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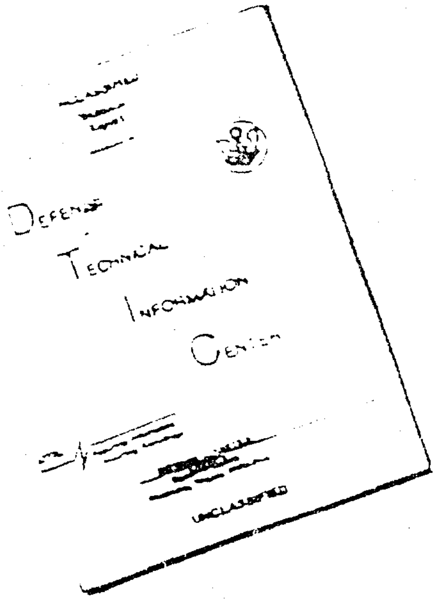
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ON HYDRAZINE
APPLICATIONS
UARY 1955

VOLUME I

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COMMITTEE ON FUELS AND LUBRICANTS
THE OFFICE OF THE ASSISTANT SECRETARY OF DEFENSE
FOR RESEARCH AND DEVELOPMENT
Washington 25, D. C.

FRO 205/3

FOREWORD

This Symposium on Hydrazine and Its Applications was sponsored jointly by the Naval Ordnance Test Station, Inyokern, China Lake, California, and the Panel on Fuels Requiring Oxidizers, of the Committee on Fuels and Lubricants, Research and Development Board. Facilities for the symposium were provided by courtesy of the Illinois Institute of Technology, Chicago, Illinois.

Papers which do not contain proprietary information constitute Volume I, for general distribution within security restrictions. Volume II contains the remaining papers, and its distribution is accordingly limited.

Donald B Brooks
DONALD B. BROOKS
Executive Director
Committee on Fuels and Lubricants (R&D)

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Table of Contents

Page

2 February 1953

I. GERMAN AND SOVIET EXPERIENCE IN THE HYDRAZINE FIELD

II. AVAILABILITY AND COST OF HYDRAZINE

Status of Raschig Process

Status of Research on Alternate Methods of Hydrazine Synthesis

Summary Report on Availability and Cost of Hydrazine

III. PROPERTIES OF HYDRAZINE AND HYDRAZINE SYSTEMS

Physical Chemistry

Chemical Problems

Analytical Problems

Safety and Handling

3 February 1953

IV. HYDRAZINE DERIVATIVES

V. APPLICATIONS OF HYDRAZINE, HYDRAZINE SYSTEMS, AND HYDRAZINE DERIVATIVES

Explosive Systems

Liquid Propellant Systems

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SYMPOSIUM ON
HYDRAZINE AND ITS APPLICATIONS
HELD AT THE ILLINOIS INSTITUTE OF TECHNOLOGY
CHICAGO, ILLINOIS
2-3 FEBRUARY 1953

MORNING SESSION, 2 FEBRUARY 1953

CHAIRMAN

DR. H. K. NASON
MONSANTO CHEMICAL COMPANY

MR. E. L. KLEIN (Research and Development Board): This Symposium is sponsored by the U. S. Naval Ordnance Test Station and the Fuels and Lubricants Committee of the Research and Development Board (particularly the Panel on Fuels Requiring Oxidizers), and is the reason we are here today.

I would like to point out that the overall classification of the session is "Confidential," although some of the papers will be classified lower. The program is also classified "Confidential."

There are two changes in the program. Dr. Eugene Lieber, head of the Chemistry Section of the Naval Ordnance Test Station, will give an address of welcome instead of Dr. Gantz, as indicated in the program.

Dr. Howard Kruse, of the Naval Ordnance Test Station, will be chairman of tomorrow morning's session.

If there are no questions, then it is my pleasure at this time to introduce to you the Chairman of the Panel on Fuels Requiring Oxidizers, of the Committee on Fuels and Lubricants, Research and Development Board, Mr. A. J. "Tony" Nerad of the General Electric Company.

MR. A. J. MERAD (General Electric Company): I am listed on the program to welcome you and, as per my usual custom, I won't take but one minute. It is grand to be able to find an auditorium to hold this Symposium that is as large and comfortable as this one.

The Panel on Fuels Requiring Oxidisers, together with the U. S. Naval Ordnance Test Station, is holding this Symposium. We have held other symposia on other subjects, and the getting together and the exchanging of ideas seemed in those cases to be so highly successful that I look for this session, to which I again welcome you, to produce the same results. I hope you take with you a great deal from this Symposium.

MR. KLEIN: Thank you, Tony.

As you all know by this time, the Symposium is being sponsored jointly by the Research and Development Board and the Naval Ordnance Test Station. A word of welcome now from the Naval Ordnance Test Station, Dr. Eugene Lieber.

DR. EUGENE LIEBER (U.S. Naval Ordnance Test Station): This is a familiar auditorium to me, having spent a few years here as a professor, and I am glad to see some of my very good friends here.

I have an announcement to make which I think we will all be sorry to hear. Professor Audrieth is ill and will be unable to attend the conference, and likewise Professor Witt of the University of Texas. Professor Watt is being represented by Mr. Chrisp, however, and I am sure he will be ably represented.

The main work of this conference lies immediately before us, and as the time is really short, with only two days for the large number of papers and I hope a considerable amount of discussion, I will also make my remarks short and concise in behalf of the Naval Ordnance Test Station.

I find it is a happy privilege indeed to welcome all of you in the name of the Bureau of Ordnance and the Naval Ordnance Test Station to this conference. I give such welcome to you from the Technical Director, Dr. Frederick Brown, and the Commander of the Station, Captain Stroup.

This conference had its inception in November of 1951 in a discussion I had with Bill Sheehan of the Bureau of Ordnance in Washington, and Bill immediately passed my suggestion along to Gene Klein. I telephoned him and the conference took birth about May 1952, in the form of a suggested agenda which I drew up with the aid of my colleagues out at the Station.

For the really hard work in organizing this conference we must compliment Gene Klein who took over the chief burden of correspondence and the other details, and NOTS' Dr. Howard Kruse, with whom you will become better acquainted later in the conference.

We should indeed express our indebtedness to our friends, Illinois Tech, for the fine facilities. Many of you here, I think, will remember the fine facilities we enjoyed at our conference on nitrogen compounds held in September 1950.

Finally, a word of thanks from NOTS to the Chicago office of ONR for their aid and the fine dinner arrangement they have made for us.

I need not say that this conference is important and timely. At present everyone is concerned with the world situation and I express the attitude of all of us in saying that we hope that what is said here will aid in solving some of the difficult military problems which confront us.

If I were asked what my high motivation was in conceiving this conference it would be to ensure scientific advancement in hydrazine chemistry by bringing together this group of workers of distinction so that they might get to know each other.

Thank you.

MR. KLEIN: I made one omission in the introduction. I want you all to meet Miss Selby, who will record the discussion of this meeting. Miss Selby is head of the Conference Reporting Unit, Research and Development Board.

It is also a distinct pleasure for me to introduce the Chairman for the first session of the Symposium, Dr. Howard K. Nason, Director of Research for the Organic Chemical Division of the Monsanto Chemical Company, and a member of the Panel on Fuels Requiring Oxidizers, Research and Development Board.

Dr. Nason

(At this point, Dr. Howard K. Nason, Monsanto Chemical Company, assumed the Chair.)

THE CHAIRMAN: Thank you very much, Gene.

Two of the hardest things to get your fingers on in the overall work in a field like this are the actual requirements of end items related to fuel properties, and information on what our competition overseas is up to.

We are very fortunate, therefore, this morning to be able to start this program with a paper on one of these two fields. Mr. Ivan Kenis, of the Air Technical Intelligence Center, of Wright-Patterson Air Force Base, will present a discussion of the "German and Soviet Experience in the Hydrazine Field."

Mr. Kenis.

GERMAN AND SOVIET EXPERIENCE IN THE HYDRAZINE FIELD

by

Ivan Kenis
Air Technical Intelligence Center

The German wartime experience with hydrazine has been well publicized in many reports prepared by the British Intelligence Objectives Sub-Committee (1,2,3,5) and the Combined Intelligence Objectives Sub-Committee (4). These reports describe the manufacture of hydrazine hydrate by the Raschig process, and minor modifications of this process, in the three German plants which were formerly at Gersthofen, Ludwigshafen and Leverkusen. In addition, the excellent monograph by Audrieth and Ogg treats the Raschig process in some detail (16). Details of the methods of manufacture are familiar to most investigators and it should suffice to touch only upon some of the problems encountered by the Germans.

The Leverkusen and Gersthofen plant operations were based on the partial oxidation of ammonia by sodium hypochlorite, whereas the Ludwigshafen plant substituted urea for ammonia as a matter of convenience. The Ludwigshafen plant, estimated at 20 tons/month capacity, produced hydrazine sulfate from which the hydrate was recovered by treatment with sodium hydroxide followed by successive distillations. The Leverkusen plant was designed to produce 50 tons/month and served as the model for the Gersthofen plant which was to produce 300 tons/month. At both plants the hydrate was produced directly without the intermediate sulfate step. The Gersthofen plant was designed as three independent 100 ton capacity units, only one of which was put into operation before the end of the war and this unit never exceeded a monthly production of 50 tons.

Perhaps the most important hydrazine development during the war was the direct rectification of hydrazine from the reaction products without the intermediate hydrazine sulfate step. It is paradoxical that this improvement was known to the Raschig firm many years before the war but was to be rediscovered by the combined efforts of the I. G. Farben Industrie and the Electrochemische Werke, Munich. Although it was Raschig who introduced hydrazine hydrate to the German Aviation Research

Institute, the Raschig plant produced less than five (5) tons throughout the whole war; however, Raschig was capable of producing only one ton per month.

Equally as important as the direct rectification process, were the yield improvements which were brought about by increasing the temperature of the hypochlorite-ammonia mixture to 160°C, and simultaneously using a high pressure (30 atm) to maintain the reactants in the liquid phase. When the Germans, in 1944, sold the hydrazine process to the Japanese, the high-pressure process was purposely omitted from the transaction. The actual transfer of technical data to Japan was delayed by the war situation until June or July 1944. The contract provided for a German technician to go to Japan, but this did not take place. As far as could be determined, the Japanese never succeeded in producing hydrazine in the short period from 1944 to the end of the war.

During the war, ten improvement patents were filed by German inventors, although all were not granted. Aside from the direct rectification, high-pressure continuous process, these patents contained little of any significance. They dealt with minor improvements of questionable value. Neither the German scientific literature of that period - there was practically none published - nor the classified intelligence documents indicated any research on the preparation of anhydrous hydrazine. Interrogations on the subject of anhydrous hydrazine directed to the principal scientists engaged in the field, confirmed that only the hydrate was considered by the German Government, although the advantages of the anhydrous product were recognized and at least one investigator considered beginning research on the synthesis of hydrazine from its elements, or from ammonia under electric discharge. The short time available for the development of commercial hydrazine hydrate, covering 1940 through 1944, and the urgency to supply this fuel to their rocket propulsion program, left little time for researches of less immediate results.

Although the principles of the Raschig process are well known it may be well to cite some of the practical difficulties the Germans experienced in producing the hydrate on a continuous basis. For example, the problem of starting up the plant required a good deal of competence in order to bring the system into equilibrium. Repeated stoppages due to bombing raids made it difficult to maintain production at a uniform rate. Furthermore, it has been reported that most of the operators were foreign prisoners of war, which should have added to the difficulty of full capacity operation.

Removal of the sodium chloride periodically from the first step in recovering the weak hydrate solution also presented a problem. Excess sodium hydroxide in the salt caused it to cake and deposit in the steam heater. This was alleviated by the maintenance of high liquid velocities through the tubes plus a control of the NaOH concentration to less than 6% in the weak liquor. The salt evaporator had to be temporarily shut down every two hours for salt removal; however, this operation did not affect the continuous concentration of the liquor.

Another problem presented itself in the concentration towers. The original distillation towers were packed with porcelain Raschig rings. However, after a period of operation the rings wore thin and were completely dissolved in three or four months. Porcelain was observed to be deposited everywhere, particularly as a coating on the heater tubes and, consequently, the Raschig rings were replaced with stainless steel turnings. However, a few days later the final concentrating column exploded. Subsequent investigation revealed that when the hydrazine hydrate vapor was passed over the steel turnings, hot spots occurred at points on the surface, and decomposition began which resulted in the explosion. This difficulty was overcome by substituting stainless steel bell plates in the bottom half of the tower where the hydrazine hydrate concentration was the highest. A slight positive nitrogen pressure was also employed to reduce the effect of oxygen explosions.

The manufacturing techniques for the production of the hydrate were not completely worked out in that the most efficient operation was never achieved. Data used in the design of the pilot plant at Leverkusen showed that the economical choice would have to be made between the concentration of hydrazine hydrate in the product liquor and the hydrazine yield based on the raw materials.

In the plant operations, hydrazine hydrate was concentrated from 3% to 15%, then to 60% and then to 80%. The plant could be operated to produce 95% hydrate. Figure 1, page 4, illustrates the effect of the hypochlorite concentration on the yield of hydrazine hydrate (1).

The defeat of Germany did not yield a great deal in the way of hydrazine hydrate production facilities or technicians for the Soviet forces since these were not in their zone of occupation. However, this fact is of little real significance since the Soviets had themselves investigated hydrazine syntheses many years prior to the war. In 1905, Schestakoff proposed a then new synthesis based on the action of hypochlorites on urea (11). In 1923, Putokhin published, for the benefit of the Soviet chemists, the complete details of the Raschig process for the preparation of hydrazine, its salts and the hydrate (12). Judging from the past Soviet claims for discoveries, we may expect to see published, at some future date, a more complete list of Soviet investigators who will, no doubt, by Soviet chronology, antedate the work of Curtius (1887) in his isolation of hydrazine and Fischer's work (1875) with organic hydrazines.

A recent review of the Soviet literature by Davis, Vesselovsky and Johnston (6, 7) showed that, based on the published work available to the Western world, there seems to be little interest in the thermodynamic properties of hydrazine. There is also a lack of contributions to the study of decomposition or the oxidation of hydrazine. Table I shows the contributions to the literature on the kinetics, thermodynamics, physical properties and manufacture of hydrazine as compiled by Davis, Vesselovsky and Johnston (7).

It will be noted that Soviet contributions number only eleven out of 172 papers from all countries; or about six percent. Judging from information received from other than scientific publication channels, these data belie the facts of what is actually occurring in USSR. And, in fact, we can conclude that the evidence of Soviet work, whether of good or bad quality, is conspicuous by the absence of the Soviet papers. Furthermore, relatively few of these papers have been observed since 1940, indicating that perhaps a high degree of security is placed on hydrazine investigations. (8, 9, 10, 11, 12, 13, 14, 15)

Notable exceptions to papers published since 1940 are those by Semishin (8) on binary systems of hydrazine and by Pleskov (9, 13) on electrode potentials in anhydrous hydrazine. Pleskov indicated, in 1945, the possibility of discharging the amide ion in liquid ammonia and postulates the formation of hydrazine from the condensation of the amide radicals (13). No further experimental evidence was presented to support this postulation.

At any rate, the Soviets did obtain quantities of hydrazine hydrate, mostly in the form of the C-Stoff* rocket propellant blend, from German supply depots. Sufficient material was available to conduct an adequate rocket engine test program until Soviet controlled production could get underway.

Simultaneously, they began a recruiting program to obtain German engineers and chemists formerly employed in the German

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* C-Stoff: 31% hydrazine hydrate, 56% methanol, 13% water plus $K_3Cu(CN)_4$ catalyst (approx. comp.)

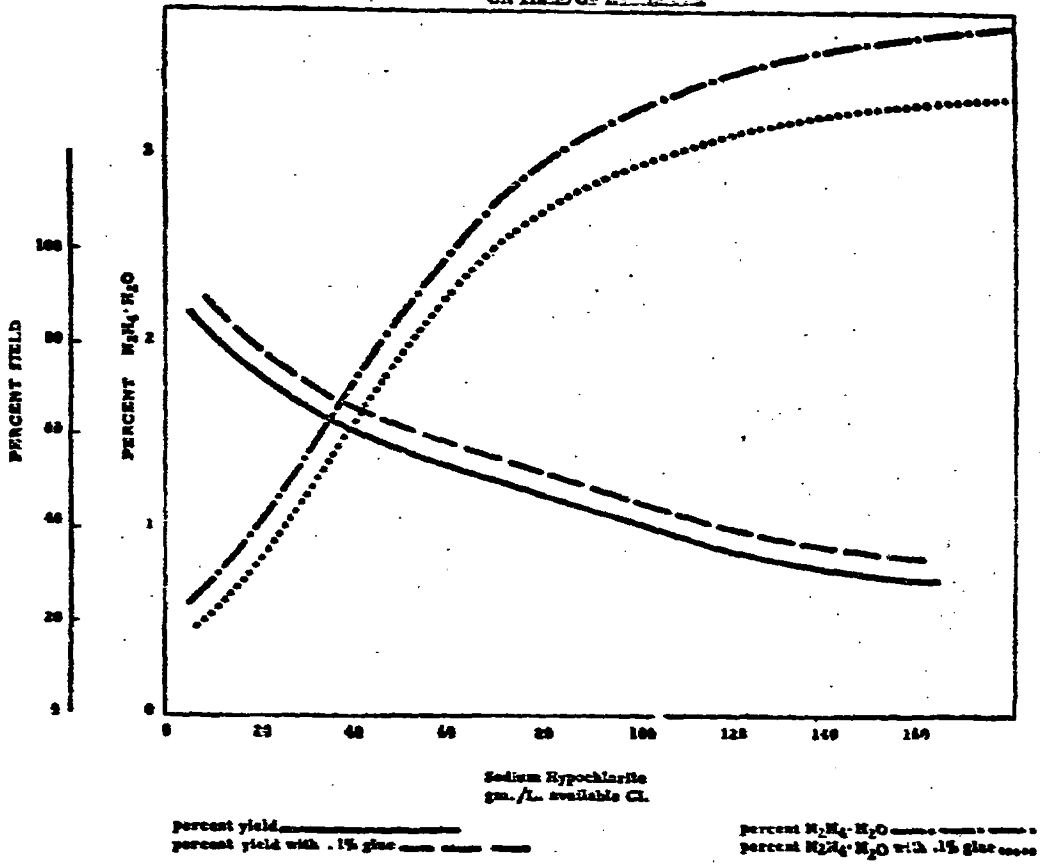
TABLE I

OVERALL CONTRIBUTIONS TO THE LITERATURE ON KINETIC, THERMODYNAMICS PHYSICAL PROPERTIES AND MANUFACTURE OF HYDRAZINE

Country	Mfr.	Misc. Process-es	Phys. constants, thermodynamic functions, thermo-chemical data	Spectroscopic data and molecular structure	Phase equilibria in hydrazine-systems	Kinetics of decomposition	Kinetics of oxidation	Ignition properties	Flame velocity	Totals
U.S.	9	12	20	7	8	9	16	1	1	83
Germany	6	10	10	13	1	2	4	0	0	46
England	1	1	1	3	0	1	2	1	1	11
Japan	3	1	2	3	0	0	0	0	0	9
Russia	3	0	2	0	4	1	0	0	1	11
France	1	1	1	4	1	0	0	0	0	8
Sweden	2	0	0	0	1	0	0	0	0	3
Australia	1	0	0	0	0	0	0	0	0	1
Denmark	1	0	0	0	0	0	0	0	0	1
Belgium	1	0	0	0	0	0	0	0	0	1
Switzerland	0	1	0	0	0	0	0	0	0	1
Italy	0	1	0	0	0	1	1	0	0	3
Turkey	0	1	0	0	0	0	0	0	0	1
Netherlands	0	0	2	0	0	0	1	0	0	3
Canada	0	0	1	1	0	0	0	0	0	2
India	0	0	0	2	0	0	0	0	0	2
	28	28	39	33	15	14	24	2	3	186

Note: Several papers are represented in more than one category, therefore the total number of papers is actually only 172.

EFFECT OF CONCENTRATION OF SODIUM HYPOCHLORITE
ON YIELD OF HYDRAZINE



hydrazine plants. This program met with little success but, in spite of this, the Soviets succeeded in putting into operation in the East Zone of Germany, a hydrazine hydrate unit at least as large as the German wartime capacity. This plant is reported to have produced in excess of 1000 tons hydrazine hydrate during 1951. Planned production for 1952 exceeds 4000 tons; all of which is to be shipped to the USSR. Such large quantities, coupled with the fact that probably less than one-tenth of these quantities could find uses other than as a rocket fuel, suggest not only an active rocket test program but probably a well planned stockpiling of this potential fuel. Furthermore, it is not unlikely that the Soviets could dehydrate the hydrazine hydrate received from Germany. Sufficient evidence is at hand to confirm Soviet intense interest in the rocket airplanes, ME-163 and the DFS-346, both of which employed hydrazine hydrate. Conversion of these craft to the use of anhydrous hydrazine, plus an adequate freezing point depressant, may be the Soviet plan.

Some of the hydrazine manufactured in Germany is produced by the hydrazine sulfate intermediary-step followed by treatment with sodium hydroxide. Analysis of the sulfate product agreed quite well with chemical handbook data; however, materials represented to be the finished hydrate have so far proven to be only ammonia solutions, probably the raw material used in the process. There are indications that hydrazine hydrate is also produced via urea and hypochlorite, as well as from ammonia and hypochlorite without the sulfate step. There are at least three plants accounted for in the East Zone of Germany which are reported to be producing hydrazine hydrate by these processes. A duplicate of the largest of these plants is being erected in the Ural mountain region of the USSR. The exact location has not yet been determined.

In summarizing, we can conclude that the Soviets have at their disposal hydrazine plant capacity as great or greater than Germany's wartime capacity; and that these plants are producing at three to four times the rate attained by Germany at the end of the war. We can assume that, as has been customary in other fields in which the Soviets had much to learn in a short time, they spent only limited time and money on processes which required much research. Instead they concentrated on duplicating known production processes. As a result, we find them probably as far along in the hydrazine field as any nation of the Western powers.

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THE DEHYDRATION OF HYDRAZINE BY AZEOTROPIC DISTILLATION

by

John W. Clegg, R. Q. Wilson, and H. P. Munger
Battelle Memorial Institute

Presented by
John W. Clegg

Anhydrous hydrazine is expensive and somewhat difficult to obtain by methods currently employed. Hydrazine is produced chiefly by the Raschig process, from which it is obtained in a low-concentration, aqueous solution. Conventional distillation methods may be used to concentrate this solution to the hydrazine-water azeotrope containing approximately 70 percent hydrazine and 30 percent water(1). Further concentration of this material is difficult because of the formation of this maximum-boiling hydrazine-water azeotrope. Several chemical dehydrating processes have been currently used, but these either employ reactive solids or proceed through the formation of a precipitate which is difficult to handle.

Exploratory work was undertaken, therefore, to determine if anhydrous hydrazine could be recovered from the hydrazine-water azeotrope by adding a third component and distilling. Of the numerous materials tested initially, aniline was the first to show real promise as an effective entrainer, and will be used as an example in describing the procedure. Aniline is known to form an azeotrope with water containing 81.8 percent water and boiling at 98.5°C. This is 21.6°C lower than the hydrazine-water azeotrope which boils at 120.1°C.

The first investigative procedure consisted of the determination of distillation curves for various mixtures of interest. These curves were obtained from a Todd "Precise Fractionation Assembly," shown in Figure 1.

