid," Ph. D. Thesis, Purdue University, 1960.

7. Gunn, S. V., "The Effects of Several Variables Upon the Ignition Lag of Hypergolic Fuels Oxidized by Nitric Acid," Jour. A.R.S., Vol. 22, pp. 33-38.

8. Ladanyi, D. J. and Miller, R. O., "Two Methods for Measuring Ignition Delays of Self-Igniting Rocket Propellant Combinations," Jet Propulsion, Vol. 26, 1956, pp. 157-163.

9. Ladanyi, D. J. and Miller, R. O., "Comparison of Ignition Delays of Several Propellant Combinations Obtained with Modified Open-Cup and Small Scale Rocket Engine Apparatus," NACA RM-E-53D03, 1953.

10. Barrere, M. and Moutet, A., "Study of the Ignition Lag of Liquid Propellants," Fifth Symposium (International) on Combustion; Reinhold Publishing Corporation, New York, 1955, pp. 170-181.

11. Fletcher, E. A. and Schalla, R. L., "The Ignition Behavior of Various Amines with White Fuming Nitric Acid," Jour. A.R.S., Vol. 29, 1959, pp. 33-39.

12. Baker, L. L., Jr. and Kilpatrick, M., "A Study of Fast Reactions in Fuel-Oxidant Systems," Fifth Symposium (International) on Combustion; Reinhold Publishing Corp., New York, 1955, pp. 196-205.

13. Altman, D. and Penner, S. S., "Combustion of Liquid Propellants," High Speed Aerodynamics and Jet Propulsion, Vol. 11, 1956, p. 471.

14. Rapp, L. R. and Strier, M. P., "The Effect of Chemical Structure on the Hypergolic Ignition of Amine Fuels," Jet Propulsion, Vol. 27, 1957, pp. 401-404.

15. Elverum, G. W., Jr. and Staudhammer, P., The Effect of Rapid Liquid-Phase Reactions on Injector Design and Combustion in Rocket Motors, JPL-CIT, Progress Report No. 30-4, 1959.

16. Carpenter, T. W., "A Photographic Investigation of the Impact and Reaction of Hypergolic Propellant Droplets," M. S. Thesis, Virginia Polytechnic Institute, 1964.

17. Mullins, B. P. and Penner, S. S., Explosions, Detonations, Flammability and Ignition, Pergamon Press, New York, 1959, pp. 197-209.

Literature Not Cited

Adams, G. K. and Stocks, G. W., "The Combustion of Hydrazine," *Fourth Symposium (International) on Combustion;* The Williams and Wilkins Co., Baltimore, 1953, pp. 239-248.

Allen, O. A., Campbell, H. C., and Rice, O. K., "The Induction Period in Gaseous Thermal Explosions," *Journal of the American Chemical Society*, Vol. 57, 1935, pp. 310-317.

Altseimer, J. H., "Two-Dimensional Transparent Thrust Chamber," *Jour. A.R.S.*, Vol. 22, 1952, pp. 86-91.

Bernard, M. L., "Hybrid Hypergolic Propellants: A Glance at their First Development," *Jour. A.R.S.*, Vol. 32, 1963, p. 956.

Collacott, R. A., "Impact of Drops," *Engineering*, Vol. 187, 1959, pp. 440-441.

Ducarme, J., Gerstein, M. and Lefebvre, A. H., *Progress in Combustion Science and Technology*, Pergamon Press, New York, 1960, pp. 183-213.

Feodosiev, V. I. and Siniarev, G. B., *Introduction to Rocket Technology*, Academic Press, New York, 1959.

Fletcher, E. A. and Schalla, R. L., "The Behavior of the System Triethylamine-White Fuming Nitric Acid Under Conditions of Rapid Mixing," *Sixth Symposium (International) on Combustion;* Reinhold Publishing Corp., New York, 1957, pp. 911-917.

Gray, P. and Harper, M. J., "The Thermal Theory of Induction Periods and Ignition Delays," *Seventh Symposium (International) on Combustion;* Butterworth's Scientific Publications, London, 1959, pp. 425-430.

Gray, P. and Spencer, M., "Studies of the Combustion of Dimethyl Hydrazine and Related Compounds." *Ninth Symposium (International) on Combustion;* Academic Press Inc., New York, 1963, pp. 148-157.

Halliday, K. C., Jr., "The Ignition of Fuels with Nitric Acic," Jour. A.R.S., Paper No. 80-52.

Hennings, G., Ladanyi, D. J. and Miller, R. O., "Ignition Delay Determinations of Furfuryl Alcohol and Mixed Butyl Mercaptans with Various White Fuming Nitric Acids Using Modified Open-Cup and Small Scale Rocket Engine Apparatus," NACA, RM-E-53E29, 1955.

Lawhead, R. B., "Photographic Studies of Combustion Processes in Liquid Propellant Rockets," Eighth Symposium (International) on Combustion, Williams and Wilkins Co., Baltimore, 1962.

McCullough, F., Jr. and Jenkins, H. P., Jr., "Studies of the Rates of Combustion of Hypergolic Fluids," Fifth Symposium (International) on Combustion; Reinhold Publishing Corp., New York, 1955, pp. 181-190.

Miller, R. O., "Ignition Delays and Fluid Properties of Several Fuels and Nitric Acid Oxidants in Temperature Range from 70° to -105°F," NACA, TN-3884, 1956.

Morrell, G., "Summary of NACA Research on Ignition Lag of Self-Igniting Fuel Nitric Acid Propellants," NACA, RM-E-57G19, 1957.

Penner, S. S., Chemical Rocket Propulsion and Combustion Research, Gordon and Breach Science Publishers, New York, 1962.

______________, Chemistry Problems in Jet Propulsion, The MacMillan Company, New York, 1957.

Pino, M. A., "A Versatile Ignition Delay Tester for Self-Igniting Rocket Propellants," Jour. A.R.S., Vol. 25, 1955, pp. 463-466.

Sutton, G. P., Rocket Propulsion Elements, John Wiley and Sons, Inc., New York, 1958.

A PHOTOGRAPHIC INVESTIGATION OF THE COLLISION, REACTION, AND IGNITION OF HYPERGOL DROPLETS

ABSTRACT

The experimental apparatus employed in this investigation permitted a fuel droplet and an oxidizer droplet to collide in a nitrogen atmosphere at temperatures from 50°C to 430°C. The resulting phenomena were photographed with a 16mm Fastax camera.

Experimentation was completed in three series of tests. The first series consisted of impacting hydrazine droplets with white fuming nitric acid droplets at an impact velocity of 35 cm/sec and at temperatures from 200°C to 425°C. The second series utilized the same fuel and oxidizer at an impact velocity of 122 cm/sec and at temperatures ranging from 50°C to 430°C. The third series employed an alcohol-aniline mixture as the fuel droplets, and white fuming nitric acid as the oxidizer droplets. The impact velocity was 35 cm/sec and the nitrogen temperature ranged from 50°C to 415°C.

Ignition was not obtained in the two series employing hydrazine as a fuel. The droplets, upon colliding, underwent a chemical reaction and were blown apart. With the series utilizing an alcohol-aniline mixture as the fuel, the

droplets, after collision, formed one large drop which vaporized rapidly. The vapors ignited with flame at temperatures over 200°C.