> The Todd fractionating column consisted of a 1/2 inch glass column packed 36 inches high with 1/16 inch glass helices. The pot had an opening for a standard-tapered thermometer and one for the entrance of nitrogen. All the vapors were condensed in the column head and the reflux was varied by adjusting a valve on the take-off line. Rubber tubing from the receiver vent to a

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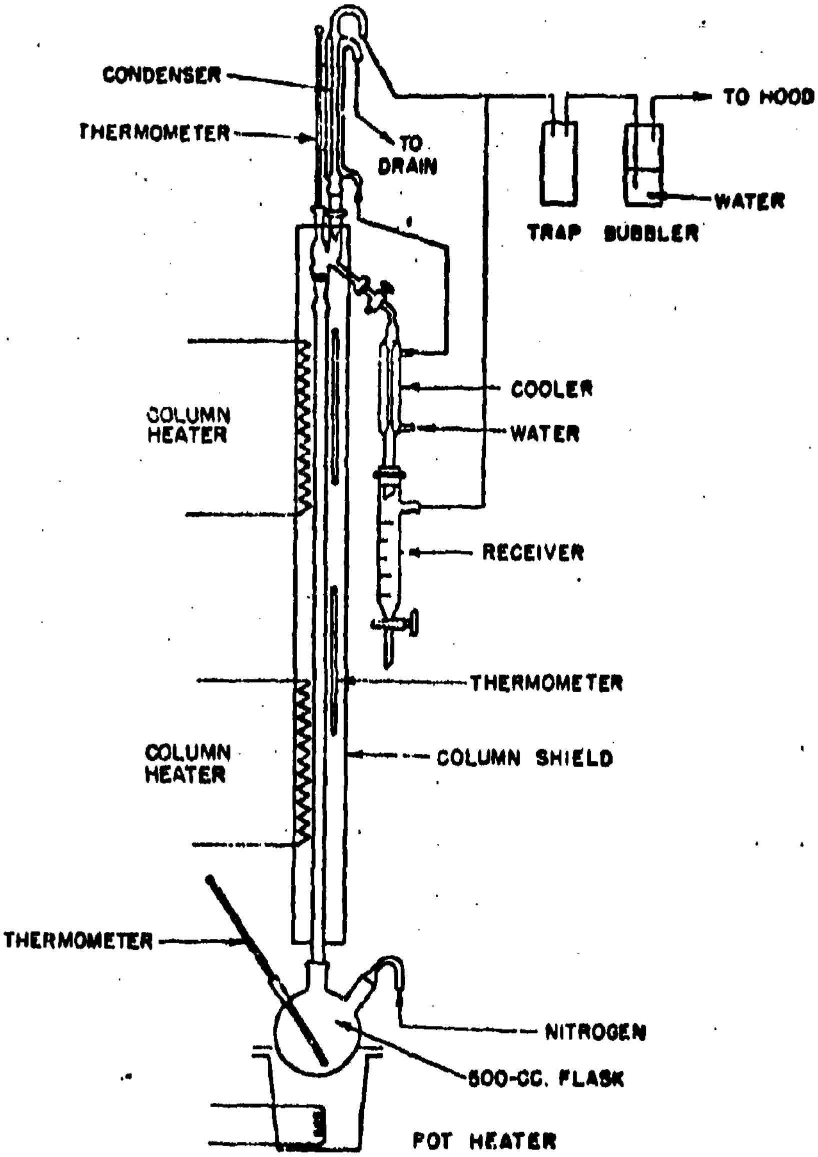


FIGURE 1. TODD FRACTIONATION ASSEMBLY

bubbler provided a nitrogen seal and assured operation under a slight positive pressure of nitrogen. Vapor temperatures were measured by a thermometer in the reflux head. The column was shielded with glass and was heated with resistance wires to minimize heat losses. Both the heat load to the pot and the column heaters were controlled by variable resistors.

Two hundred grams of material was used for each run. A reflex ratio (total vapor to distillate) of 5 to 1 was used. The distillate was collected in a receiver which was changed for each temperature change, and the samples were weighed and analyzed. A typical distillation curve for the system hydrazine-water-aniline is shown in Figure 2. This shows that the first material to distill over was the aniline-water azeotrope at 98.5°C. The next 23 grams came over in the temperature range from 116-118°C. Analysis of this fraction showed increasing contamination with hydrazine, probably in the form of the hydrazine-water azeotrope. Twice during the distillation it was noted that the temperature fell from 118 to 115°C for a short time in this region. After this point, the distillate all came over at 118.0 to 118.5°C until all of the hydrazine and water were distilled. All cuts taken in this third temperature range except one analyzed more than 72 percent hydrazine, indicating that a mixture of the hydrazine-water azeotrope (69.8 weight percent hydrazine) and anhydrous hydrazine was coming over.

A material balance on this experiment indicated that 96 percent of the hydrazine, 101 percent of the water, and 94 percent of the aniline were accounted for.

Since anhydrous hydrazine was not obtained directly from distillations of the type described above, it was thought advisable to determine the exact mechanism of the distillation by following the course of the fractionations on a ternary diagram. Some degree of dehydration was certainly occurring.

Figure 3 is a plot of the ternary diagram of hydrazine-water-aniline showing the boiling temperatures of the pure compounds and the two azeotropes formed. An inspection of this diagram suggests the presence of a high-temperature region connecting the compositions of the hydrazine-water azeotrope and aniline. In similar systems, Ewell and Welch(2) found the presence of ridges in the vapor and liquid surfaces extending across the diagrams. These ridges were usually curved and formed a distillation barrier, but they could be crossed from the concave side by rectification. They could not be crossed, however, from the convex side. In the region of these ridges the vapor and liquid surfaces were rather flat, and therefore, they could not be represented by a sharp

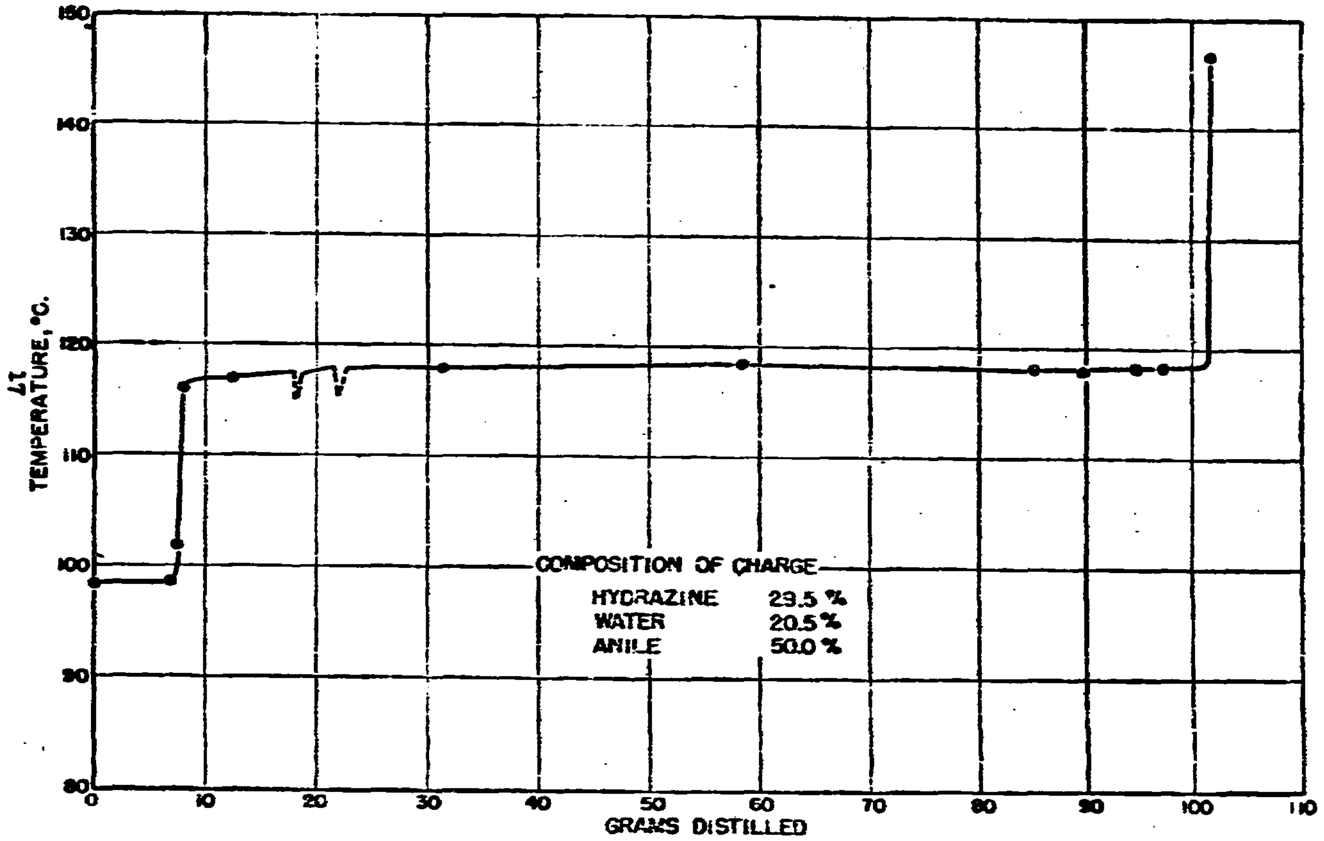


FIGURE 2. RECTIFICATION DATA FOR HYDRAZINE, WATER, AND ANILINE

line. The results from several experiments like the one described above indicated the presence of such a ridge in this system, extending from the composition of the hydrazine-water azeotrope to the composition of aniline.

In Figure 3, lines have been drawn connecting the invariant compositions of the azeotropes together with the ridge area. These divide the diagram into three areas. Any ternary mixture lying in Area I, where hydrazine, the hydrazine-water azeotrope, and aniline are in equilibrium will, when fractionated, give pure hydrazine in the first overhead vapors. This is because hydrazine is the most volatile component in this particular ternary mixture. A mixture with a composition falling in Area II will give the aniline-water azeotrope as the first fraction, and likewise a mixture with a composition lying in Area III will give the aniline-water azeotrope in the first fraction. A mixture with a composition falling on the ridge, where aniline and the hydrazine-water azeotrope may be said to be in equilibrium, will yield the hydrazine-water azeotrope first, when fractionated.

The course of the above-described distillation was followed on the diagram in Figure 3 by calculating and plotting the pot compositions throughout the experiment. Assuming that there is a ridge in the vapor and liquid surfaces of this system, the mechanism of the distillation may be explained as follows.

The original composition lies in Area II, and the first material to distill over should be the lowest boiling; that is, the aniline-water azeotrope. Inspection of the distillation curve shows that this was the case. As long as the pure aniline-water azeotrope was coming over, the composition of the pot shifted rectilinearly in the opposite direction. After a few grams of this material was distilled over, the overhead vapor temperature started to rise rapidly, indicating a change in composition. The composition of the pot at this time is shown by Point 5. There was no hydrazine present in this fraction. The composition of the pot was calculated by subtracting the weight of aniline and water in this fraction from the original pot composition, and a new composition of the pot was calculated, all on a weight percent basis. The next three fractions showed increasing amounts of hydrazine by analysis, and came over in a fluctuating temperature range close to the boiling point of the hydrazine-water azeotrope. The pot compositions at the end of these fractions were still in Area II on the diagram, as indicated by the presence of aniline in the distillate. When the composition of the pot reached Point 5, it approached the ridge area, where aniline and the hydrazine-water azeotrope were in equilibrium. Since the hydrazine-water azeotrope was the lower boiling of the two, it appeared in the vapors. This is shown by the overhead vapor temperature of 116°C. While this

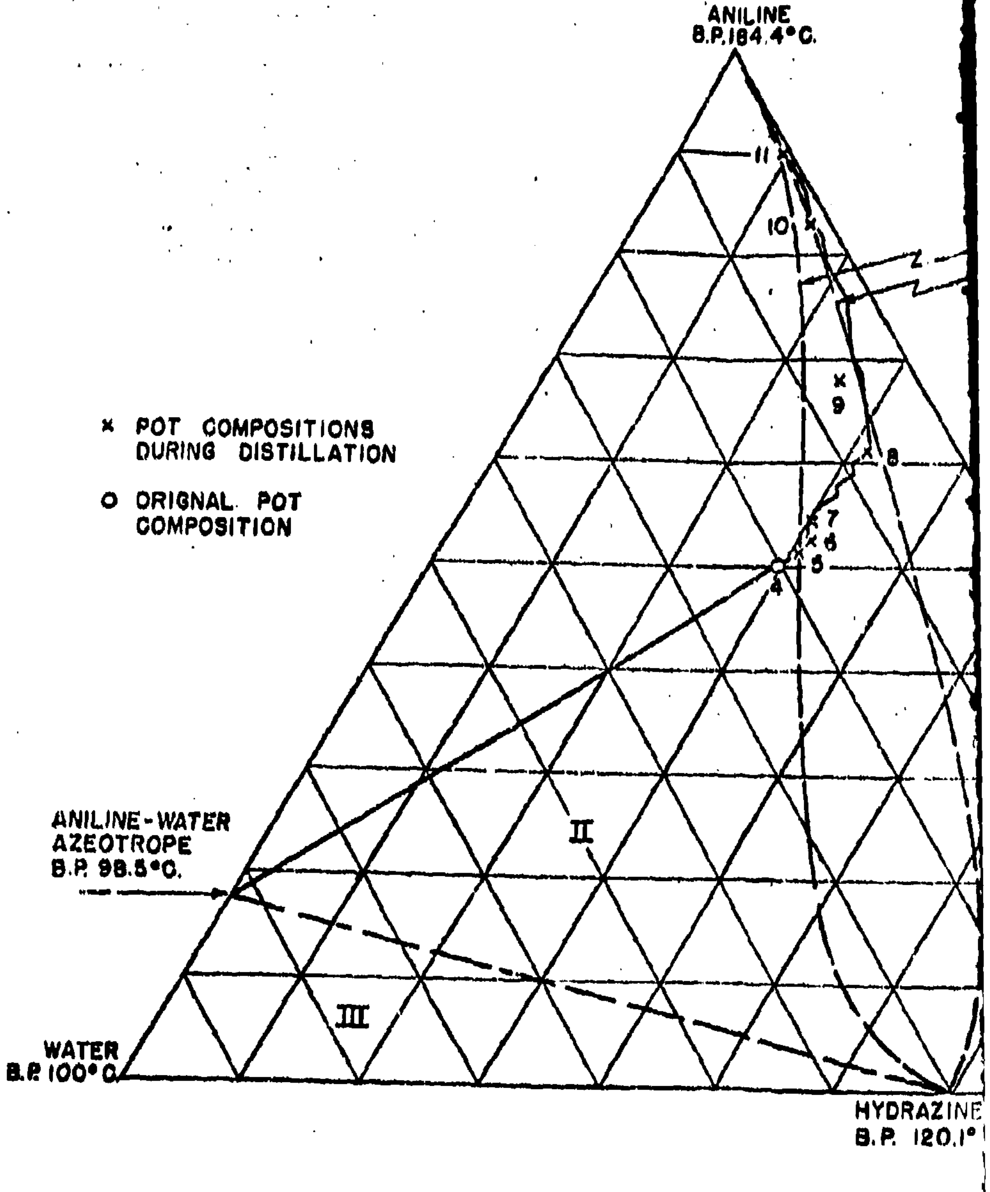
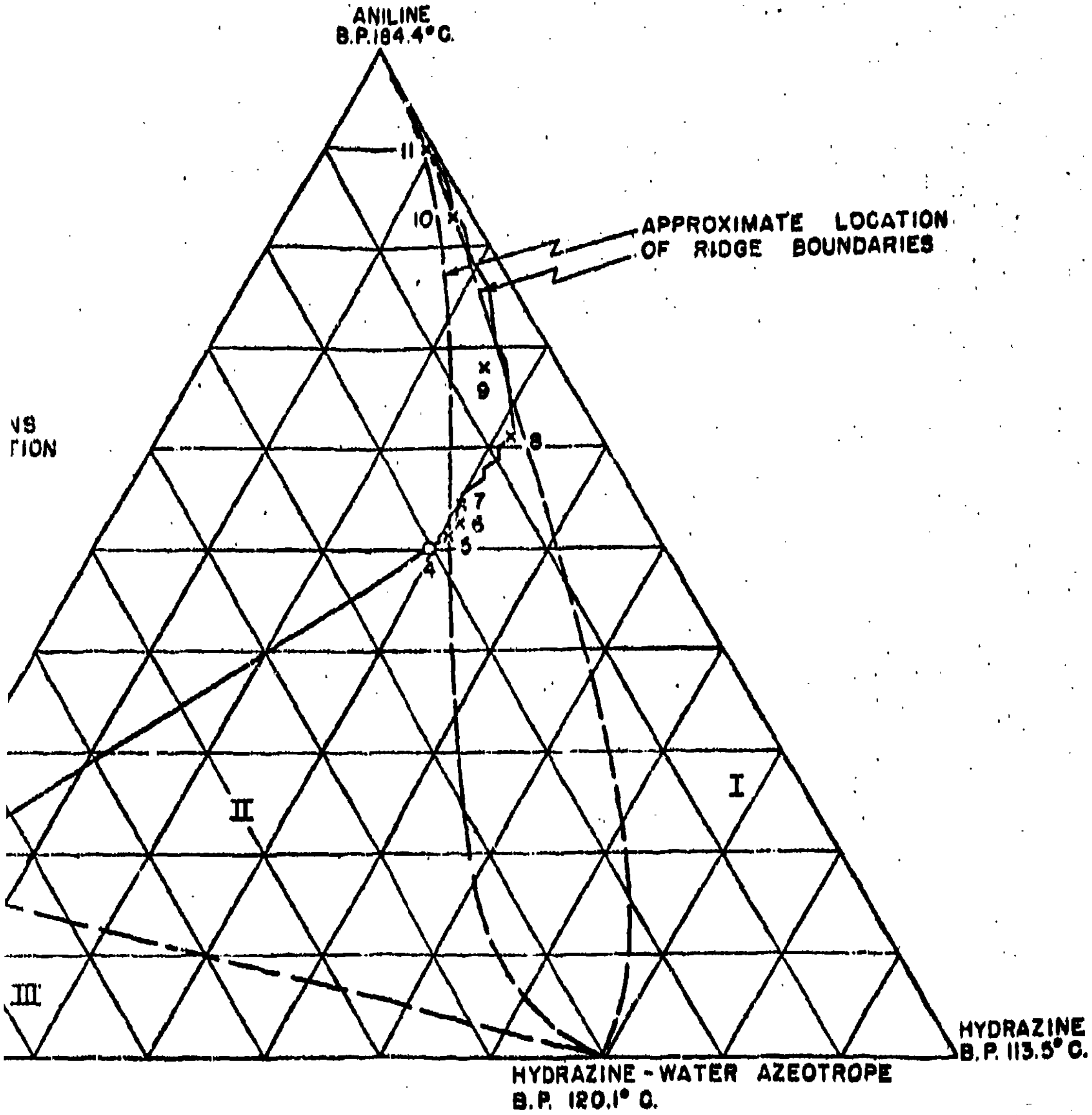


FIGURE 3. TERNARY EQUILIBRIUM DIAGRAM FOR SYSTEM HYDRAZINE



2

EQUILIBRIUM DIAGRAM FOR SYSTEM HYDRAZINE, WATER, ANILINE. BASIS: WEIGHT PER CENT

98276
0-15693

material was distilling, the pot composition shifted rectilinearly in the opposite direction until its composition moved off the ridge into the area where again the aniline-water azeotrope was the lowest boiling component. After a small amount of the aniline-water azeotrope came over, the pot composition moved back upon the ridge, and the hydrazine-water azeotrope again appeared in the overhead vapors. This stepwise shifting of distillate composition continued until the ridge was crossed. The crossing evidently occurred shortly after the end of the fifth cut. The pot composition at this time is plotted as Point 8.

As stated earlier, a ridge of this type can be crossed only from the concave side. Once the ridge is crossed, it is impossible to shift the composition back into Area II. The pot composition arrives in Area I, where anhydrous hydrazine is the lowest boiling material which can distill. The pot composition at Point 8 is nearly across the ridge. Hydrazine-water azeotrope distilled until the pot compositions shifted into Area I, as shown in Figure 3. As soon as the pot composition arrived in Area I, anhydrous hydrazine appeared in the distillate. This material continued to distill until the pot composition shifted back to the ridge, where the hydrazine-water azeotrope started coming over again. Thus, the course of the distillation from this point to the end seemed to occur in infinitesimal steps owing to this shifting of the distillate composition, until all the hydrazine and water had been removed.

The temperature of the overhead vapors that came off after the ridge was crossed was in the 118.-118.5°C range, showing that some of the hydrazine-water azeotrope was present. The composited distillate contained much more hydrazine than the azeotropic composition, however, so that the azeotrope had been "broken."

Location of the Ridge

Optimum recoveries of high-purity hydrazine depended upon the location of the ridge and ridge boundary. To find this quantitatively, several distillation experiments were made in the Todd column with varying amounts of hydrazine, water, and aniline. These are shown in Figure 4.

The straight line between the compositions of aniline and the hydrazine-water azeotrope represents all possible ternary mixtures obtainable by adding aniline to the azeotrope. This line is called the "aniline addition line" in Figure 4. In this figure, the ridge area is wide at low aniline concentrations. This area could be narrowed by using higher reflux ratios. At any reasonable reflux ratio, however, there would be a wide area at low aniline concentrations which would act as an effective distillation barrier.

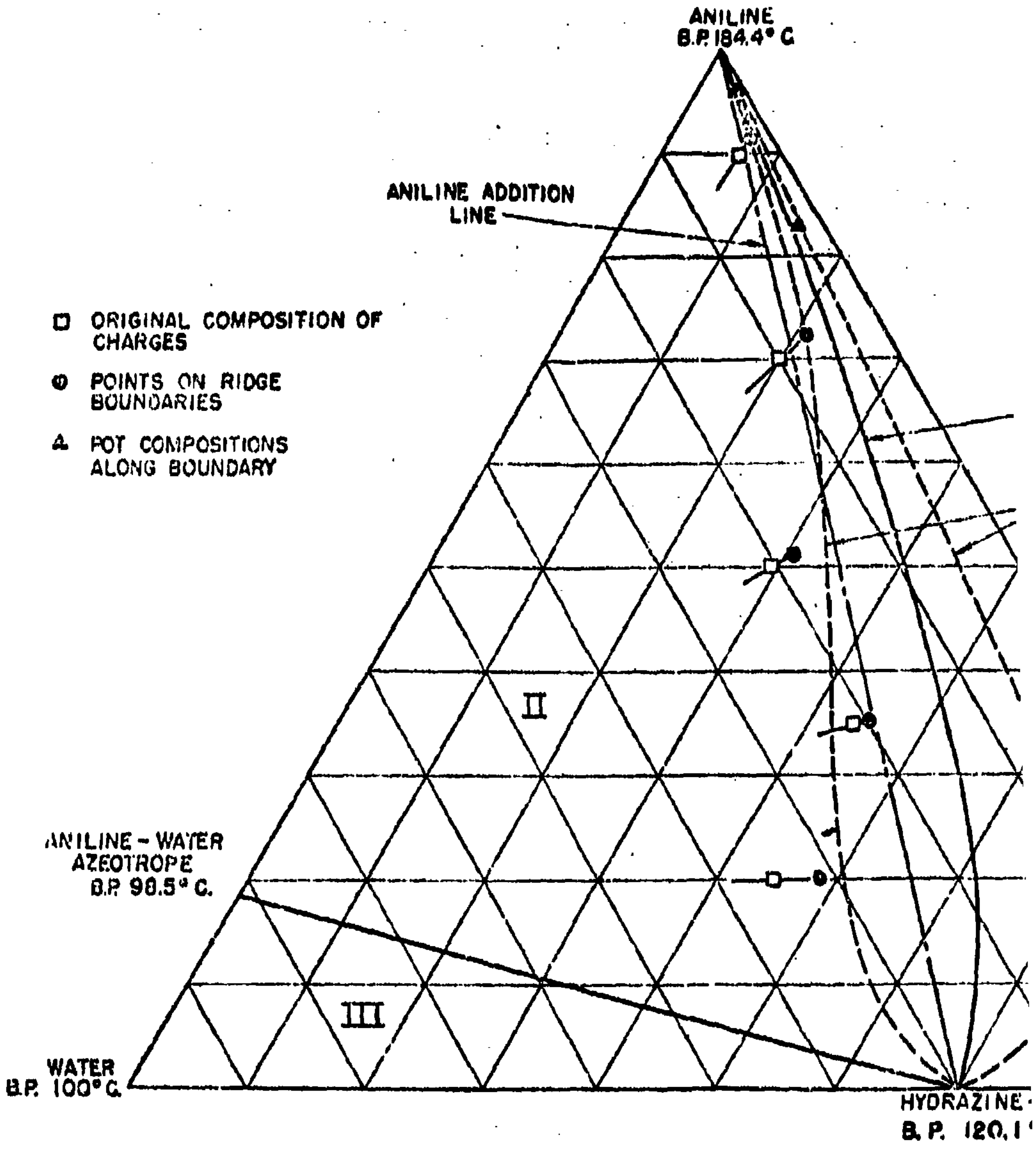
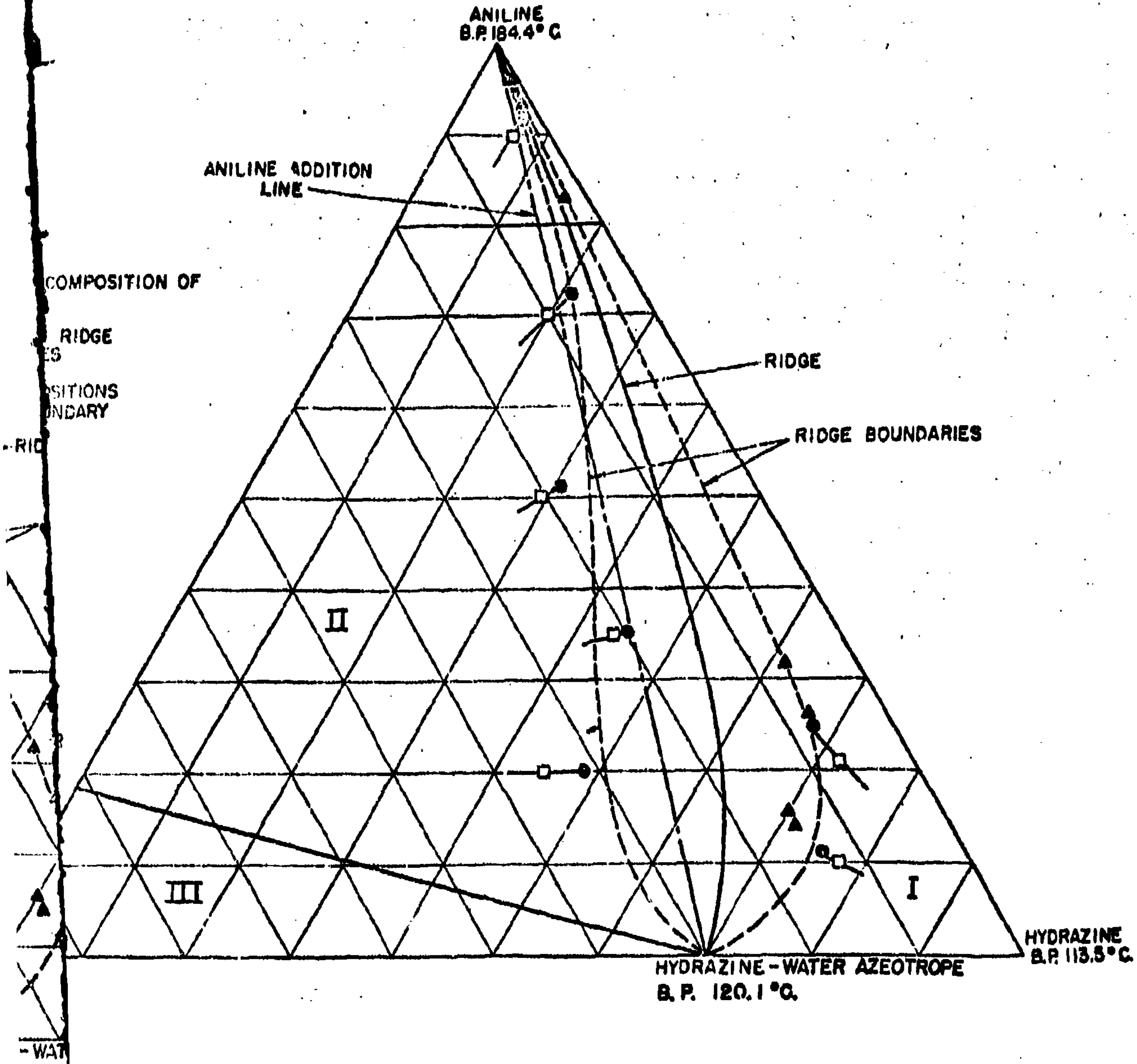


FIGURE 4. TERNARY EQUILIBRIUM DIAGRAM FOR SYSTEM HYDRAZINE, WATER, ANILINE.



EQUILIBRIUM DIAGRAM FOR SYSTEM HYDRAZINE, WATER, ANILINE. BASIS: WEIGHT PER CENT

2

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0-13780

[redacted]

At low aniline concentrations, the "aniline addition line" was inside the ridge area. Under these conditions, very little water could be removed before the distillate became contaminated with hydrazine. At high aniline concentrations, however, both the ridge and the ridge boundary were some distance from the "aniline addition line." Since the primary objective was to remove water, the optimum recovery of anhydrous hydrazine would be obtained by distilling a charge farthest removed from the ridge boundary. This would be a charge that would probably contain more than 60 percent aniline.

Apparently it was not going to be possible in this system to remove all the water before the desired product, anhydrous hydrazine, began to appear in the distillate. This meant that a certain amount of recycling of materials was going to be necessary. It was, therefore, important to find out to what extent the system could be dehydrated before recycling became necessary. In other words, how much of the water can be removed from the system before anhydrous hydrazine appears in the distillate?

Table 1 shows the amount of water removed in the first fraction for different concentrations of aniline. A maximum of about 68 percent of the water in the hydrazine-water azeotrope could be removed in a column as efficient as the Todd column used, with aniline as the entrainer. This means that, if the enriched hydrazine could be separated from the entrainer and redistilled, approximately 68 percent of the original hydrazine could be recovered as anhydrous material. The balance would have to be recycled.

Evaluation of Entrainers

In order to find a more efficient entrainer, a literature survey was made of 213 compounds that were known to form azeotropes with water. On the basis of the results of work with aniline, benzene, ethylenediamine, chlorobenzene, and toluene, it was possible to accept or reject materials according to their boiling points and the azeotropes they formed. Figure 5 shows some of the systems studied experimentally. Systems which form saddle-point azeotropes with compositions falling near the entrainer addition line would not make good entrainers. Here the aqueous distillate would have a considerable amount of hydrazine in it -- usually near 70 percent. Ethylenediamine would not be useful. The problem of removing water from the ethylenediamine-water azeotrope, to permit reuse of the ethylenediamine, would be as difficult as removing the water from the hydrazine-water azeotrope in the first place. A number of petroleum-distillate fractions were also studied. In general, they gave poor efficiency because of the location of the ternary saddlepoint azeotrope which always formed.

[redacted]

TABLE 1

QUANTITY OF WATER REMOVED FROM HYDRAZINE-WATER AZEOTROPE BY AZEOTROPIC DISTILLATION WITH INDICATED ANILINE CONCENTRATIONS

Amount of Aniline Used as an Entrainer, Percent	Water Removal as the Aniline-Water Azeotrope, Percent
90	0-12
80	48-61
70	60-68
60	57-61

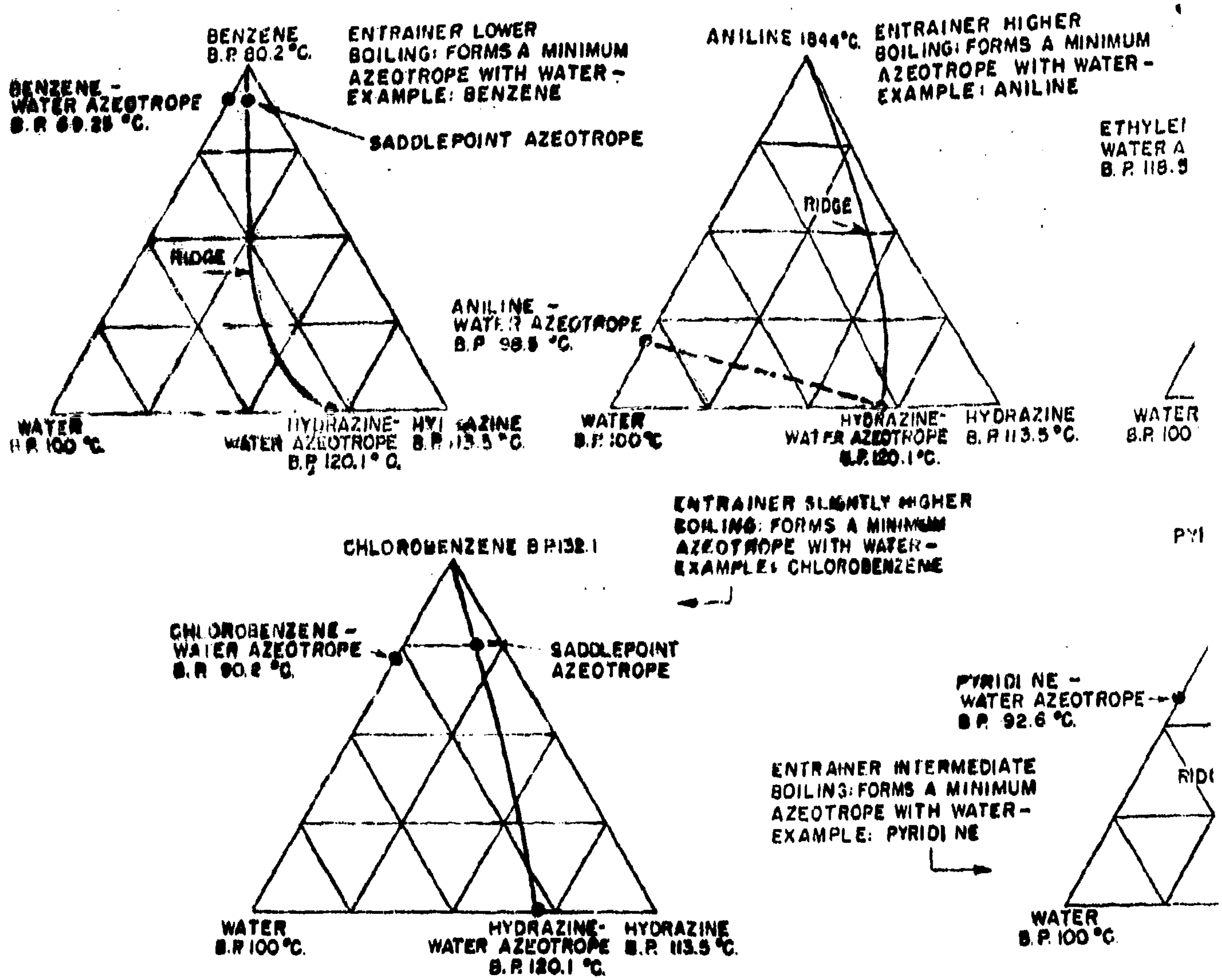
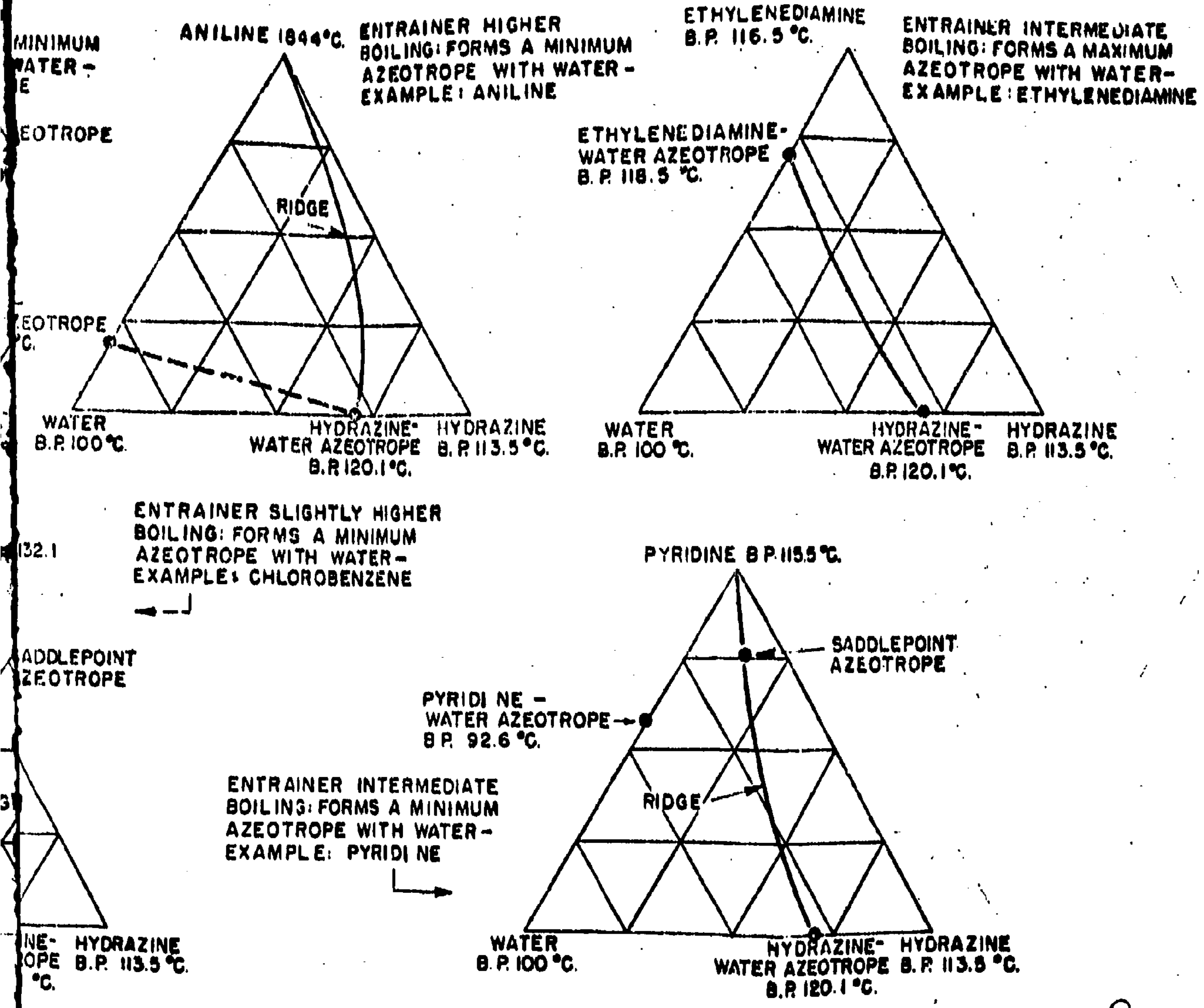


FIGURE 5. TYPES OF TERNARY EQUILIBRIUM DIAGRAMS FOR INDICATED



ENTRAINER HIGHER BOILING: FORMS A MINIMUM AZEOTROPE WITH WATER - EXAMPLE: ANILINE

ENTRAINER INTERMEDIATE BOILING: FORMS A MAXIMUM AZEOTROPE WITH WATER- EXAMPLE: ETHYLENEDIAMINE

ENTRAINER SLIGHTLY HIGHER BOILING: FORMS A MINIMUM AZEOTROPE WITH WATER- EXAMPLE: CHLOROBENZENE

ENTRAINER INTERMEDIATE BOILING: FORMS A MINIMUM AZEOTROPE WITH WATER - EXAMPLE: PYRIDINE

2

ES OF TERNARY EQUILIBRIUM DIAGRAMS FOR INDICATED SYSTEMS.

91200
0-14067

On the basis of this survey, it was concluded that compounds with physical properties similar to aniline were the only suitable materials for entrainers. If the ridge in the vapor and liquid surfaces is far removed from the entrainer addition line, the formation of a saddlepoint azeotrope would not be objectionable. No substances of this sort were found in the search.

Development of the Process

To obtain more precise and larger-scale results than was possible in the Todd column, a two-inch column was built to study the entire process. Figure 6 is an illustration of the two-inch column.

> This column was packed 37 inches with 1/4-inch glass Raschig rings. There were thermocouple wells equally spaced in the packed section. Opposite each thermocouple well was an opening which could be used either for the entrance of feed or as a sampling port. The reflux head was designed to split the overhead vapors into reflux and product in the vapor phase. An orifice in the product line maintained a 9 to 1 reflux ratio (total vapor to distillate) which was very nearly independent of the boil-up rate. The insulation on the column was heated with resistance windings to reduce the heat losses. The still pot was a 5-liter, 3-necked flask fitted with a thermocouple well and a nitrogen inlet. For continuous operations, an opening in the side of the flask provided for gravity flow out of the pot. The feed flowed to the column from a storage tank through a rotameter and a heater which was made of stainless steel tubing wrapped with resistance wire. A 10-point Micromax (Leeds and Northrup) recorder measured and recorded temperatures throughout the system.

Some of the earlier results were checked with greater precision in this column. In a continuous operation, three columns would be required for the following steps:

1. Removal of 60 to 70 percent of the water as the aniline-water azeotrope.

2. Separation of the resulting enriched hydrazine solution from the entrainer.

3. The distillation of anhydrous hydrazine from the enriched hydrazine solution.

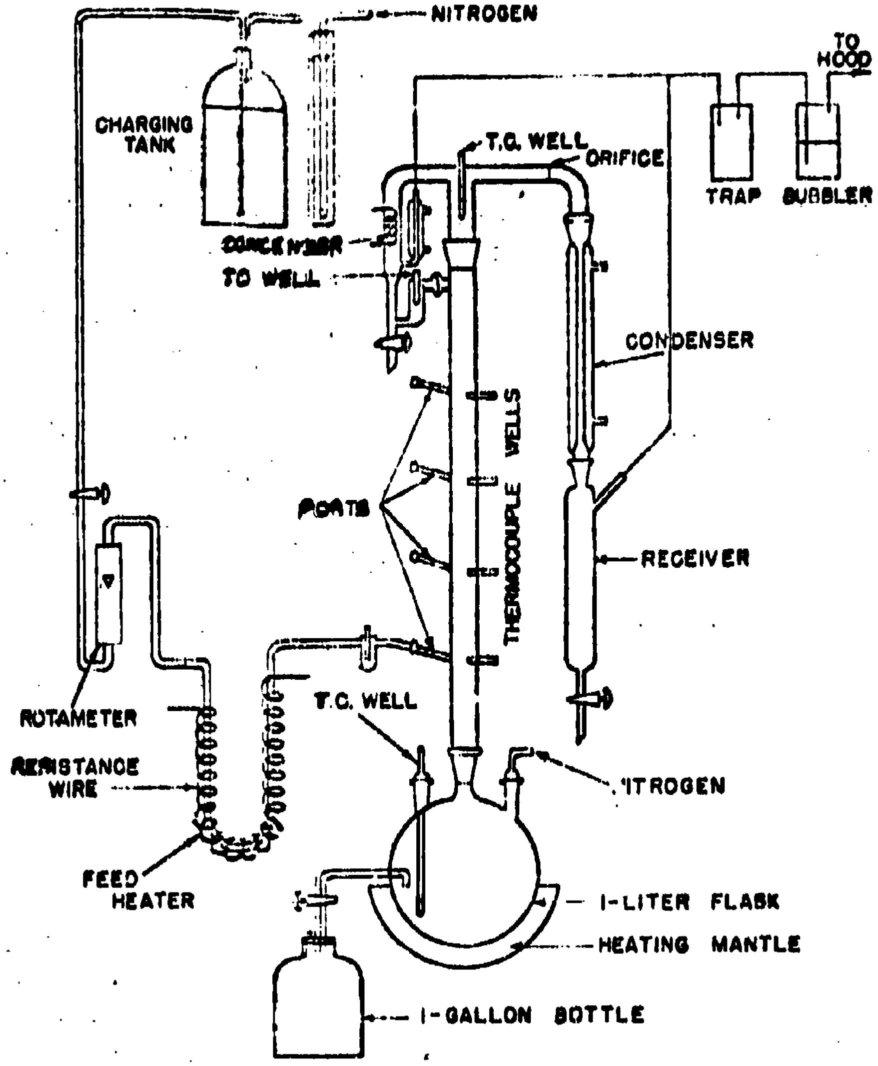


FIGURE 6. THE 2-INCH DISTILLING COLUMN

[illegible]
[illegible]

Each step in this process was performed both batchwise and continuously in the 2-inch column. In batchwise experiments, Step 2 was actually a continuation of Step 1 but, in continuous operation, it had to be carried out separately. Three continuous distillations were made on the first, or water-removal step. The fraction of the total water removed in these experiments was 65, 74, and 67 percent. The 74 percent figure may be somewhat high because of difficulty in adjusting the rate of feed at the beginning of one experiment. The bottoms from Step 1 were fed continuously to Step 2, where the overhead analyzed 87.3 percent hydrazine. This overhead was fed continuously to Step 3, where it was distilled to remove anhydrous hydrazine overhead. Over 500 grams of material analyzing 39.9 percent hydrazine was produced in this series of experiments. The same column, incidentally, was used in all three steps. The intermediate products were stored and used as feed for the subsequent steps. All hydrazine analyses were made by the method of iodate titration described by Penneman and Audrieth(3).

Proposed Process

Figure 7 is a line drawing of a pilot plant distillation for carrying out this distillation process. The feed to Column 1 contains 20 percent of the hydrazine-water azeotrope and 80 percent aniline. (Possibly 70 percent aniline would give better results.) All the aniline charged is recycled, except a small quantity lost because of its solubility in water. The first column removed about 60 percent of the water charged to the column, as overhead in the form of the aniline-water azeotrope. This is a conservative estimate, since a larger fraction of water has been removed experimentally. The water is separated from the aniline in a phase separator and discarded. The aniline is recycled. The balance of the hydrazine, water, and aniline is taken off as bottoms and charged to Column 2. This column separates the entrainer (aniline) from the 83.4 percent aqueous hydrazine solution. The hydrazine solution is taken overhead, and the aniline bottoms are recycled to make up part of the feed to the first column. The enriched hydrazine solution from the second column is fed to Column 3, where it is separated into anhydrous hydrazine as overhead and the hydrazine-water azeotrope as bottoms. The bottoms, which contain about 40 percent of the hydrazine feed to the first column, are recycled.

Estimated steam costs for these three distillations were calculated to be less than one cent per pound of anhydrous hydrazine produced. These calculations were based on a steam cost of 60 cents per 1000 pounds of steam, a reflux ratio of 5 to 1 in all columns, and 60 percent water removal in the first column. Sizing the columns and determination of the optimum reflux ratios and

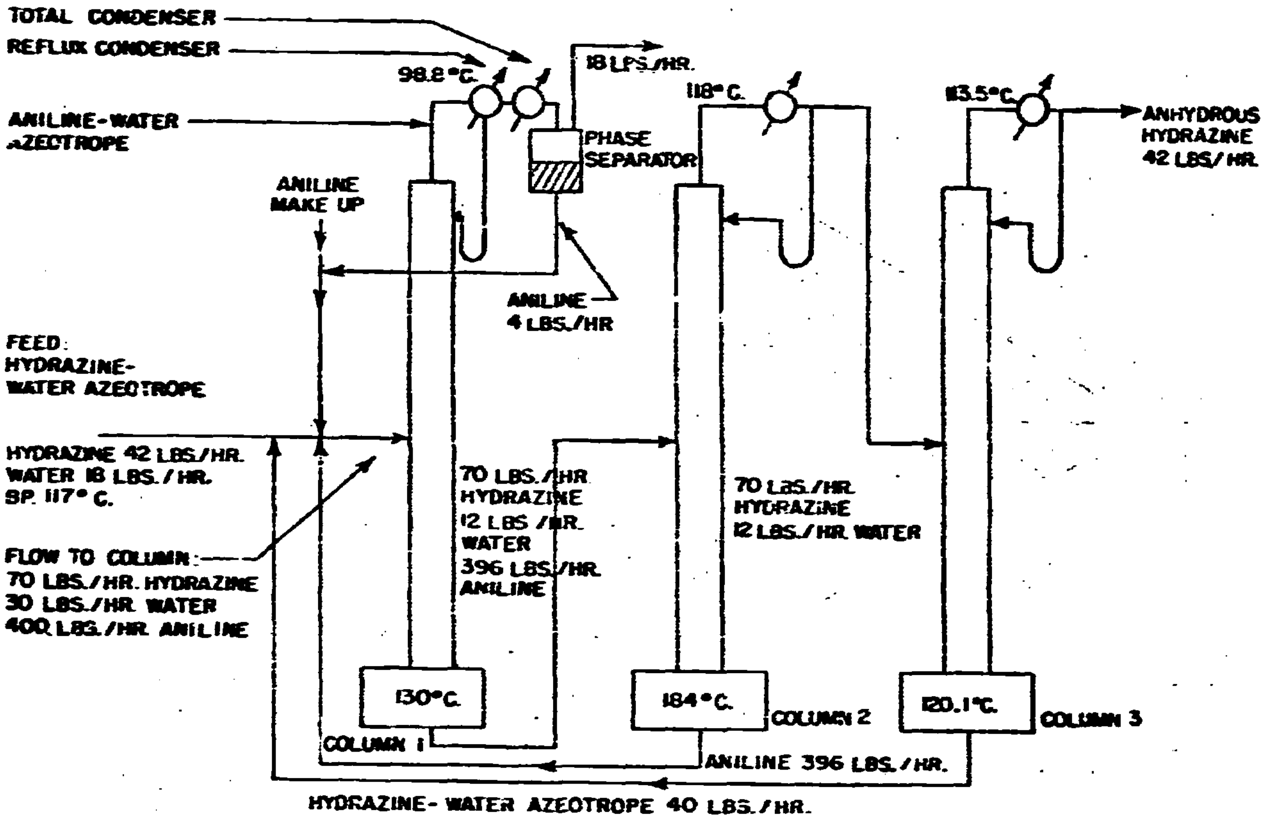


FIGURE 7. PROPROSED PROCESS FOR DEHYDRATING HYDRAZINE HYDRATE BY AZEOTROPIC DISTILLATION WITH ANILINE AS AN EXTRAINER.
BASIS: 42 POUNDS OF ANHYDROUS HYDRAZINE PER HOUR.

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number of plates for a commercial installation is beyond the scope of this paper. It requires detailed knowledge of the vapor-liquid equilibria in the ternary system hydrazine-water-aniline, for one thing. This we have determined, and it is the subject of another paper now in preparation.

A patent has been applied for on this method of dehydrating hydrazine solutions to produce anhydrous hydrazine.

This research was sponsored by the Mathieson Chemical Corporation at Battelle Memorial Institute. The authors wish to thank them for their permission to present the results at this meeting.

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HYDRAZINE FROM THE SOLVOLYSIS OF SEMICARBAZIDE

by

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The formation of hydrazine in substantially quantitative yield by the acid hydrolysis of semicarbazide has been reported by Harlay(1) and the hydrolysis in basic media has been suggested as a possible basis for the development of a practical process for the production of hydrazine(2). The formation of hydrazine sulfate by the hydrolysis of semicarbazide with dilute sulfuric acid(3), followed by ammonolysis of the resultant salt with liquid ammonia(4) appears to provide a route to substantially anhydrous hydrazine that is worthy of further study.

The production of hydrazine by a closed cycle process based upon the ammonolysis of semicarbazide by means of liquid ammonia has been considered(5) as a possibly practical method but there is no evidence that the reactions in question have been studied at all thoroughly. In this case, the separation of the hydrazine would be followed by recycling the urea to the well known steps required to produce semicarbazide.

The kinetics of the reactions involved in both the hydrolysis and ammonolysis of semicarbazide are currently under investigation in our laboratories. The present paper includes only an account of preliminary studies; work on the problem as a whole is far from complete.

EXPERIMENTAL

Pyrolysis of Semicarbazide. Since some of the temperatures anticipated for use in the study of the solvolysis of semicarbazide (m.p., 96°) were considerably above the melting point of this starting material, it seemed worthwhile at the outset to determine whether hydrazine results from the pyrolysis of semicarbazide or its hydrochloride under anhydrous conditions. Accordingly, dry semicarbazide hydrochloride was heated in a sealed tube at 105° for 13 hrs.; hydrazine was not produced. The same results were obtained when mixtures comprising one mole of semicarbazide and two moles of ammonium chloride were treated similarly. (It has been observed elsewhere(5) that hydrazine does not result from the thermal decomposition of semicarbazide hydrochloride at 260°.) When dry semicarbazide was heated for 13 hrs. at 105°, a 3-4 percent yield of hydrazine resulted.

Hydrolysis of Semicarbazide. Unless otherwise indicated, these reactions were carried out by refluxing 3.0 g. of semicarbazide hydrochloride in a known volume of either 3 or 6M sulfuric acid for the reflux times shown in Table 1. Thereafter, the reaction mixtures were cooled, hydrazine was separated by crystallization as the sulfate, and this was washed with ethanol, dried at 140°, and weighed. Yields were determined both by a spectrophotometric method(6) for total hydrazine formed and in terms of the weight of hydrazine sulfate isolated; the two methods gave results that were in good agreement.

Table 1

Effect of Time and Acid Concentration upon the Hydrolysis of Semicarbazide

Reflux Time (hrs.)	Hydrazine Yield (percent) as a Function of Volume and Molarity of Sulfuric Acid Used			
	3M		6M	
	15 ml.	30 ml.	15 ml.	30 ml.
0.25[a]				49
.5	27	30	76	91
.75				98
1.0	49	54		99
4.0		93		99

[a] Reaction vessel was cooled in ice water at end of reflux time.

Ammonolysis of Semicarbazide. The experimental methods employed in this case were essentially the same as those that have been described in connection with the study of the interaction of urea and ammonia(7). All ammonolysis reactions were carried out under strictly anhydrous conditions. In a typical case, 1.4 g. of semicarbazide hydrochloride and sufficient liquid ammonia (ca. 1 mole) to give a total solution volume of 25 ml. at -70° were placed in a glass tube which was subsequently sealed and heated in an autoclave at a known temperature for a predetermined period of time. At the end of the run, the ammonia was evaporated, the residual products were dissolved in water, and hydrazine was determined spectrophotometrically.

Exploratory experiments on the effect of time and temperature upon the yield of hydrazine showed that hydrazine is not formed after 30 hrs. at 25-30°, a 15 percent yield results after 13 hrs. at 75°, 34 percent after 13 hrs. at 90°, 43 percent after 13 hrs. at 105°, and 44 percent after 24 hrs. at the same temperature. Using the free base rather than the hydrochloride as the starting material, heating for 13 hrs. at 105° gave a 37 percent yield of hydrazine. Data relating to hydrazine yield as a function of time, temperature, and ammonium chloride concentration are given in Table 2.

The effect of added salts other than ammonium chloride was studied briefly; the resulting data are given in Table 3. Attention is called to the fact that in these runs, NH_4Cl was also present to the extent of 1 mole per mole of semicarbazide.

DISCUSSION

The preliminary experiments on the thermal decomposition of semicarbazide hydrochloride at 105° show that hydrazine is not formed under these conditions. Hence, hydrazine produced in the subsequent experiments must be attributable to solvolysis rather than simple thermal decomposition.

Optimum conditions for the quantitative hydrolysis of semicarbazide to hydrazine, ammonia and carbon dioxide appear to involve refluxing for one hour with 6M sulfuric acid (10 ml./g. of CH_6ON_3Cl). This reaction yields pure hydrazine sulfate. Although data on the ammonolysis of this product to yield hydrazine and ammonium sulfate are not sufficiently extensive for inclusion here, the work that has been done thus far indicates that this reaction will probably provide a nearly quantitative yield of substantially anhydrous hydrazine.

The work on the ammonolysis of semicarbazide hydrochloride is obviously incomplete; further experiments are in progress. It appears, however, that at 105° there results either an equilibrium the products of which are hydrazine, urea, and unchanged semicarbazide, or the formation of hydrazine together with another product that is not subsequently convertible to hydrazine, either in the presence or absence of ammonium salts. The data of Tables 2 and 3 show that the reaction is influenced little, if indeed at all, by the presence of appreciable concentrations of ammonium salts or sodium chloride.

ACKNOWLEDGEMENT

This work is supported by the U. S. Navy Bureau of Ordnance, Contract Nl[illegible]s-67363.

TABLE 2

Effect of Time, Temperature, and Ammonium Chloride Concentration upon the Yield of Hydrazine from the Ammonolysis of Semicarbazide with Liquid Ammonia at 105 C.

Time (hrs.)	[a]Total moles NH_4Cl/ mole CH_6ON_3Cl	N_2H_4 Yield, (percent)
1	1	24
3	1	33
6	1	39
	3	39
8.5	1	40
	3	40
13	1	43
	1.2	44
	1.5	44
	2	47
	3	48
24	1	44
	3	51

[a] Includes 1 mole of NH_4Cl arising from use of semicarbazide as the hydrochloride.

TABLE 3

Effect of Added Salts upon the Yield of Hydrazine from the Ammonolysis of Semicarbazide with Liquid Ammonia for 13 hrs. at 105°C.

Added Salt		
Formula	Moles/mole CH_6ON_3Cl	N_2H_4 Yield (percent)
NH_4Cl	3	48
NH_4Br	4	53
NaCl	5	46
NH_4NO_3	2	43
$(NH_4)_2SO_4$	5	52

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THE PHOTOLYSIS OF AMMONIA AT 1849 Å IN A FLOW SYSTEM*

by

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Presented by H. E. Gunning

ABSTRACT

An investigation has been made of the photolysis of ammonia at 1849 Å in a flow system at room temperature. The products of the reaction were found to be hydrazine, hydrogen and nitrogen. The rate of decomposition of ammonia was independent of the linear flow rate, but depended upon the ammonia pressure in the reaction zone. The fraction of ammonia decomposed which was recovered as hydrazine, while independent of ammonia pressure, increased markedly with increasing linear flow rate from zero in the static system to 0.84 at a linear flow rate of 1750 cm/sec.

It was found that the quantum yield of ammonia consumption under flow conditions was consistently higher by a factor of approximately two than for the static conditions at the same pressures.

A separate system was used to determine the extinction coefficient of ammonia at 1849 Å over the pressure range of the experiments. The value obtained was 1.21×10^3 liters-mole^{-1} cm^{-1}.

A mechanism has been proposed which is in qualitative agreement with the observed facts.

INTRODUCTION

The photolysis of ammonia has been extensively investigated in static systems, under which conditions the final products are nitrogen and hydrogen[1]. It is generally agreed that the primary process involves the formation of an amino radical and a hydrogen atom. The subsequent elementary reactions leading to the formation of stable products are apparently partially

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heterogeneous so that, despite many excellent studies made on the static photolysis, a definitive reaction mechanism has not been established.

Differences in the final products under flow conditions were found by Gedye and Rideal[2]. They obtained identifiable quantities of hydrazine as a third product in the flow system. Other investigators have also reported small or trace quantities of a reducing substance, presumable hydrazine, for the flow photolysis[3,4].

The present investigation was undertaken in the hope that some additional insight could be obtained into the mechanism of the reaction by a systematic study under flow conditions. The shorter wavelength resonance line of mercury, at 1849 Å, was chosen for the photolysis since it falls within the region of maximum absorption for ammonia[1]. In view of the fact that no previous photochemical studies have been made on ammonia at this wavelength, it was necessary to measure the extinction coefficient of ammonia at 1849 Å. In addition, data on the static reaction, for comparison purposes, have been obtained. The details of the investigation follow.

EXPERIMENTAL

Apparatus for Measuring the Extinction Coefficient of Ammonia at 1849 Å.

For these measurements an independent mercury-free high-vacuum system was used. The light source was a Hanovia "Biosteritron" mercury-in-quartz resonance discharge, operated by a Sola neon sign transformer with a 3000 volt, 30 Ma secondary, coupled with a Sola constant voltage transformer. Two absorption cells were used, a Hanovia Biosteritron cell, with path length of 0.02 ± 0.003 cm., and an Aminco precision quartz absorption cell, style F, class 3, with a path length of 1.0002 ± 0.0005 cm. A Westinghouse WL789 platinum cathode phototube, which shows no response above 2100 Å, was used to measure the intensity at 1849 Å. The minute currents from the phototube were conveniently measured with a Beckman Ultrohmeter. Satisfactory collimation was obtained by interposing sets of apertures between the lamp and cell, and between the cell and phototube. The lamp-cell-phototube assembly was rigidly mounted within a brass box, blackened on the inside with Kodacoat. During the measurements nitrogen was passed through the box to eliminate absorption of the 1849 Å radiation by oxygen in the optical path.

The absorption cell was connected to the manifold of the high-vacuum system. High vacua were achieved with a three-stage, all-glass, oil diffusion pump, backed by a Welch two-stage mechanical pump. Pressure measurements were made with an Alphatron radio-ionization gage for the low pressure region, and a mercury manometer, with the mercury in each limb covered by a 10 cm. layer of Octoil manometer fluid, for the high-pressure region.

The Light Source for the Photolyses

A mercury-in-quartz rare gas resonance lamp was designed for use as an internal source, eliminating thereby any air path between the light source and the reaction cell. The lamp is shown in Figure 1. It consisted essentially of a U-tube fabricated of 10 mm. I.D. Hanovia, S.R. grade optical quartz, with 1 mm. walls. The electrode arms were ring-sealed into the tubing attached to a male quartz 45/50 standard taper joint. One of the electrode arms was provided with a 5 mm. I.D. side arm for filling the lamp. The large male joint was fitted into a Pyrex reaction tube by means of a female, 45/50, Pyrex standard taper joint. The lamp, as finally used, contained a drop of mercury and 4 mm. of argon.

The discharge was maintained by a General Electric luminous tube transformer with a 5000 volt, 120 Ma secondary. The primary input to the transformer was stabilized by interposing a Sola constant voltage transformer between the line and the transformer primary. The lamp intensity could be changed by varying the primary voltage with a Variac transformer.

The lamp is essentially dichromatic, emitting the two resonance lines of mercury at 1849 Å and 2537 Å. Since ammonia is transparent at 2537 Å, the discharge can be regarded as a monochromatic source at 1849 Å, with respect to ammonia. During operation the lamp temperature did not exceed 40°C. The design of the lamp as an internal source was dictated by the fact that 1849 Å radiation is strongly absorbed by oxygen and furthermore is strongly absorbed by quartz. It was therefore necessary to eliminate the air path, and keep the thickness of quartz traversed by the radiation at a minimum to obtain photochemically useful intensities. Such an arrangement lacks the flexibility of the external collimated source; for example the zinc and cadmium spark sources in the 2100-2200 Å region used, among others, by Wiig[1] in his important series of studies on the static photolysis of ammonia.

The ammonia used throughout the investigation was the highest purity obtainable from the Matheson Company, East Rutherfor, N. J. It had a minimum purity of 99.5% and gave no test for the presence of trace quantities of hydrazine or other reducing materials.

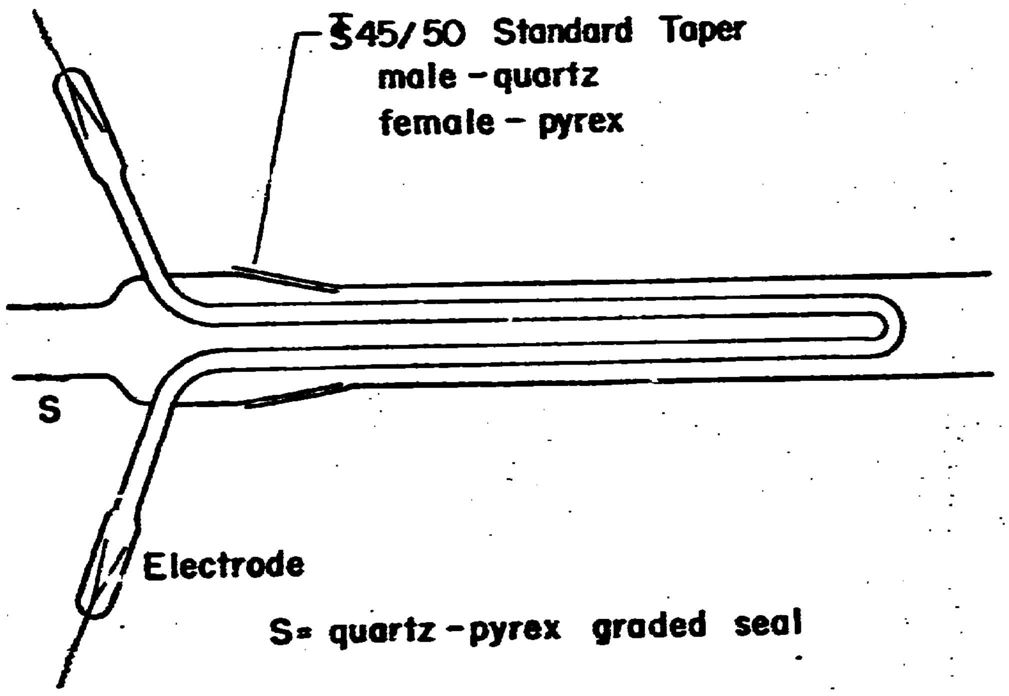

FIGURE I. THE LAMP SYSTEM

Flow Experiments at Atmospheric Pressure

The apparatus for these runs was briefly described in an earlier communication[5]. These preliminary runs were designed to ascertain whether the lamp would produce sufficient quantities of hydrazine for chemical characterization, and for accurate analytical determination. The ammonia, at atmospheric pressure and at a measured flow rate was allowed to traverse the irradiated zone of the lamp-cell assembly, whereupon it condensed together with any hydrazine formed on a large cold finger containing dry ice-acetone slush at -78°C. The liquid ammonia-hydrazine mixture dripped from the cold finger into a removable collector below through a drip tube. Sufficient liquid ammonia was condensed in the collector before the lamp was turned on to cover the exit of the drip tube. Excess ammonia gas was vented into a fume hood at such a rate that the liquid level in the collector remained constant during an experiment. The flow rate of ammonia was measured by a capillary manometric flow meter.

In one series of experiments, a trap containing hydrazine of determined purity was connected to the apparatus described above so that the hydrazine was injected into the flow stream at a point before the irradiation zone. This trap was maintained at 0°C. by an ice-water bath. Both ammonia and nitrogen were used as carrier gases to sweep the hydrazine through the system so that its photolytic decomposition could be studied. The amount of hydrazine passed through the system was determined by the change in the weight of the trap containing hydrazine. The amount of hydrazine swept over was sufficiently large so that the quantity of hydrazine produced by the photolysis of the ammonia carrier gas was negligible. When ammonia was used as the carrier gas the effluent gases passed through liquid ammonia, but when nitrogen was used as the carrier gas the gases passed through a dilute solution of hydrochloric acid.

The hydrazine in the collector flask was analyzed by titration as described in the following section.

Flow Experiments in the Closed System

This part of the investigation was designed to study variations in the rates of formation of hydrazine, hydrogen and nitrogen as a function of reaction pressure and linear flow rate in the photolysis of ammonia. A large number of modifications of the original system were made during the course of the investigation to improve the precision of the analyses of the products and to obtain better control of the flow variables. The final modification of the apparatus, and that which was used for the main body of results to be reported here, is shown in Figure 2.

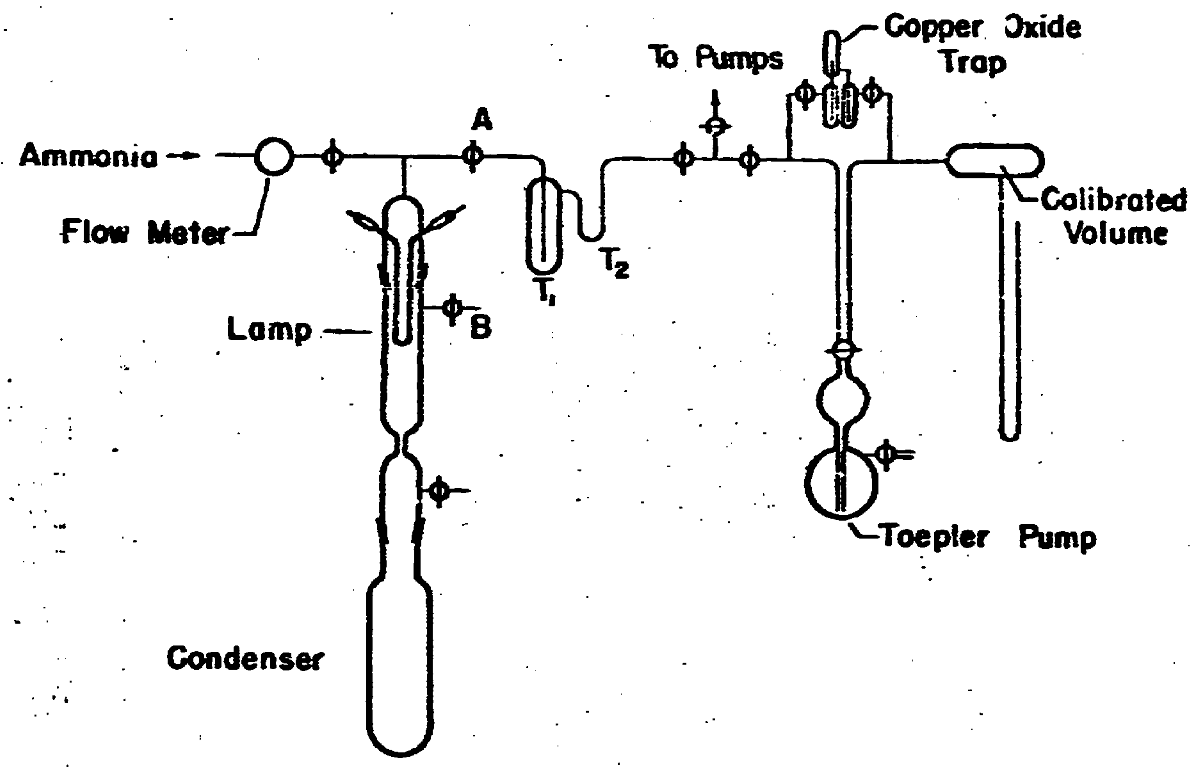

FIGURE 2. FLOW PHOTOLYSIS APPARATUS

The system was evacuated by a two-stage mercury diffusion pump, backed by a Welch Duoseal mechanical pump. Traps T1 and T2 were kept immersed in liquid nitrogen whenever stopcock A, leading to the photolysis system, was opened. Previous work had shown that under these conditions no mercury photosensitization occurs in the reaction system.

The lamp was operated at a current of 90 Ma, using a Variac transformer to control the current. The pressure measurements were made with an Alphatron radio-ionization gage, and an Octoil-mercury manometer as in the absorption measurements. The pressure measuring devices were connected to the system via stopcock D.

Variations in linear flow rates were achieved by altering the diameter of the orifice immediately below the lamp-cell assembly.

The mass flow of ammonia through the system was read from a calibrated Hoke flow meter covering the range from 5 to 35 cu.ft./hr. for ammonia. The inlet needle valve was used to vary the mass flow rate.

Before making an experiment the system was evacuated and the condenser flask was surrounded with liquid nitrogen. The system was flushed out with ammonia to saturate the walls and was evacuated again. The lamp was then turned on and warmed up to constant intensity. Isolation of the photolysis system was achieved by closing stopcock A. An electric timer was started simultaneously with the flow of ammonia through the reactor via the flow meter. The liquid nitrogen was maintained at a fixed level about the condenser flask in which the ammonia was condensed. At the end of the run the timer and lamp were shut off. Ammonia was allowed to flow for several more minutes while the walls of the reaction system were gently heated to drive off adsorbed hydrazine.

After the ammonia flow had been stopped, the condensables were frozen down for an additional hour. The non-condensables were transferred to a calibrated volume by the Toepler pump and their pressure in this calibrated volume was measured. Hydrogen was removed by combustion over cupric oxide, deposited on glass wool. The resulting water vapor was frozen out in a trap surrounded by liquid nitrogen. The pressure of the residual gas was measured in the calibrated volume and was assumed to be nitrogen. Repeated blank runs showed that no detectable quantities of non-condensables were present in the original ammonia.

For the hydrazine analysis, the condenser was removed and the ammonia allowed to evaporate until only a few ml. remained. It was found that up to 10% of the hydrazine could be carried off with the volatilising ammonia. Tests showed that the loss of hydrazine could be prevented simply by allowing the effluent vapor to bubble through a trap containing distilled water. The residue in the condenser and the contents of the water trap were combined, diluted with water and acidified with concentrated hydrochloric acid. This solution was made up to a known volume and aliquots were titrated with 0.1 N potassium iodate following the method of Penneman and Audrieth[6]. Analyses made with synthetic solutions of hydrazine at concentrations similar to those obtained in the photolyses showed that the error in the titrations did not exceed 2%.

Static Experiments

To compare relative quantum yields under static and dynamic conditions, a series of runs was done in the above apparatus under static conditions.

A sample of ammonia was subjected to two trap-to-trap distillations, a middle fraction being saved in each case. The desired pressure of ammonia was admitted to the system from a storage reservoir and the photolysis was carried out on the static sample with the condenser at room temperature. At the end of a run the non-condensable and condensable products were analysed in the same manner as in the flow runs. It should be noted that the results obtained with the ammonia, which had been subjected to two trap-to-trap distillations, were identical, within experimental error, to those found for the ammonia taken directly from the tank.

A static photolysis was also done on hydrazine to determine whether it was decomposed by 2537 Å radiation. A sample of Matheson's anhydrous hydrazine was thoroughly degassed and the hydrazine vapor, at 14 mm. pressure, was admitted to an evacuated quartz tube attached to a mercury-free vacuum system. The tube was closed off from the liquid hydrazine and was exposed to the radiation from a mercury resonance lamp fashioned of Vycor 7910. The Vycor glass removes 1849 Å radiation but transmits 2537 Å radiation. At the end of the experiment, a side arm from the tube was immersed in dry ice and acetone for 30 minutes. The non-condensable products were transferred by Toepler pump to a calibrated volume and measured. These gases were then passed through a trap at liquid nitrogen temperature to remove ammonia and the residual non-condensable gas was analyzed for nitrogen and hydrogen as in the ammonia photolysis experiments.

RESULTS

The Extinction Coefficient of Ammonia at 1849 Å

The extinction coefficient, $\mathcal{E}$, is defined by the relation

$$I_t \equiv I_o\, 10^{-\mathcal{E}cd}.$$

where I_o and I_t are the intensities of the 1849 Å radiation incident on and transmitted through the quartz absorption cell containing ammonia. The optical path length through the ammonia at a concentration of c moles/liter is d cm.

In Figure 3, the results of absorption measurements using the Aminco cell with d = 1.0002 cm. are shown as a plot of $\frac{\log I_o/I_t}{d}$ vs. c. The left hand ordinate figures and the lower abscissa figures represent the results for the 1.000 cm. cell. The concentration range corresponds to ammonia pressures from 1 to 40 mm. Within experimental error the points fall on a straight line the slope of which gives a value of $\mathcal{E}$ of 1.21×10^3 liters-moles^{-1} cm^{-1}.

The absorption of ammonia in the range from 40 to 200 mm. was measured with the Hanovia quartz cell which had a d value of 0.02 ± 0.003 cm. The values of $\mathcal{E}$ calculated therefrom agree within experimental error with the value reported for the 1.000 cm. cell. Beer's Law is therefore obeyed at least over the range from 1 to 200 mm. pressure of ammonia.

From the value, 1.21×10^3 liters-moles^{-1} cm^{-1} for the extinction coefficient, and the geometry of the reactor, it was estimated that a minimum ammonia pressure of 8-10 mm. was required for complete absorption of the 1849 Å radiation.

Preliminary experiments on the absorption of 1849 Å radiation by hydrazine indicate that the extinction coefficient is about six times as large as the corresponding ammonia value.

Flow Experiments at Atmospheric Pressure

The results obtained in these experiments are summarized in Table 1.

The hydrazine formed in the reaction was characterized by preparing the derivative with benzaldehyde. The benzalazine obtained had a melting point of 91-92°C. in agreement with reported values for the melting point of this compound. Furthermore,

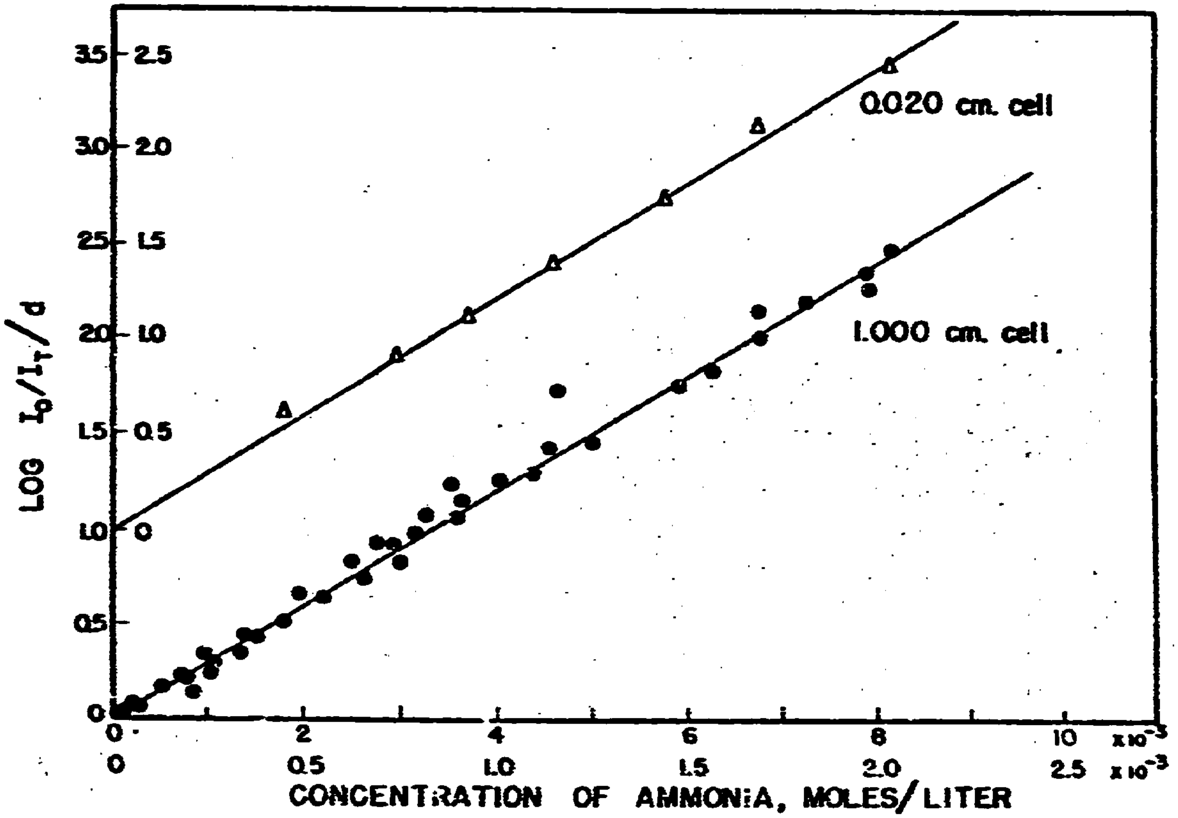

FIGURE 3. THE EXTINCTION COEFFICIENT OF AMMONIA AT 1849 Å

mixed melting point determinations, made by admixing a pure sample of benzalazine, showed no depression of the melting point.

These experiments showed that the system was capable of producing hydrazine in sufficient quantities for accurate analysis. The rates of hydrazine formation are in agreement with those in the closed systems if the pressure and linear flow rates used are considered. The linear flow rate in these experiments was about 7 cm/sec.

Table 1

Production of Hydrazine in the Photolysis of Ammonia at 1849 Å in an Open Flow System at Atmospheric Pressure.

Mass Flow Rate moles/hr.	Lamp Current MA	Rate of Hydrazine Formation moles/hr.x10^4
7.7	30	0.32
13.4	30	0.39
13.4	115	0.85

Flow Photolysis of Hydrazine

The results of the experiments in which hydrazine was swept through the irradiated zone by a carrier gas are recorded in Table 2.

The amount of hydrazine passing the lamp per unit time was about 100 times greater in these experiments than the amount produced in unit time in the ammonia photolysis. It should be emphasized that the hydrazine may be decomposed by the 2537 Å radiation from the lamp as well as by the 1849 Å radiation. When the runs were repeated with the lamp off, no hydrazine was decomposed. The accuracy of the measurement of the hydrazine decomposed is estimated to be ± 5%.

These runs, while of a qualitative nature, show that hydrazine is extensively decomposed on flowing through the irradiated zone.

Table 2

The Photolysis of Hydrazine in the Presence of a Carrier Gas at Atmospheric Pressure

Mass Flow Rate of Carrier Gas moles/hr.	Carrier Gas	Hydrazine Flow Rate moles/hr.x10^4	Hydrazine Decomposed %
13.4	NH_3	49	24
13.4	NH_3	32	20
13.4	N_2	46	27

The Flow Photolysis of Ammonia in the Closed System

The mass flow rate of ammonia was converted to volume flow at the temperature and pressure of the reaction zone. This quantity divided by the cross-sectional area of the irradiated zone gave the linear flow rate of the ammonia.

In the range of mass flow rates and ammonia pressures used the linear flow rate depends essentially on the resistance to flow of the tubing between the lamp and the ammonia condenser. Thus, the linear flow rate could be varied by changing the diameter of an orifice in this tubing. With a given orifice size, the pressure rise in the reaction zone on increasing the mass flow rate was just that required for the linear flow rate to remain constant. Fluctuation of the calculated linear flow rate for one orifice size at various mass flow rates in the results may therefore be attributed to error in the readings of the mass flow rates and reaction pressures.

The linear flow rates were varied from 7.05 to 11,150 cm/sec. The contact time for the gas in the irradiated zone obtained by dividing the length of the irradiated zone (26 cm.) by the linear flow rate varied from 3.69 to 2.33x10^{-3} sec.

In the analysis of the products, the amounts of the total non-condensable gas, the nitrogen and the hydrazine produced per unit time were measured. Two quantities of interest can be calculated from these data using the stoichiometric equations

$$2NH_3 \dashrightarrow N_2 + 3\,H_2$$

$$2\,NH_3 \longrightarrow N_2H_4 + H_2$$

1. The apparent amount of ammonia decomposed is given by twice the sum of the hydrazine and nitrogen produced.

2. The fraction of the ammonia decomposed which is recovered as hydrazine is given by the ratio of the hydrazine to the sum of the hydrazine and nitrogen.

Since the total non-condensable gas minus the nitrogen gives the quantity of hydrogen produced, the amount of hydrazine produced can be calculated from the gas analysis only since from the stoichiometry

$$(N_2H_4) = (N_2 + H_2) - 4(N_2)$$

It was found that more accurate values for the amount of hydrazine produced were obtained by calculation from the gas analysis in the above manner than by recovery and titration of the hydrazine. Both procedures were followed in each run, but the value for the hydrazine used in calculating the ammonia decomposed and the percentage of the decomposed ammonia recovered as hydrazine was the value calculated from the gas analysis. The error in the recovery and titration of the hydrazine was shown to arise largely from loss of hydrazine in the evaporation of the liquid ammonia. When the ammonia was bubbled through water in the later runs, and this water was added to the residual hydrazine, the measured and calculated amounts of hydrazine agreed within about 5%.

A summary of the results of the flow photolysis of ammonia in the closed system is given in Table 3. The runs are grouped according to the orifice size (i.e., with the same linear flow rate). Within the groups, the mass flow rate and hence the reaction pressure was varied over the range permitted by the apparatus.

It is evident that the percentage of the decomposed ammonia which is recovered as hydrazine (% hydrazine) is essentially independent of the reaction pressure at any given linear flow rate but increases with the linear flow rate. The percentage conversion to hydrazine and linear flow rate values were averaged in each group. Figure 4 is a plot of percentage conversion to hydrazine vs. log (linear flow rate) based on these averaged results. A relationship, which is approximately linear, is obeyed up to a linear flow rate of about 1750 cm/sec., at which value the conversion is about 34%. Runs 31 and 32 were carried out at considerably higher linear flow rates but the conversion did not increase. To achieve these high linear

Table 3 Results from the photolysis of ammonia at 1849 Å in a closed flow system.

Run No.	Mass Flow Rate moles/hr.	Reaction Pressure mm.	Linear Flow Rate m/sec.	Total Gas per hr. moles x10⁴	N_2 per hr. moles x10⁴	Measured hydrazine per hr. moles x10⁴	Ammonia Decomp. per hr. moles x10⁴	% Hydrazine
30	12.7	560.	7.05	13.15	2.91	1.27	8.22	36.2
28	12.7	183.	21.0	14.07	2.87	2.30	10.92	47.4
25	12.7	52.2	75.3	15.51	2.90	3.50	13.82	53.
26	25.3	104.	76.2	13.23	2.59	3.11	10.92	53.6
27	38.2	159.	76.6	11.62	2.18	2.71	10.16	57.2
24	6.33	22.5	87.7	16.60	2.85	4.45	14.50	61.7
20	19.0	56.8	104.	14.62	2.62	4.06	13.52	61.2
21	31.7	94.0	105.	12.85	2.34	3.23	11.66	55.9
23	38.2	112.	106.	11.91	2.35	3.00	9.72	51.7
22	44.3	131.	106.	11.75	2.33	----	9.52	51.0
18	12.7	13.8	235	15.12	2.35	4.30	16.40	71.4
19	19.0	20.3	232	15.21	2.38	4.90	16.14	70.5
13	25.3	26.9	291	15.35	2.45	5.19	16.00	73.4
14	31.7	34.5	279	13.99	2.15	4.78	15.08	71.6
15	38.2	40.6	235	13.46	2.06	5.04	14.56	71.8
16	44.3	48.2	284	12.88	1.82	4.56	14.84	75.5
5	19.0	6.51	803	12.80	1.56	5.53	16.75	81.5
6	25.4	11.6	685	13.97	1.60	6.34	18.34	82.5
8	38.2	15.7	755	14.39	1.69	6.34	16.70	76.0
9	44.3	19.2	721	14.42	1.64	7.08	17.84	79.3
29	44.3	8.	1750	15.07	1.59	8.03	20.60	84.7
2	44.3	7.5	1850	12.82	1.25	7.55	18.14	85.2
3	44.3	7.5	1870	12.96	1.06	6.96	16.94	82.2
31	12.7	0.5→2.5	7810→1580	4.30	0.48	----	5.72	83.3
32	25.3	.79→.85	11,150→9200	3.28	0.41	.66	4.10	80.1

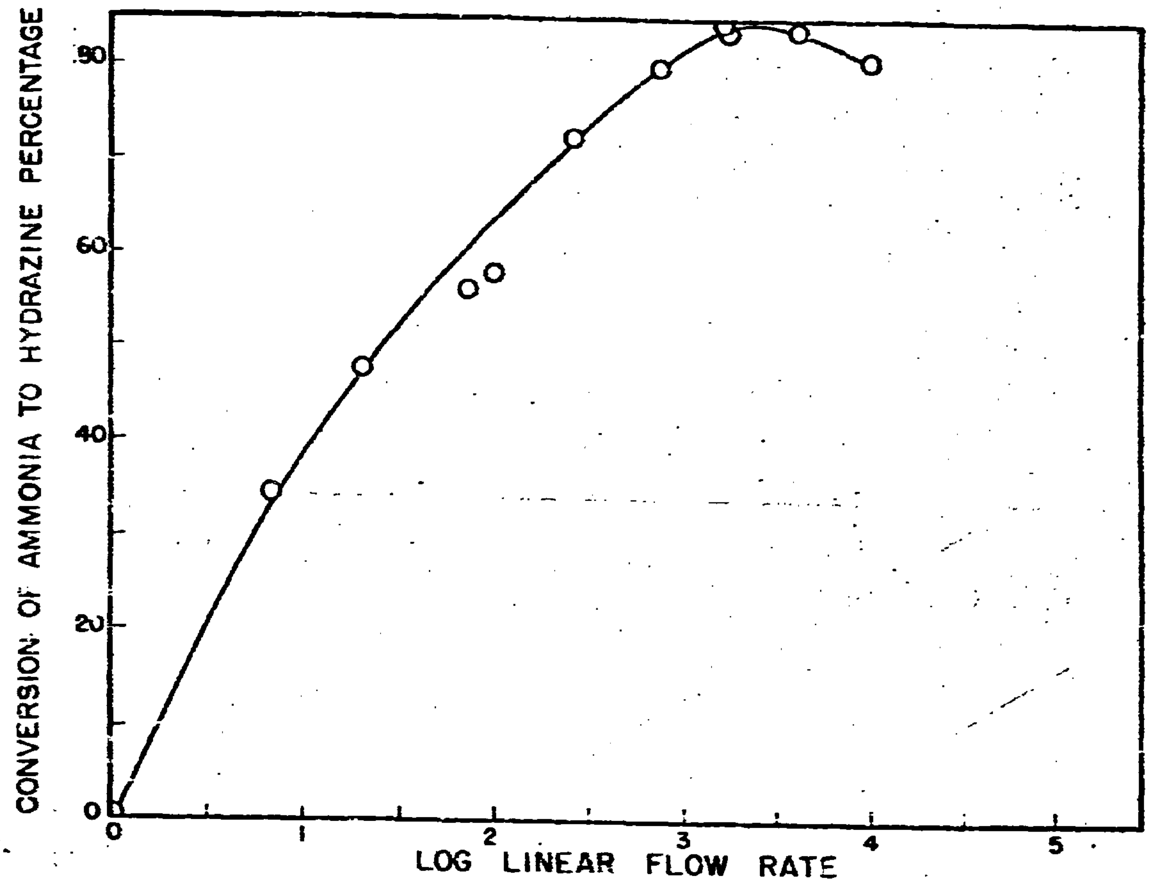

FIGURE 4. CONVERSION OF AMMONIA TO HYDRAZINE.

flow rates, these runs had to be carried out at such low reaction pressures that there was incomplete absorption of the 1849 Å radiation. Small amounts of non-condensable gas were therefore obtained and the error in analysis was larger than in the other runs. Thus it is not clear whether the % hydrazine would increase to 100% with high linear flow rates or whether it does in fact level off at about 84%.

The amount of ammonia decomposed in each run was plotted against reaction pressure in Figure 5. The points fall on a smooth curve, independent of the linear flow rate of the run. Thus the relative quantum yield for ammonia decomposition is independent of linear flow rate and has a constant value of about 10×10^{-4} moles/hr. from 100 mm. to 560 mm. pressure of ammonia in the reaction zone (Run 30 at 560 mm. pressure is not shown in Fig. 5). At lower pressures, the relative quantum yield rises rapidly to a value almost twice that at 100 mm. Below about 10 mm. pressure there is incomplete absorption of the 1849 Å radiation and therefore the ratio falls off.

For the runs reported in Table 3, the surface-to-volume ratio in the zone between the lamp and the orifice was 0.95 cm^{-1}. Two experiments were made with this zone packed with Pyrex rods, thereby increasing the surface-to-volume ratio to 8.65 cm^{-1}. The results for these runs are given in Table 4 together with the comparable data for the unpacked system.

While these experiments, in which the surface-to-volume ratio was changed, were not extensive, the results indicate that neither the amount of ammonia decomposed nor the percentage conversion to hydrazine was greatly affected by packing the volume immediately following the radiation zone.

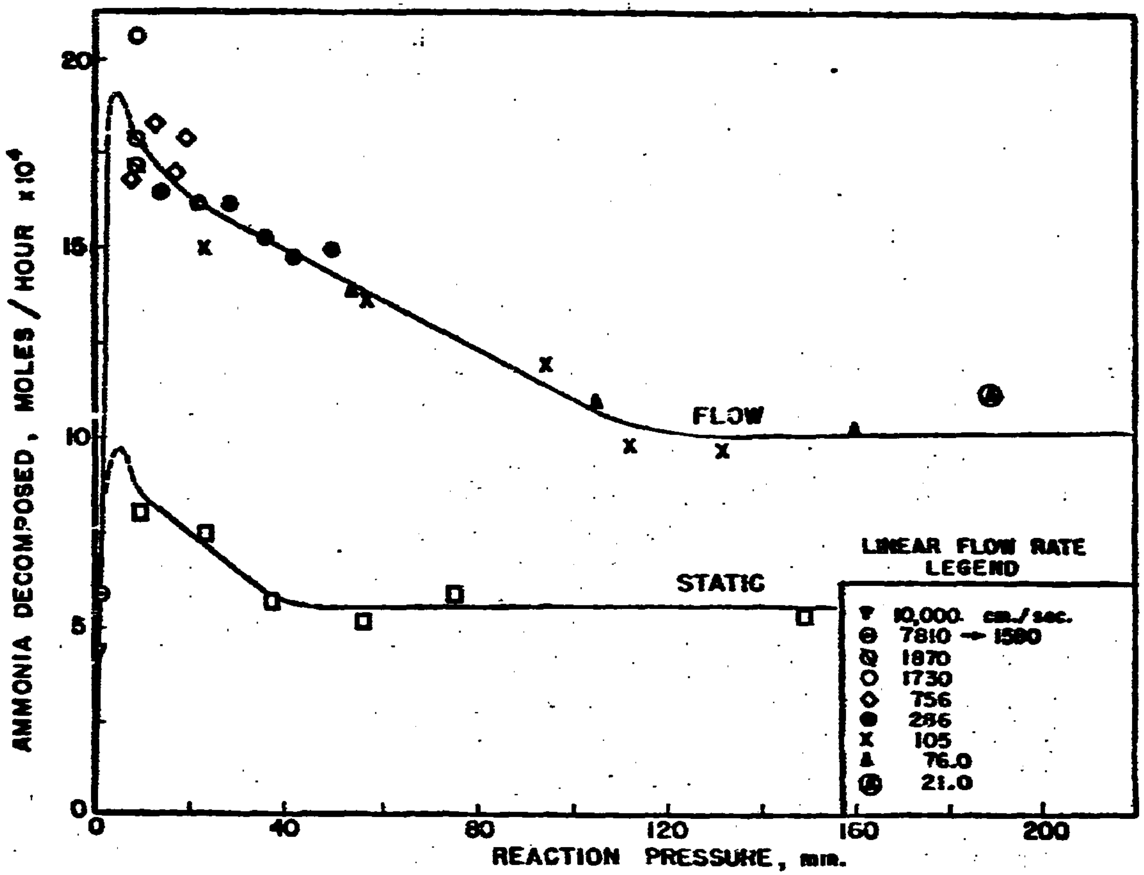

FIGURE 5. RATE OF AMMONIA DECOMPOSITION AS A FUNCTION OF PRESSURE

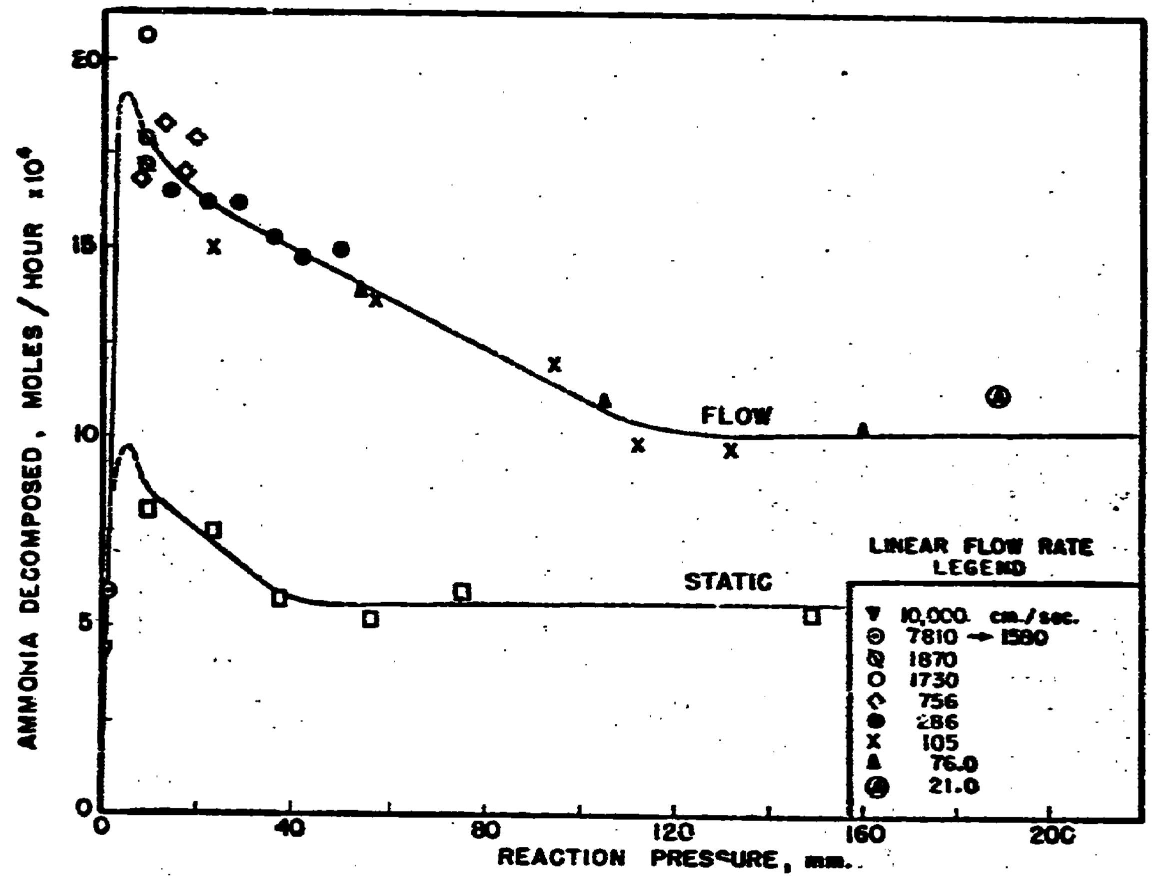

FIGURE 5. RATE OF AMMONIA DECOMPOSITION AS A FUNCTION OF PRESSURE

Table 4

Effect of Altering Surface-to-Volume Ratio

Run No.	Mass Flow Rate moles/hr.	Reaction Pressure mm.	Linear Flow Rate cm/sec.	Total Gas/hr. molesx10^4	N_2/hr. molesx10^4	Measured N_2H_4/hr. molesx10^4	Ammonia Decomposed per hr. molesx10^4	% Hydrazine
33	25.3	15.8	455	14.76	1.83	7.04	18.30	80.0
Unpacked		15.8	495				17.00	77.0
34	31.6	56	159	12.92	2.00	5.32	13.84	71.1
Unpacked		56	159				13.75	67.5

Static Photolysis of Ammonia at 1849 Å

The summary of the analyses of the non-condensable products of a series of static photolyses of ammonia is given in Table 5. The condensable residue gave no test for hydrazine.

Table 5

The Static Photolysis of Ammonia at 1849 Å

Ammonia Pressure mm.	Total Gas per hr. moles x10^4	% N_2 in total gas	Ammonia Decomposed per hr. moles x10^4
10	16.14	25.0	8.07
24	15.12	25.0	7.56
38	11.41	25.0	5.71
57	10.60	24.8	5.30
76	11.80	--	5.90
150	10.52	--	5.26
264	11.70	--	5.70

The relative quantum yield for ammonia decomposition is plotted as a function of pressure in Figure 5. The same pressure variation as in the flow runs was observed. At comparable pressures the relative quantum yield in the static system is about half the value obtained in the flow system.

The fact that the nitrogen is almost exactly 25% of the total non-condensable product indicates the absence of hydrazine and shows that the gas analysis is reliable.

The products of the static photolysis of hydrazine at 14 mm. pressure by 2537 Å radiation were in exact agreement with the following equation.

$$2\ N_2H_4 \longrightarrow 2\ NH_3 + H_2 + N_2$$

In a similar experiment with no radiation, no hydrazine was decomposed. The light intensity at 2537 Å was 4×10^{-4} einsteins/min. and 5×10^{-6} moles of hydrazine were decomposed per minute. If the quantum yield of the hydrazine decomposition was about 2, as found by Wenner and Beckman[7] the rate of radiation absorption was 2.5×10^{-6} einsteins/min. From the cell geometry, the percentage absorption of the 2537 Å radiation, and the hydrazine pressure the extinction coefficient of hydrazine at 2537 Å was estimated to be 5 liters-mole^{-1} cm.$^{-1}$.

DISCUSSION

Any discussion of the mechanism of the secondary reactions in the photolysis of ammonia at 1849 Å must be in consonance with the following facts:

(1) The rate of ammonia decomposition in the flow system is independent of linear flow rate.

(2) From 560 mm. to 100 mm. pressure the rate of ammonia decomposition is constant. At lower pressures the rate rises to a value which is almost twice the rate at 100 mm. pressure. Below 10 mm. pressure the rate of decomposition decreases again because of incomplete absorption of the 1849 Å radiation.

(3) The percentage conversion of the ammonia to hydrazine is independent of the reaction pressure but increases almost linearly with the logarithm of the linear flow rate. This conversion increases from zero in the static system to 84% at a linear flow rate of 1750 cm/sec. but may not increase further at greater flow rates.

(4) The rate of ammonia decomposition in the flow system is about twice that in the static system at the same pressure. This relationship holds over the whole of the pressure range investigated.

(5) A tenfold increase in the surface-to-volume ratio in the zone immediately following the irradiated zone has very little effect on the rate of ammonia decomposition or on the conversion to hydrazine.

(6) The extinction coefficient for ammonia at 1849 Å is 1.21×10^3 liters-moles^{-1} cm^{-1} between 1 mm. and 200 mm. pressure. The extinction coefficient of hydrazine at 1849 Å is about six times that for ammonia and at 2537 Å has a value of about 5 liters-moles^{-1} cm^{-1}.

(7) When hydrazine was passed through the flow system at a pressure some one hundred times greater than the partial pressure of hydrazine in the ammonia photolysis experiments, twenty-five percent of this hydrazine was decomposed by photolysis.

(8) The static photolysis of hydrazine at 2537 Å obeyed

the equation

$$2\ N_2H_4 \longrightarrow 2\ NH_3 + N_2 + H_2$$

(9) If the static quantum yield for ammonia decomposition at 100 mm. is about 0.25 as proposed by Wiig and others[1], then the quantum yield in the flow system approaches unity at low pressures.

The investigation of the flow photolysis of ammonia has shown that hydrazine and hydrogen can be the major products of the reaction. The percentage of the decomposed ammonia that is recovered as hydrazine depends only on the linear flow rate of the ammonia through the system. An increase in the linear flow rate dilutes the radicals and products of the reaction with ammonia and also causes them to spend a shorter time in the irradiated zone. Dilution of the radicals and hydrazine would decrease the decomposition of hydrazine by radical attack if the radicals also disappear on collision with the wall. A decrease in the hydrazine partial pressure and a shorter contact time in the irradiated zone would lead to less photolysis of the hydrazine by the 1849 Å and 2537 Å radiation. It seems probable, therefore, that the relatively large amounts of nitrogen obtained at low linear flow rates arise from the decomposition of hydrazine either by photolysis or by radical attack. Some nitrogen may also arise by an independent reaction path since the minimum conversion of ammonia to nitrogen was 15%.

The overall quantum yield of ammonia decomposition appears to approach unity at low pressure in the flow system. It is probable, therefore, that the primary quantum yield for the photolysis of ammonia into hydrogen atoms and amino radicals is unity. The lower experimental quantum yields then arise from ammonia reforming steps. These steps are pressure dependent but are independent of the linear flow rate. Since the conversion to hydrazine does depend on the linear flow rate, the decomposition of hydrazine in the flow system does not produce ammonia. The hypothesis that the hydrazine produced is partially decomposed in the flow system by photolysis was examined. It was shown that, when relatively large amounts of hydrazine were swept through the system by nitrogen or ammonia, twenty-five percent of the hydrazine was decomposed. Moreover, 2537 Å radiation decomposed hydrazine to produce ammonia, hydrogen and nitrogen.

First the possibility of hydrazine photolysis by the 1849 Å radiation was investigated. The assumption was made that the rate of ammonia decomposition (1.5x10^{-}[illegible] moles/sec.) at 100 mm. pressure in the static system represented a quantum yield of 0.25. The 1849 Å radiation intensity incident on the flowing gas was therefore 6.0×10^{-7} einsteins/sec. Next, it was necessary to calculate the maximum possible partial pressure of hydrazine in the flow stream at various linear flow rates. It was assumed that the initial step was

$$NH_3 + h\nu_{1849} \longrightarrow NH_2 + H$$

with a quantum yield of one and that all the amino radicals recombined to give hydrazine. The maximum rate of production of hydrazine was, therefore, 3.0×10^{-7} moles/sec. From the volume flow rate of the ammonia through the reaction zone, it is possible to calculate the volume in which this amount of hydrazine was distributed, assuming a uniform distribution, and hence the partial pressure of the hydrazine in the flow stream. This partial pressure varied from 4.8×10^{-2} mm. at a linear flow rate of 7 cm/sec. to 2.5×10^{-5} mm. at a flow rate of 10,000 cm/sec.

If the ammonia and hydrazine are in competition for the 1849 Å radiation, the absorption equation is given by the following equation

$$I_t = I_o \, 10^{-\varepsilon_1 c_1 d - \varepsilon_2 c_2 d}$$

1 represents ammonia
2 represents hydrazine

The fraction of the 1849 Å radiation available to the hydrazine is approximately $\varepsilon_2 c_2 / \varepsilon_1 c_1$. For the experiment with the highest partial pressure of hydrazine in the flow stream this fraction is 5×10^{-4}.

Thus 3×10^{-11} einsteins/sec. were available to the hydrazine, and if the quantum yield for hydrazine decomposition was unity, less than .01% of the hydrazine produced was photolyzed.

The mercury lamp puts out about ten times as much radiation at 2537 Å as at 1849 Å and at this wavelength the ammonia does not compete with the hydrazine for the radiation. The possibility of photolysis of the hydrazine by 2537 Å radiation was therefore examined. Using a value of 6×10^{-6} einsteins/sec. as the input intensity of 2537 Å radiation, the extinction coefficient from the static photolysis of hydrazine (5 liters-mole^{-1} sec.$^{-1}$) and the calculated partial pressure of hydrazine in the slowest linear flow rate experiment, it was calculated that less than 1% of the hydrazine could be decomposed by the 2537 Å radiation. This result was not in conflict with the experiments in which hydrazine was decomposed when swept through the lamp zone in a carrier gas because in these experiments the partial pressure was about one hundred times greater than in the ammonia photolysis experiments. The same method of calculation, when applied to these hydrazine flow runs, predicts that 26% of the hydrazine should be decomposed.

As a result of the above calculations it seems reasonable to say that the photolysis of hydrazine in the flow system cannot account for the decomposition of hydrazine and thus the hydrazine must be decomposed as a result of radical attacks.

In view of the experimental results and calculations discussed above, the following reaction mechanism was adopted as the basis for a qualitative explanation of the flow photolysis of ammonia.

(1) $NH_3 + h\nu_{1849} \longrightarrow NH_2 + H$

(2) $H + NH_2 \longrightarrow NH_3^*$

(3) $NH_3^* + M \longrightarrow NH_3 + M$

(4) $NH_3^* \longrightarrow NH_2 + H$

(5) $NH_2 + NH_2 \longrightarrow N_2H_4$

(6) $N_2H_4 + H \longrightarrow N_2H_3 + H_2$

(7) $N_2H_3 + H \longrightarrow N_2 + 2\ H_2$

(8) $N_2H_3 + N_2H_3 \longrightarrow 2\ NH_3 + N_2$

(9) $H + \text{wall} \longrightarrow 1/2\ H_2 + \text{wall}$

According to this mechanism, if hydrazine is a product of the reaction, there is an excess of hydrogen atoms which diffuse to the wall and form molecular hydrogen. The amino radicals are removed rapidly by combination to hydrazine, whereas the homogeneous recombination of hydrogen atoms requires a three body collision and is therefore negligible. Since there is an excess of hydrogen atoms, the attack of amino radicals on hydrazine and hydrazyl radicals is unimportant. Moreover, reaction (8) is unimportant compared to reaction (7).

The assumption has already been made that the quantum yield of reaction (1) is unity. If (8) is neglected, the only ammonia reforming reaction is (3) which is pressure dependent. The flow experiments indicate that, at pressures higher than 100 mm., reaction (3) is much more important than reaction (4). At lower pressures, reaction (4) becomes important and the overall quantum yield approaches unity.

If hydrogen atom removal by reactions (6) and (7) is neglected, the statistical rate for the ratio of ammonia reformation compared to the rate of hydrazine formation by reactions (3) and (5) is two to one above 100 mm. pressure. Thus, one-half of the amino radicals reform ammonia and the rate of ammonia decomposition at pressures over 100 mm. is about one-half the maximum value obtained at low pressures.

Reaction (3), the ammonia reforming step, depends on the hydrogen atom concentration which is turn depends on the extent of reactions (6) and (7). It will be shown below that the latter reactions depend only on the linear flow rate. Thus, the hydrogen atom concentration and hence the net rate of ammonia decomposition should depend on the linear flow rate. This effect was not found experimentally and the explanation may be that in the range of linear flow rates used the total concentration of hydrogen atoms did not vary by more than 25% due to removal in reactions (6) and (7).

As the linear flow rate is increased, the reaction products are diluted with ammonia causing a reduction of the partial pressure of hydrazine in the flow stream. Reactions (6) and (7) become less important compared to reaction (9) as the hydrazine partial pressure is decreased. Thus the conversion to hydrazine increases with linear flow rate and is independent of the reaction pressure.

The experiments in which the surface-to-volume ratio was increased in the zone following the lamp indicate that most of the reaction is complete in the irradiated zone. If this were not the case, the increase in the rate of hydrogen atom removal would result in an increase in the net rate of ammonia decomposition and in the conversion to hydrazine. A small increase may be noted in these experiments but the increase is scarcely greater than the experimental error.

In the static photolysis of ammonia, the mechanism must explain the fact that no hydrazine is obtained and that the rate of ammonia decomposition is lower than in the flow runs although it has the same pressure dependence. The partial pressure of hydrazine is probably much higher in the static system than in the flow system and the hydrazine formed must remain in the reaction zone. Hence reaction (6) is very important and causes a decrease in the hydrogen atom concentration. Reaction (8) is then able to compete successfully with reaction (7) and, since reaction (8) results in ammonia reformation, the net rate of ammonia decomposition is decreased. This effect is pressure independent but reaction (3) is also in operation so that the rate of ammonia decomposition has the same pressure dependence as it has in the flow experiments. It is possible that the photolysis of hydrazine may also become important in the static system.

While the mechanism which has been presented is in qualitative agreement with the experimental facts, it is quite possible that complex homogeneous and heterogeneous reaction steps are involved which would give a more complete explanation of the results which have been obtained in the ammonia photolysis. Since the apparatus used in this investigation was somewhat different from that used by other investigators, a quantitative comparison with their results does not seem justified.

ACKNOWLEDGMENTS

The authors wish to thank Dr. C. Luner of this Department for assistance in the measurement of the extinction coefficient of ammonia. They also wish to thank Dr. H. Oppenheimer, Michael Reese Hospital, Chicago, for the loan of apparatus used in these measurements.

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HYDRAZINE FROM THE ACTION OF LIQUID CHLORINE ON LIQUID AMMONIA

by

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Abstract

An attempt was made to synthetize hydrazine by the interaction of liquid chlorine with a large excess of liquid ammonia at 35°C and about 200 psi. The best yield obtained was 2.7 percent of theoretical. Nitrogen was formed by a side reaction which could not be suppressed by any mixing conditions tried. The project was dropped as commercially unattractive.

Introduction

In 1949 a group at the Naval Ordnance Laboratory became interested in the synthesis of hydrazine. The reaction of liquid ammonia and chlorine was selected for exploration. During the summer of 1950, apparatus was set up by Hubert Tatum, detailed to NOL from the Bureau of Ordnance. A short investigation of the reaction was completed during the period by Mr. Tatum and Dr. George Bryan of NOL. At the time this project was begun we had no knowledge of the work of Mattair and Sisler of Ohio State(1).

Certain rigid restrictions were laid down at the start of the investigation:

1. Experiments would be terminated unless there were indications that a yield of 90% or better (based on chlorine) could be obtained.

2. The reaction was to be run with a large excess of ammonia to minimize side reactions.

3. The reaction was to be carried out under pressure in the liquid phase at a temperature of 30° - 45°C so that mill water could be used for cooling. Any attempt to use refrigeration for dissipating the heat of reaction was regarded as leading to excessive capital and power costs. We felt that vapor phase reaction would lead to excessive localized heating and that clouds of NH_4Cl produced would be hard to handle. In addition, plant equipment would be bulky.

4. Temperature rise during reaction was to be held to 5° - 10°C partly by dilution with ammonia and partly by external cooling with mill water.

5. No diluents, either liquid or gaseous, were to be employed. An inert gas diluent, in particular, could lead to excessive recovery costs.

6. The entire operation was regarded as a logical adjunct to an existing chlorine plant and projected recovery processes were based on chemicals available within such a plant.

A cost estimate was prepared for a plant producing 1000 pounds per hour of hydrazine at 90% efficiency. For 1950 prices materials cost was estimated at 18.7 cents per pound with a selling price of about 37 cents. Capital costs seemed to be in line with those for other heavy chemical processes. Laboratory apparatus was designed to produce 0.1 pound per hour of hydrazine at the reactor end. No attempt was made at this point to test the feasibility of projected recovery processes.

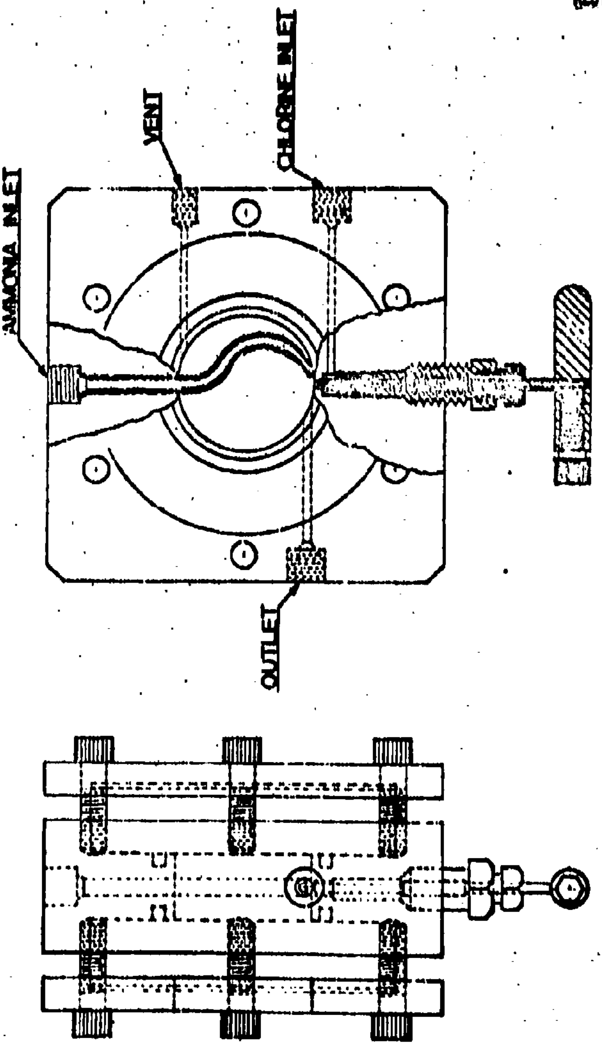
Experimental

Several reactor designs were tried; the final one is shown in Figure 1. Reaction occurred in a 2" hole drilled in a block of stainless steel 1 inch thick. The front and rear faces of the cell were made of 4 1/2 inch discs of 1 inch thick Herculite glass with O-ring seals. Chlorine was metered through a stainless valve built into the block, the spindle projecting just inside the cylinder wall. A thin, flat, jet of ammonia was fed at right angles to the chlorine inlet.

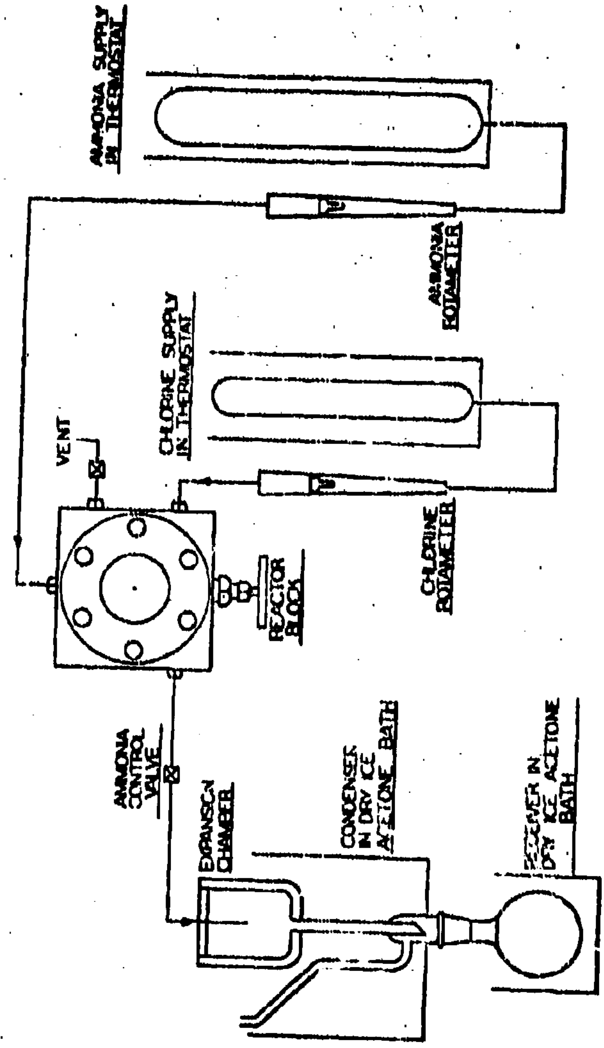
A simplified flow diagram is shown in Figure 2. Certain valves used for safety and convenience have been omitted.

Both the ammonia and chlorine tanks were immersed in thermostats to develop the proper vapor pressure over the liquids. Armored rotometers registered flows. Chlorine was controlled with the valve at the reactor block, while ammonia flow was controlled by the outlet valve to the recovery system. Operating pressures were from 180 to 250 psi. The chlorine pressure was kept about 10 psi higher than ammonia to prevent back-up into the chlorine lines. The ammonia tank was made of carbon steel, the rest of the system of 316 stainless.

The recovery system consisted of an insulated chamber (Dewar type) in which ammonia expanded to atmospheric pressure. The



REACTOR VESSEL
FIGURE I



SIMPLIFIED FLOW DIAGRAM
FIG. 2

cooled product dropped through a condenser into a receiver; inert gases were vented through a second condenser attached to the receiver. Both condensers and receiver were cooled in a dry ice - acetone mixture. The apparatus was properly armored and vented to protect operating personnel.

On completion of a run ammonia was removed in a still giving separation at least equivalent to one theoretical plate. In most cases the residue was dissolved in water and an aliquot taken for analysis. Sometimes an aliquot of the concentrated ammonia solution was removed and dissolved in dilute acid and the resulting solution analyzed.

Hydrazine was determined by titration with iodate. A check analysis was made by reducing silver ion and weighing the silver precipitate. Benzalazine was prepared in one instance to identify the reducing agent.

Results

Disappointing yields of hydrazine were encountered under all conditions tried. Results are summarized in Table I.

Table I

Hydrazine Yields (Based on Chlorine)

Operating Pressure 180-200 psi. Temperature, 35°C

NH_3/Cl_2 Ratio	NH_3 Fed moles/hr.	Cl_2 Fed moles/hr.	Yield hydrazine, percent
31	93	3	0.0
100	18	0.18	1.0
330	15	0.045	2.7
830	20	0.024	2.0
900	19	0.021	2.0

In view of the findings of Mattair and Sisler that chloramine reacts slowly with excess ammonia it is possible that reaction time was insufficient in these experiments. Our operating temperature, however, was somewhat higher, and should have led to faster reaction.

Nitrogen was formed rapidly in the reaction chamber and no conditions of mixing were found which prevented the unwanted side reaction. An analysis of the inert gas with a mass spectrometer showed only a trace of hydrogen. There was never any evidence of nitrogen trichloride being formed. Heavy metal ions were present in the effluent from the reactor. Nickel and iron were identified. Molybdenum was absent. No test for copper was made.

No attempt was made to dilute the chlorine with a solvent such as carbon tetrachloride.

Substitution of bromine for chlorine gave a slower, smoother reaction but yielded no hydrazine.

<u>Miscellaneous Observations</u>

In connection with this project certain other observations were made.

A 30% yield of hydrazine was obtained from the reaction of 15 g. of semicarbazide hydrochloride and 80 cc of anhydrous ammonia heated for 2 hours at 100°C and 700 psi.

Phenyl hydrazine and liquid ammonia failed to react under the above conditions.

A mixture of 5 g. of nitrobenzene, 0.5 g. of NH_4I and 75 cc of anhydrous ammonia heated to 100°C for 2 hours did not show hydrazine. This experiment was performed to see whether nitrobenzene would oxidize HI to I_2; and if this, in turn, would oxidize ammonia to hydrazine.

This work was supported by BuOrd Task NOL-13-Re2d-02-1.

<u>Reference</u>

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DISCUSSION

Dr. Noonan asked if anyone had attempted to produce hydrazine from hydroxylamine and ammonia. NOL had tried the reaction with no success.

MR. D. W. RYKER (Olin Industries, Inc.): We did some work of a preliminary nature involving the reaction of ammonia and hydroxylamine to make hydrazine. The results, however, were negative.

I am interested in the statement that you ought to be able to make hydrazine cheaper from hydroxylamine. It is my impression that hydroxylamine is an expensive material at the present time. I think it is almost as hard to make as hydrazine.

DR. NOONAN: It can be made by the cathodic reduction of NO, I believe. It seems to me by using a Gardner type cell you ought to be able to get hydroxylamine, and with the present knowledge in the chlorine industry of the liquid ammonia extraction of sodium hydroxide you ought to be able to get it out easily.

SUMMARY REPORT ON AVAILABILITY AND COST OF HYDRAZINE

by

Russell B. Goodman
The Ralph M. Parsons Company

Abstract

The present production of anhydrous hydrazine totals about 650 pounds per day, which will be increased to 12,600 pounds per day early this spring.

The current selling price is $4.50 per pound, which will be reduced to $2.50 per pound or less when the new production facilities are put in operation.

The modified Raschig process offers the lowest cost established production method, and will account for about 95 percent of the total production. The Urea-Hypochlorite process will supply the balance.

An estimate of absolute minimum production cost in Government-operated plants utilizing the Raschig process at a rate of 50 tons per day indicates:

1. A cost of 30.5¢ per pound if all raw materials are supplied at cost in Government-operated plants.
2. A cost of 46.6¢ per pound if raw materials are purchased at market prices.

* * *

It is apparent from the papers which have been given in this Symposium that a great deal of research work has been done in the attempt to develop a process for the production of anhydrous hydrazine at a lower cost than the existing commercial processes.

Some of this work may ultimately succeed in this objective; however, at the present time all of the commercial production of hydrazine is divided about equally between the modified Raschig process and the urea-hypochlorite process.

The present production totals about 650 pounds per day, but additional plant facilities are now under construction which will increase this to about 12,600 pounds per day by early this spring, at which time the Raschig process will account for approximately 95 percent of the total production.

The current selling price for anhydrous hydrazine is about $4.50 per pound in stainless steel drums at the plant. However, it is estimated that after the new facilities are put in operation the price can be reduced to about $2.50 per pound at the Lake Charles plant of Mathieson, and at the Newark, New Jersey plant of Fairmont.

In the spring of 1950 The Ralph M. Parsons Company completed a study under the sponsorship of the Navy Department Bureau of Aeronautics to determine what processes could be employed and what the minimum cost would be if the Government required hydrazine in large quantities.

Bases for Design and Cost Estimates

Raw Material Costs -- The raw material costs are determined on two bases. The most desirable from the hydrazine cost standpoint is where ammonia, chlorine, caustic and urea are produced in Government plants and charged to the hydrazine plant at "cost," and this has been designated as Case A. These raw material "costs" would include all manufacturing costs and normal plant depreciation, but no general overhead, interest, sales expense, income tax, or profit. To actually realize this low cost raw material source would require the construction of Government chlorine, caustic, and ammonia facilities. Sulfuric acid and glue are not considered critical items and could be purchased on the open market.

The other case, designated as Case B, assumes that all raw materials would be purchased at prevailing market prices.

Freight is estimated at $5.00 per ton on ammonia, urea, and sulfuric acid only, with no freight charged for chlorine or caustic. This is also an average condition between a completely integrated plant and an isolated hydrazine synthesis unit.

Utilities -- The primary utility is natural gas for steam generation. The steam cost is not determined separately since the steam plant investment and the operating cost are included as part of the overall hydrazine plant. The same is true for water cost. No charge is made for raw water, but the cost of treating makeup cooling water and boiler water is shown. It is assumed that the small amount of electricity required will be purchased.

Processing and Non-Processing Costs -- These are based on the estimated labor and supervisory forces required and the operating conditions anticipated for this type operation. The item "Miscellaneous" includes general engineering and maintenance, office supplies and expenses, medical, fire and security protection, stores and salvage, transportation, janitor service (outside processing area), moving and living expenses of employees, maintenance of grounds and roads, non-operating vehicles, and laboratory.

Amortization -- Amortization is taken at 10 percent per year in Case A and 20 percent per year in Case B. The resulting dollar figures are therefore higher than the reserve-for-depreciation figure of perhaps 7 percent per year which would be used in normal accounting procedures. However, one of the primary purposes of the cost estimates in this report is to determine the cost of hydrazine to the Government should it become involved in the manufacture of this material for military use. Since hydrazine thus far has no large scale non-military use, it is believed that more realistic cost figures will be obtained by including in these costs the effects of amortization at 10 percent and 20 percent per year rather than the lower normal depreciation figures which are used for ammonia and chlorine-caustic plants, the products from which are in large scale peace-time demand.

By-Product Credit -- Both the Raschig Ammonolysis and the Urea-Hypochlorite Ammonolysis processes will yield a commercially saleable ammonium sulfate by-product. The Urea-Hypochlorite Ammonolysis process will also yield a saleable 28 percent aqueous ammonia solution as will the Urea-Hypochlorite Caustic Dehydration process. The credit for these by-products is conservatively taken at about one-half of the present market value, or $20 per ton for ammonium sulfate and $32 per ton (anhydrous basis) for the 28 percent aqueous ammonia. Salt (sodium chloride) is produced as a by-product in the Raschig Ammonolysis process, and a sodium chloride-sodium carbonate mixture is produced in the two Urea-Hypochlorite processes. The cost of recovery and purification of these materials is estimated to be more than the sale value, hence no by-product credit is allowed.

Not Included -- The cost of producing anhydrous hydrazine as determined in this report does not include head office salaries and expenses, processing royalties, interest on working capital, interest on plant investment, sales expense, income tax, or profit.

This study brought out the following conclusions:

1. At the existing state of development the Raschig process could produce hydrazine at a lower cost than any other process.

2. A minimum cost of about 27¢ per pound of anhydrous hydrazine could be realized if all raw materials could be supplied from Government plants and charged to the hydrazine plant at cost.

3. The production of hydrazine by the urea-hypochlorite process was about 10¢ per pound higher than the Raschig process in large-scale plants.

Economic evaluations were made on the basis of various process units designed for 50 tons of anhydrous hydrazine per day.

These data are presented in Tables 1, 2A, 2B, and 2C.

Three different methods for the dehydration of the hydrazine hydrate azeotrope were studied and it was concluded that caustic dehydration and azeotropic dehydration were about equal on a cost basis, while ammonolysis of hydrazine sulfate was somewhat more costly and introduced problems of by-product disposal.

These relationships are shown in Table 5.

The Urea-Hypochlorite Process

The production of hydrazine by the urea-hypochlorite process is somewhat simpler than by the Raschig process in the respect that solid urea can be stored and reacted at atmospheric pressure while liquid ammonia requires pressure equipment. However, it is a more costly process because of the higher cost of urea than ammonia and because it requires more caustic soda.

A cost comparison of the two processes is given in Table 3.

Decomposition of Semicarbazide

The ammonolysis of semicarbazide appears to offer an attractive means of producing hydrazine. Although there is no commercial production of hydrazine by this process, it may be of interest to present an estimated cost comparison with the Raschig process, Table 4.

Conclusions

If hydrazine is to be produced by the Raschig process in quantities of 50 tons per day or more, the unit costs corrected from the 1950 index to November 1952, would be as follows:

	Case A	Case B
Raw Materials	16.4¢/lb	29.0¢/lb
Utilities	2.5	2.5
Processing	4.7	4.7
Non-Processing	3.4	3.4
Amortization	3.5	7.0
	30.5	46.6

TABLE 1

PLANT INVESTMENT

RASCHIG CAUSTIC DEHYDRATION - 50 TON PER DAY PLANT

Land and Improvements		$ 200,000
Buildings		400,000
Machinery and Equipment		
Process Units	$ 4,300,000	
Utilities (Steam, Cooling Water, Etc)	4,100,000	
Storage and Handling	1,400,000	
Miscellaneous Laboratory, Shop and Yard Equipment	300,000	
		10,100,000
TOTAL		$ 10,700,000

TABLE 2A

PRODUCTION COST ESTIMATE

RASCHIG CAUSTIC DEHYDRATION PROCESS

Production Cost Items	Quantity Per Day	Case A Total Cost $/Day	Case B Total Cost $/Day
Raw Materials			
Ammonia at $ 32/Ton (A), at $75/Ton (B)	69	2,208	5,175
Chlorine at $ 30/Ton (A), at $54/Ton (B)	185	5,550	9,990
Caustic at $30/Ton (A), at $48/Ton (B)	212	6,360	10,176
Glue at $200/Ton	0.37	74	74
Freight	—	345	345
TOTAL RAW MATERIALS		14,537	25,760
Hydrazine Unit Cost ¢/Lb		14.5	25.7

TABLE 2B

PRODUCTION COST ESTIMATE

RASCHIG CAUSTIC DEHYDRATION PROCESS

Production Cost Items	Quantity Per Day	Case A Total Cost $/Day	Case B Total Cost $/Day
Utilities			
Fuel (Natural Gas) at $ .12/MCF	18,200	2,184	2,184
Electricity at $ .005/Kwh	16,896	85	85
Water Treating at $ .033/M Gal.	880	29	29
TOTAL UTILITIES		2,298	2,298
Hydrazine Unit Cost ¢/Lb		2.3	2.3
Processing			
Operating Labor (Incl. Pay Roll Burden)		2,288	2,208
Plant Supervision and Office Labor		377	377
Operating Supplies		256	256
Plant Maintenance (Labor and Materials)		1,022	1,022
TOTAL PROCESSING		3,943	3,943
Hydrazine Unit Cost ¢/Lb		4.0	4.0

TABLE 2C

PRODUCTION COST ESTIMATE

RASCHIG CAUSTIC DEHYDRATION PROCESS

Production Cost Items	Quantity Per Day	Case A Total Cost $/Day	Case B Total Cost $/Day
Non-Processing			
Insurance		292	292
Ad Valorem Taxes		236	236
Gen. Admin. and Gen. Office Overhead		391	391
Miscellaneous		1,954	1,954
TOTAL NON-PROCESSING		2,873	2,873
Hydrazine Unit Cost ¢/Lb		2.9	2.9
Amortization			
10 per cent per year (Case A)		2,932	
20 per cent per year (Case B)			5,864
Hydrazine Unit Cost ¢/Lb		2.9	5.8
TOTAL COST			
Total Hydrazine Unit Cost ¢/Lb		26.6	40.7

TABLE 3

COMPARISON OF

HYDRAZINE PRODUCTION COSTS AND PLANT INVESTMENT

RASCHIG AND UREA-HYPOCHLORITE PROCESSES

Process	Hydrazine Production Cost Case A ¢/lb	 Case B ¢/lb	Hydrazine Plant Investment
Raschig, Caustic Dehydration			
Total Cost (No By-Product Credit)	26.6	40.7	$10,700,000
Urea-Hypochlorite, Caustic Dehydration			
Total Cost (Before By-Product Credit)	36.8	57.0	9,500,000
Less By-Product Credit	0.6	0.6	
Total Cost	36.2	56.4	

TABLE 4

COST COMPARISON OF

RASCHIG AND SEMICARBAZIDE PROCESSES

Production Cost Items	Raschig Process Caustic Dehydration ¢/Lb	Semicarbazide Process Ammonolysis Chlorourea Route ¢/Lb	Semicarbazide Process Ammonolysis Nitrourea Route ¢/Lb
Raw Material Cost	14.5	14.3	24.5
Plant Amortization at 10%/Year	2.9	2.5	2.5
Utilities	2.3	1.2	1.2
Processing Costs	4.0	3.8	3.8
Non-Processing Costs	2.9	2.8	2.8
TOTAL COST/LB OF HYDRAZINE	26.6	24.6	34.8

TABLE 4

COST COMPARISON OF

RASCHIG AND SEMICARBAZIDE PROCESSES

Production Cost Items	Raschig Process Caustic Dehydration ¢/Lb	Semicarbazide Process Ammonolysis Chlorourea Route ¢/Lb	Semicarbazide Process Ammonolysis Nitrourea Route ¢/Lb
Raw Material Cost	14.5	14.3	24.5
Plant Amortization at 10%/Year	2.9	2.5	2.5
Utilities	2.3	1.2	1.2
Processing Costs	4.0	3.8	3.8
Non-Processing Costs	2.9	2.8	2.8
TOTAL COST/LB OF HYDRAZINE	26.6	24.6	34.8

TABLE 5

COMPARISON OF HYDRAZINE

PRODUCTION COSTS AND PLANT INVESTMENTS

RASCHIG PROCESS WITH VARIOUS DEHYDRATION MODIFICATIONS

Process	Hydrazine Production Cost Case A ¢/Lb	Hydrazine Production Cost Case B ¢/Lb	Hydrazine Plant Investment
Raschig, Azeotropic Dehydration Total Cost (No By-Product Credit)	27.1	41.1	$11,400,000
Raschig, Caustic Dehydration Total Cost (No By-Product Credit)	26.6	43.7	10,700,000
Raschig, Ammonolysis Total Cost (Before By-Product Credit)	32.8	49.3	11,100,000
Less By-Product Credit	4.0	4.0	
Total Cost (Less By-Product Credit)	28.8	45.3	

DISCUSSION ON PAPERS BY
MR. J. W. CLEGG, MR. JOSEPH D. CHRISP, MR. HARRY E. GUNNING,
DR. EVAN O. NOONAN, AND MR. RUSSELL GOODMAN

VOICE: The mechanism you had on the slide indicated that hydrogen atoms contributed materially to the modification of the yield by intermediate steps, yet you find that although hydrazine is presumed to be removed by reactions the yield is unaffected by a very large increase in the surface volume ratio. How do you explain that?

PROFESSOR GUNNING (Illinois Institute of Technology): I don't think that particular reaction is important under our conditions. I put that in as a possibility but actually the hydrogen atoms are largely destroyed there. That is to say, if you look at it this way, consider the infinitely high flow rates, you have hydrogen atoms produced. There is no other place for them except the wall if they did not react with hydrazine. Consequently, the wall then becomes unimportant. It is only where the wall competes with some other process that you could say this would affect it. If the wall is competing with hydrazine that would be true because in the case where you have abstraction processes forming H_2, then that would become true, but actually in the very high flow rates the wall doesn't, as far as we can see -- now we way this with a certain degree of humility -- contribute.

VOICE: Kinetically speaking, that reaction does not exist.

PROFESSOR GUNNING: Look at it this way. Suppose you write down the reaction and you get 100 percent hydrazine and you get hydrogen. How else can the hydrogen molecules form if they do not react with hydrazine, unless that is by abstraction? You could perhaps use ammonia as a third body combination in the gas phase, with ammonia as a third body, but we don't believe that is true.

You hit a point that we are not sure about. This problem of the heterogenous process puzzles us a great deal. It is one of the basic problems I think in the interpretation of the ammonia photolysis; we do not know the actual role of the heterogenous processes. I agree there is some question in so far as what the hydrogen atoms do.

VOICE: The reason I ask is that one is to increase, the other decrease. It would seem peculiar, therefore, that you should have found, if this mechanism that you described is correct, that large an increase if the surface volume ratio is as you say.

PROFESSOR GUNNING: I agree with you. These are the facts though, as far as I know them.

DR. FRED VON HESSERT (Fairmount Chemical Co., Inc.): In the azetropic dehydration of hydrazine what is the over-all loss of aniline per ton of hydrazine produced?

MR. NICOLAISEN (Mathieson Chemical Corporation): This question will be answerable only after commercial production of hydrazine is begun. Theoretically, the loss should be nil, since aniline is completely stable under the conditions of operation. However, actual loss will depend upon the efficiency with which the aniline can be recovered from the waste water, and upon the handling losses. Pilot plant operation does not accurately pin either of these factors down. In any event, the loss of aniline anticipated in the plant does not contribute appreciably to the production cost.

DR. VON HESSERT: You must have some figure to base your loss on.

MR. NICOLAISEN: As I say, we have no actual basis for proving the loss.

THE CHAIRMAN: I would just like to caution you who enter the discussion that you will have to correct the stenotype record. We would appreciate it if you would make your remarks as loud as you can.

MR. MEYER STEINBERG (Guggenheim Bros.): I would like to ask Dr. Gunning what concentrations of hydrazine were obtained in his experiments. Is there any indication as to a theoretical maximum possible concentration?

PROFESSOR GUNNING: Now the concentration of the hydrazine in the reaction zone, of course, affects the extent of decomposition. As you scale up the unit one of the things you do and the reason we are doing it, is to increase the actual extent of the decomposition.

I think the crux of the whole thing lies in this -- can we increase the amino radical concentration, therefore the hydrazine concentration, and still maintain the same over-all yield.

In other words, you must realize that in this process at this stage there is no precedent for this type of work. Therefore, we don't scale up, that is, at least to where Mr. Goodman can do it because of the great deal of industrial know-how and precedent. There is none in this; consequently, we don't know.

What we are doing now is increasing the light intensity, therefore increasing the concentration of hydrazine, you see, in the total amount formed, to see if we can maintain by a factor of 100 a quantity yield. We have reason to believe we have increased the yield under those conditions because we can get higher flow rates.

MR. STEINBERG: What are the values of the stationary concentrations of hydrazine?

PROFESSOR GUNNING: They are extremely low; we are only decomposing about 0.1 percent of the ammonia. Under our conditions that is limited by the light intensity. As we scale it up, we will increase that.

THE CHAIRMAN: Anyone else?

DR. EUGENE MILLER (Redstone Arsenal): I have a general question on the problem of dehydration of hydrazine. I wonder if anybody has considered the possibility of operating the distillation at lower temperatures and pressures in order to break the hydrazine azeotrope. Theoretically there is a possibility and it can be done.

MR. CLEGG: We have given it brief consideration theoretically and find there is little point in going to lower pressures. There is some indication that a break would be obtained at about 10 atmospheres, but as far as I know, no experimental work has been done.

MR. DANIEL B. MURPHY (Picatinny Arsenal): I would like to ask Dr. Noonan whether the chlorine and ammonia used were of commercial purity?

DR. NOONAN: Yes, they were. That is what you would use ordinarily. Actually, they did go through one distillation, because we distilled them into our receivers, and may have purified them slightly. We didn't intend to do it, however.

THE CHAIRMAN: Mr. Nicolaisen, do you want to comment on the question by Dr. Miller of Redstone?

MR. NICOLAISEN: No, sir.

MR. M. P. DUNNAM (Wright Air Development Center): I had a comment on the Redstone question. We ran the distillation down to 10 millimeters. It didn't change the azeotrope composition appreciably.

THE CHAIRMAN: Anyone else?

DR. A. M. BALL (Hercules Powder Company): I am curious to know whether the Mathieson people regard the Parsons figures as a reasonable goal for that scale production.

THE CHAIRMAN: Which figures, A or B?

DR. BALL: Either one.

DR. TROYAN (Mathieson Chemical Corporation): I might speak for Mathieson under advisement.

I believe the higher figures that were shown are more realistic. It is a rather synthetic case where everything is manufactured by the Government at no profit, starting with coal, air, water and salt. I believe that the $0.50 a pound price is a rough figure that in our economic evaluations looks attainable at this scale of operation.

DR. BALL: Did you mean the plant that you are building now is for 50 tons a day?

MR. TROYAN: Six tons a day.

THE CHAIRMAN: If I may abuse one of the duties of the Chairman not to make gratuitous comments, I would like to say that this highly controversial matter of profit or no profit to the Government is tied up with return on the money that is used. Actually I think we confuse figures of no profit with figures of no profit plus no charge for the capital that is used. That is something I certainly would like to see clearly defined in figures of this type.

I think we can fool ourselves by looking at capital figures and cost figures where actually the Government's costs are not all in. The Government doesn't get money for free any more than anyone else does.

DR. W. E. LAWSON (E. I. du Pont de Nemours & Company): A man can always comment on that, I suppose, and indeed I should like to.

The costs in question carried nothing for working capital, even for erection of the plant. Surely one has to pay the laborer before the money for the operation comes in.

Furthermore, there must be an amount sufficient for thirty or thiry-five days' operation. This is a portion of your capital, and it is not included in the summary.

THE CHAIRMAN: No working capital, in other words?

DR. LAWSON: No, none whatsoever was included. I noticed the prices for electricity, which were down as low as 5 mils. There is no place in the United States where power can be obtained at the present time at this figure, with the possible exception of TVA, which does not include the entire costs.

Without including the entire capital, there is no way of calculating return, and it is necessary to get a return on the investment, whichever route is used for calculations. Furthermore, this includes all starting materials, and I note that these were at cost without return. I would suggest that we look at them with a jaundiced eye.

THE CHAIRMAN: Mr. Goodman, you are entitled to rebuttal.

MR. GOODMAN: Dr. Lawson undoubtedly knows more realistic figures about profits and losses than I do. They were based on 1950 as a minimum on instructions from our agency, the Bureau of Aeronautics. We were to calculate a minimum figure with no profits. I would grant they may not be realistic today.

THE CHAIRMAN: We could find common agreement that they are minimum figures.

MR. GOODMAN: They are unquestionably minimum figures.

MR. V. R. BONNETTE (Mathieson Chemical Corporation): Mr. Goodman, you didn't say whether 10-year amortization or 20-year. Was it 20 years in case "B"?

MR. GOODMAN: 10 percent per year or 20 percent per year.

THE CHAIRMAN: 10-year and 5-year periods.

DR. J. F. HALLER (Mathieson Chemical Corporation): I would like to ask Dr. Gunning whether he has ever exceeded the approximate conversion of the 0.2, or thereabouts, percent of the ammonia. I suspect there is a ceiling there that I would be interested in having explained.

PROFESSOR GUNNING: Actually the fact of the matter is we are, as I said before, limited by our light intensity. We have to maintain a certain linear flooring. You see, we want to have a complete set of data in one reactor to keep everything the same.

This question, I hope to be able to answer for you within about one month. I can give you an experimental answer to this question, but I don't feel any other answer has any meaning as it stands now. As I say, I feel that this is one of the most complex reactions. In photolysis nobody agrees with anybody. We only make our mechanism to fit our particular apparatus.

I think it can be done, let's put it that way. I am sufficiently encouraged by what we have got up to this stage, the extent of decomposition, maintaining the same flow rate. I think that we can go farther. That is a big question, I would grant you.

THE CHAIRMAN: Anyone else?

DR. NOONAN: The Mathieson figure on power per pound of hydrazine must be around 6 kilowatts. Is that right?

MR. TROYAN: I don't believe we have the data right at hand. That probably sounds in the right range.

DR. NOONAN: I just want to point out Dr. Gunning has an awfully long way to go. Down to 6 kilowatts is quite a long way.

PROFESSOR GUNNING: I would like to point out other things in my own defense. What I based it on was the power requirement of 100 kilowatt hours per pound. As it stands now it is a most conservative estimate.

When comparing the Raschig Process we are dealing with anhydrous ammonia. We go to anhydrous hydrazine. We have not the elaborate recovery cost associated with the Raschig Process, as we will see. I argue this will be the determining factor. We have a leeway that we can move up to a yield of one, at least. Now we think we can increase this. Every time we increase from .1 to .2, say, we cut it down from 100 to 50.

There is a great deal of exploration work that has to be done on a semi-pilot scale with large reactors and high flow rates, but this will be the determining factor. There are a lot of material costs that come into the Raschig Process that we haven't got.

That is the only reason we feel encouraged in going on.

DR. NOONAN: Well, again, I think for every 10 kilowatts of power you use up you have got to give up so many pounds of aluminum or so many pounds of chlorine or so many pounds of calcium carbide, and as I pointed up before, power plant facilities are not quickly expanded in war time. You can put in cells rapidly; you can't expand a power plant in short order.

MR. GOODMAN: I might point out, Dr. Noonan, putting in chlorine cells also requires power.

DR. NOONAN: I mean this: You can put in a cell, but you can't build the powerplant for it.

MR. CLEGG: I don't want to enter into a controversy. However, recovery costs of hydrazine from concentrations of a fraction of one percent in ammonia may be as much as the recovery cost of the hydrazine in the Raschig Process. They are substantial. I believe that Mr. Goodman will back me up on that.

MR. GOODMAN: It is very true.

MR. RYKER (Olin Industries, Inc.): I want to ask a question which is in direct line with Mr. Clegg's comment. I want to ask Dr. Gunning, with only one-tenth of 1 percent conversion, there will be something less than one-tenth of 1 percent of hydrazine in the ammonia, I think you are going to have difficulty finding it. How do you expect to get it out of the ammonia?

PROFESSOR GUNNING: Simply by condensing the ammonia. In other words, you have your refrigeration unit there. As you pump out ammonia, hydrazine is coming down with the ammonia and concentrating.

MR. RYKER: At what pressures?

PROFESSOR GUNNING: We have operated at a large number of pressures. As a matter of fact, we have explored, as I say, quite a range of pressures. We could go up on atmospheric pressures without any trouble. We have been working at lower pressures recently because we were interested in the problem of changing quantities, but any pressure from 10 millimeters up to atmospheric can be done at convenience.

MR. RYKER: Then your entire system will have to be a low temperature system, -30 degrees F. or lower.

PROFESSOR GUNNING: For the recovery, the whole thing is done at low temperature. In freezing the ammonia you have to liquefy the ammonia.

I won't argue about that. You people are much more competent than I am. I am just a university professor.

MR. GALE (McCord Corporation): I would like to address this question to Dr. Noonan.

Did subsequent work by other investigators indicate that the process described in your paper was thermodynamically out of the question?

DR. NOONAN: Referring to the ammonia-chlorine reaction, no; I think Mattair and Sisler got about 30 percent yield. However, they did it in two steps. They allowed the ammonia and chlorine to react in the vapor phase and held it in the chloramine form at low temperatures to contact the ammonia at -70°C. for several hours. Apparently this reaction is rather slow.

MR. GALE: The reason I bring that question up is the design of the reactor which you showed is perhaps only a schematic representation. I wondered whether the method by which you introduced your streams might not have produced effects similar to that found in the Hilsch tube.

DR. NOONAN: What is that?

MR. GALE: That's a tube in which gases are introduced tangentially at high pressures and velocities and the resulting effect, while not thoroughly described yet by anyone, produces a cold stream on one side and a hot stream on the other side.

DR. NOONAN: I am sure under no circumstances could this have happened in our apparatus; some of the runs were at extremely low flow rates.

THE CHAIRMAN: This will be our final question.

DR. HARRY H. SISLER (Ohio State University): I think that I should make some remarks about this. We hoped to present a discussion to this group but it did not seem just quite the thing to do at the time.

I would like to say, however, that the work reported in the paper which you quoted, Doctor, has been continued, and the results obtained have been improved considerably to put it mildly, and that the 30 percent yield is a very small figure.

As I say, I wish that I could give more information but I can't at this time, but that is not to be considered something tried and failed.

THE CHAIRMAN: We will look forward to a contribution from you at some future symposium.

It is time for lunch. I want to thank the participants of this morning's session. We will have a new chairman this afternoon.

AFTERNOON SESSION
2 February 1953

CHAIRMAN, DR. EUGENE LIEBER
U. S. NAVAL ORDNANCE TEST STATION

THE CHAIRMAN: The meeting should start promptly. We have a large number of papers to cover. The first speaker is scheduled to take off at 1400.

The next phase of our conference concerns itself with "Properties of Hydrazine and Hydrazine Systems." For the afternoon session we will consider various phases of physical chemistry of hydrazine, chemical problems, analytical problems and safety and handling and toxicity.

In order to end the afternoon session at a reasonable period for the number of papers and the discussion we should get out of these papers, and in fairness to all of the speakers this afternoon, I would suggest that each of the speakers try to restrict his own presentation to approximately fifteen minutes. Depending on the length of the discussion, we can allow for a plus or minus five minutes.

As in our morning session, we will present each group of papers, followed by a discussion. We will start off promptly. The first paper is on the "Thermal Analysis of Hydrazine Systems," a contribution from the Naval Ordnance Test Station, by Jane M. Corcoran, N. Ogimachi, Howard W. Kruse, Sol Skolnik, and myself. Sol Skolnik, as most of you know, is now located at the Naval Powder Factory, Indian Head, Maryland. The paper will be presented by Dr. Kruse.

THERMAL ANALYSIS OF SOME HYDRAZINE SYSTEMS

by

Jane M. Corcoran, N. Ogimachi, Howard W. Kruse,
Sol Skolnik and Eugene Lieber
U. S. Naval Ordnance Test Station, Inyokern
Presented by Dr. Howard W. Kruse

ABSTRACT

As a part of an investigation of low-freezing fuel mixtures containing hydrazine, phase diagrams of a number of binary systems were determined. These included hydrazine with aniline, methanol, ethanol, n-propyl alcohol, isopropyl alcohol, allyl alcohol, propargyl alcohol, and 5-aminotetrazole. The ternary system hydrazine nitrate-water-hydrazine also was investigated by means of thermal analysis and a phase diagram was constructed from these data.

INTRODUCTION

During the past several years there has been a growing interest in the use of anhydrous hydrazine as rocket fuel. The favorable properties which recommend it are well known. Among these are high specific impulse; low vapor pressure, low flame luminosity, and smokeless exhaust. With commonly used oxidants, such as RFNA, WFNA, or hydrogen peroxide,hydrogen ignites spontaneously with a very short ignition delay.

In selecting any material for propellant use, however, various physical properties must be taken into consideration. One of the most important of these is the freezing point, especially when the fuel is to be employed in packaged missiles. The potential employment of a fuel in arctic regions and in air-launched rockets requires that the material remain liquid down to temperatures in the neighborhood of -65°F. Hydrazine, with a freezing point of 34.7°F, would solidify under such conditions. Therefore, in order to extend the temperature range over which hydrazine may be used, it is necessary to add other materials to depress the freezing point. A part of the work of the Inorganic Chemistry Branch of the Chemistry Division at NOTS has been directed toward accomplishing this purpose.

This investigation has included a literature survey of previous work on mixtures of hydrazine with additives, and preliminary survey work in the laboratory on additives not studied before. A number of the more promising materials have been investigated in some detail and the results of this work are described in this paper. The method employed was that of thermal analysis. From the melting point-composition data which were obtained, phase diagrams of these hydrazine systems were constructed.

EXPERIMENTAL PROCEDURE

Materials

Hydrazine. Anhydrous hydrazine was used in all of the work described here except where otherwise indicated. The anhydrous hydrazine was prepared by dehydration of Airmount commercial hydrazine (95%). Three parts by weight of hydrazine were added to two parts of freshly fused potassium hydroxide which had been ground in a desiccator box. After the mixture had been allowed to stand for two hours, the hydrazine was distilled in an all-glass apparatus under a nitrogen atmosphere at a pressure of 60-80 mm. Hg. In order to minimize the explosion hazard of hydrazine distillation, nitrogen was admitted into the system before heating, and the flow was allowed to continue until the apparatus had cooled at the end of distillation. A safety shield was used during the entire operation. Approximately 75 percent of the hydrazine was distilled from the mixture. If analysis did not indicate substantially complete dehydration, distillation from fused potassium hydroxide was repeated. Analysis was made by the direct iodate method using chloroform as an indicator (1). Hydrazine purified in this manner analyzed 99.9+ percent N_2H_4 and had a freezing point of 1.52°C.

Aniline. Aniline, prepared from aniline sulfate, was purified by distillation in a nitrogen atmosphere at 60-80 mm. pressure through a 3-foot column packed with glass helices. Middle fractions were collected at a reflux ratio of 5:1. The combined material from several distillations was then fractionated and middle fractions again collected. The purified product had a refractive index of 1.5860 $^{20}_{D}$ and a freezing point of -6.00°C.

Alcohols. Most of the alcohols were purified according to procedures given by Weissberger and Proskauer (2). Refractive index and density were used to check the purity. Briefly, the methods employed for each alcohol were as follows: A.C.S. Reagent-grade, acetone-free methanol was distilled at atmospheric pressure from magnesium. Absolute ethanol was purified by distillation from freshly calcined calcium oxide. For the preparation of pure propyl alcohol, Eastman White Label material was first distilled from magnesium and iodine. The resulting product was then fractionated through a 4-foot column packed with 1/8-inch glass helices. Middle fractions were collected and employed in the work described here. Isopropyl alcohol was first refluxed with aluminum amalgam for four hours and then fractionated in the column used for n-propyl alcohol. Allyl alcohol was given a preliminary purification by fractionation in an 18-inch column packed with 1/8-inch glass helices. Middle fractions were collected and finally distilled from freshly dried potassium carbonate. Purification of propargyl alcohol was effected by first drying with magnesium sulfate. The alcohol was then distilled from 1-2 percent succinic acid through an 18-inch column packed with 1/8-inch helices. Middle fractions from several batches were collected and again fractionated. Physical constants of the product prepared in this manner agreed well with those given in the literature. The freezing point, however, was slightly higher, a value of -51.5°C. being obtained compared to -51.8°C. reported by Henne and Greenlee(3).

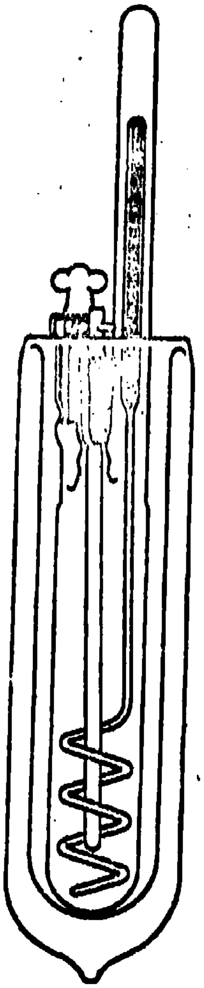
All purification procedures used for the alcohols were carried out with suitable precautions to exclude moisture. Subsequent operations employed a desiccator box filled with an atmosphere of dry nitrogen.

Five-Aminotetrazole. The mono-hydrate of 5-aminotetrazole obtained from Fairmount Chemical Company was dried in an oven at 100°C. to remove the water of hydration. The resulting product was then employed without further purification.

Hydrazine Nitrate. Hydrazine nitrate was prepared by neutralization of Fairmount hydrazine with fresh, colorless C.P. nitric acid. Both the hydrazine and the acid were diluted by an equal weight of ice before mixing was started. Further additions of ice were made as necessary in order to keep the solution cool. After neutralization was complete, part of the water was removed by evaporation at 80-90°C. on a hot plate. The solution was then placed in a filter flask, connected to a water aspirator, and evaporated at 68-72°C. by immersion in a water bath. A slow stream of nitrogen was allowed to bubble through the solution to hasten evaporation. When evaporation had ceased, the resulting syrupy solution was cooled in an ice bath with constant stirring. After crystallization had begun, absolute methanol was added in sufficient quantity to give a smooth slurry when the mixture had cooled. The crystals were then filtered on a sintered glass filter, washed three times with absolute methanol, and allowed to remain on the filter until most of the methanol had been removed by suction. After air-drying, the hydrazine nitrate was given a final drying of 6-8 hours in a vacuum oven at 50°C. Analysis for hydrazine by the direct iodate method indicated 33.69 percent N_2H_4; the theoretical value is 33.71 percent.

Apparatus

Freezing and melting points of most of the pure compounds and mixtures were determined in cells of the type shown in Figure 1. Two sizes were employed. The larger size, used for study of the first three systems was constructed of 25 mm Pyrex tubing and the main body of the cell was 120 mm long. Later it was found that a slightly smaller cell could be handled more readily, and that it was easier to obtain a smooth slurry of crystals. The remainder of the systems was, therefore, studied using the smaller cell. The main body of this cell was constructed of 20 mm Pyrex tubing and was 110 mm long. A thermocouple well was inserted through one of the two standard-taper joints in the top. The other opening was used for introducing the components and was closed with a standard-taper plug. Stirring of the mixtures during freezing and melting was accomplished by means of a solenoid acting intermittently on the iron bar sealed into the upper end of the spiral glass stirrer. The current to the solenoid was interrupted by a multivibrator circuit. In order to provide slow, uniform changes in temperature when the cell was immersed in cooling or warming baths, it was placed in the clear-glass Dewar flask shown in the figure. The temperature in the cell was measured with a calibrated copper-constantan thermocouple inserted into the well, which contained n-propyl alcohol as a thermal conducting medium. The thermocouple potential was continuously recorded on recording potentiometers with the exception of the work on the hydrazine-ethanol system. In the work on this system the thermocouple potential was measured with a Leeds and Northrup Portable Precision Potentiometer. Temperature in the systems of hydrazine with methanol, allyl alcohol and hydrazine nitrate and water, were recorded on a Leeds and Northrup Type G Speedomax recorder. A low-level amplifier specially designed for work of this type was employed. This made it possible to vary the chart scale on the Speedomax from 50 to 2000 microvolts. In most of the work the 200-microvolt scale was used, making it possible to read thermocouple potentials to 1 microvolt. Thermocouple potentials during melting in the systems of hydrazine with propyl alcohol, isopropyl alcohol, propargyl alcohol, and 5-aminotetrazole were determined on a Brown Elektronik recording potentiometer having a one millivolt chart scale.



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Leeds and Northrup Portable Precision potentiometers were used as zero-point suppressors for both the Speedomax and Brown Elektronik recording potentiometers.

Procedure for Melting Points and Freezing Points

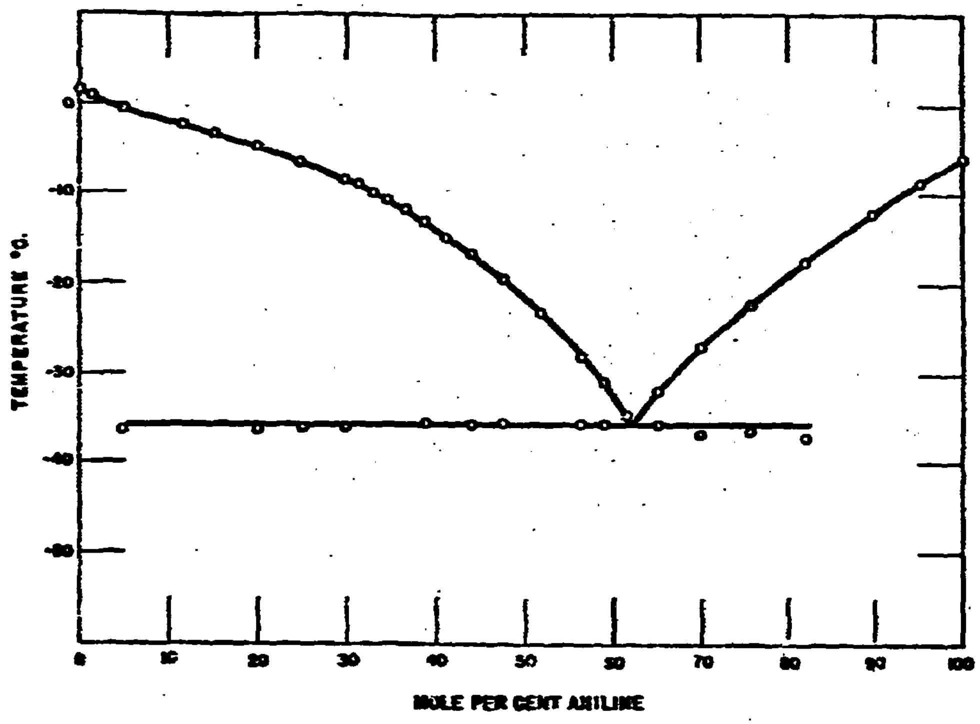
The mixtures of hydrazine with the various additives used in this study were prepared directly in the freezing point cell, using an analytical balance. Compositions were calculated from the weights thus obtained. For the experiments employing purified materials, the components were added to the cell while it was in the desiccator box. The commercial materials were handled in air.

Attempts to determine freezing points of mixtures of hydrazine with most of the additives were unsatisfactory. Supercooling took place to such an extent that reproducible freezing points could not be determined. Therefore almost all of the thermal analysis data presented in this report were obtained from warming curves. This procedure consisted of freezing the mixture with constant stirring and noting the approximate freezing point. The cell assembly was then placed in a warming bath which was a few degrees above the freezing point, and the temperature was allowed to rise. A warming rate of 0.1 - 0.2°C. per minute was obtained. Stirring of the mixture was continued until the melting point was passed. This procedure gave warming curves which were reproducible, and from which both eutectic points and points on the liquidus line could be determined readily. In some cases, however, especially during the early part of this study, data were obtained from cooling curves. Where this method was employed, it is indicated in the discussion.

RESULTS AND DISCUSSION

A phase diagram, plotted from thermal analysis data, of the system aniline-hydrazine is shown in Figure 2. The temperature-composition diagram indicates that aniline and hydrazine form a simple eutectic system. The mixture with minimum freezing point, that of the eutectic composition, contains 38 mole percent (17.3 weight percent) hydrazine and freezes at -35.9°C. Although a fuel having this freezing point may not be suitable for extreme temperature conditions, the melting point of the mixture shows definite improvement over pure aniline. The possibility of lowering the freezing point further by addition of a third component may possibly merit further investigation.

Because of the general availability of the lower alcohols, a number of binary systems of these materials with hydrazine were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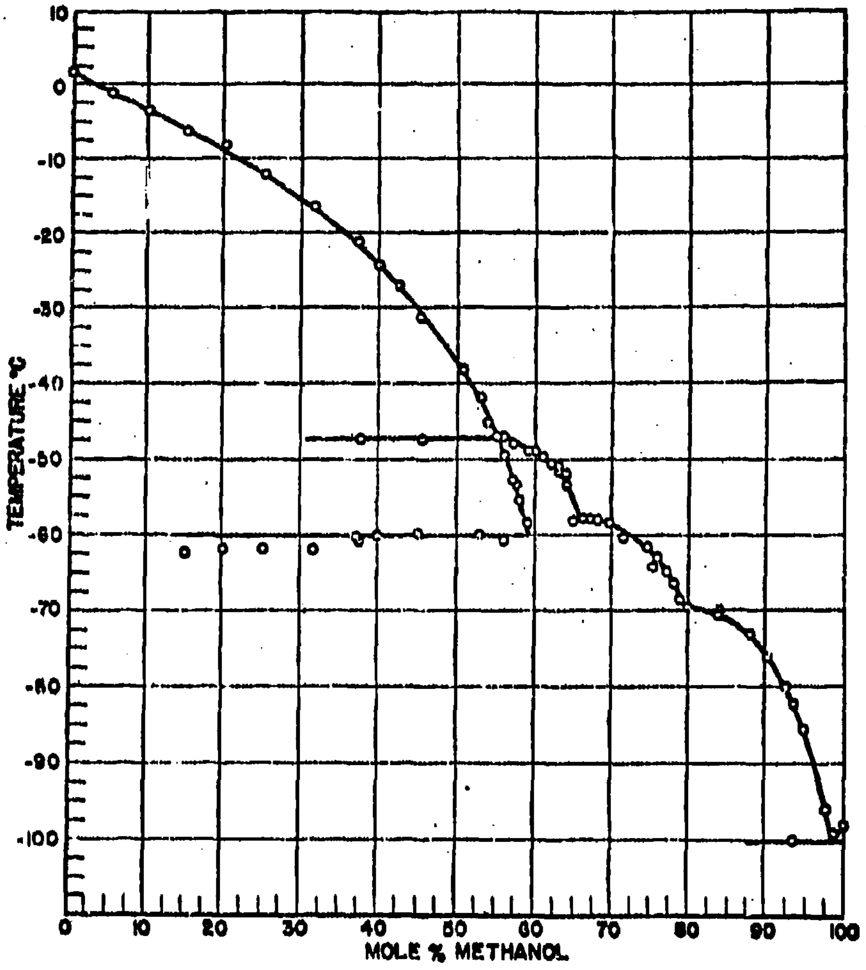
MOLE PER CENT ANILINE

investigated.

Melting point-composition data for the system hydrazine-methanol are plotted in the phase diagram given in Figure 3. Three addition compounds, $N_2H_4 \cdot CH_3OH$, $N_2H_4 \cdot 2CH_3OH$, and $N_2H_4 \cdot 4CH_3OH$ are found. Melting points of these compounds are -47.3°C., -57.8°C., and -69.5°C., respectively. The two eutectics melt at -60.0°C. and -100°C. The compound $N_2H_4 \cdot CH_3OH$ exhibits an incongruent melting point; its existence was established by isolation and analysis of the solid phase separating from a cooled mixture containing 59.4 percent methanol. Over the range of 55 - 59 mole percent methanol, two curves were obtained in the phase diagram. Points on the lower curves were found when the mixtures were melted immediately after freezing. When the frozen mixtures were allowed to stand for three or more hours, points were obtained on the upper liquidus line. Because a phase diagram of this type could also represent a transformation in the solid state, an analysis of the solid phase was made to establish definitely the existence of a compound. The upper liquidus line, therefore, represents a stable equilibrium between liquid and solid phases while the lower curve indicates a metastable equilibrium. Above a temperature of -47.3°C. the compound $N_2H_4 \cdot CH_3OH$ cannot exist, but decomposes into solid hydrazine and methanol. Because of the slow formation of this compound, equilibrium was not always reached before the mixtures were melted, and points on the eutectic line between $N_2H_4 \cdot CH_3OH$ and $N_2H_4 \cdot 2CH_3OH$ were found for mixtures containing less than 50 methanol.

The phase diagram for the system hydrazine-ethanol was determined largely from freezing points obtained from cooling curves. These data are plotted in Figure 4. This system forms one addition compound, $N_2H_4 \cdot 2C_2H_5OH$, which has a melting point of -31.2°C. The eutectic between hydrazine and this compound contains 55 mole percent ethanol and freezes at -33.7°C. The eutectic between ethanol and the compound, which contains approximately 98 mole percent ethanol, freezes at -117.3°C. Mixtures containing more than 90 mole percent ethanol exhibited such excessive supercooling that data in this region of the phase diagram were obtained only with great difficulty from cooling curves. The usual methods for inducing crystallization, such as producing cold spots on the freezing-point cell, were ineffective.

Both of these systems showed a drifting of the eutectic line toward lower temperatures as the mixtures became richer in hydrazine. This behavior was probably due to the frequent use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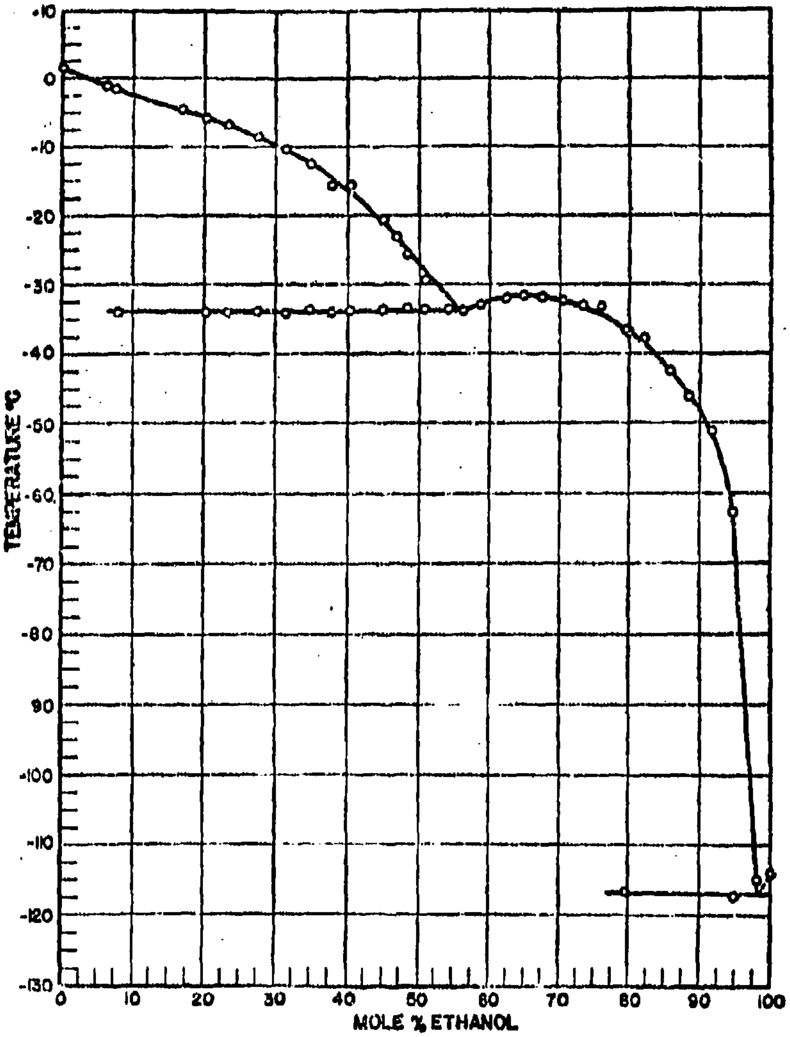
MOLE % METHANOL



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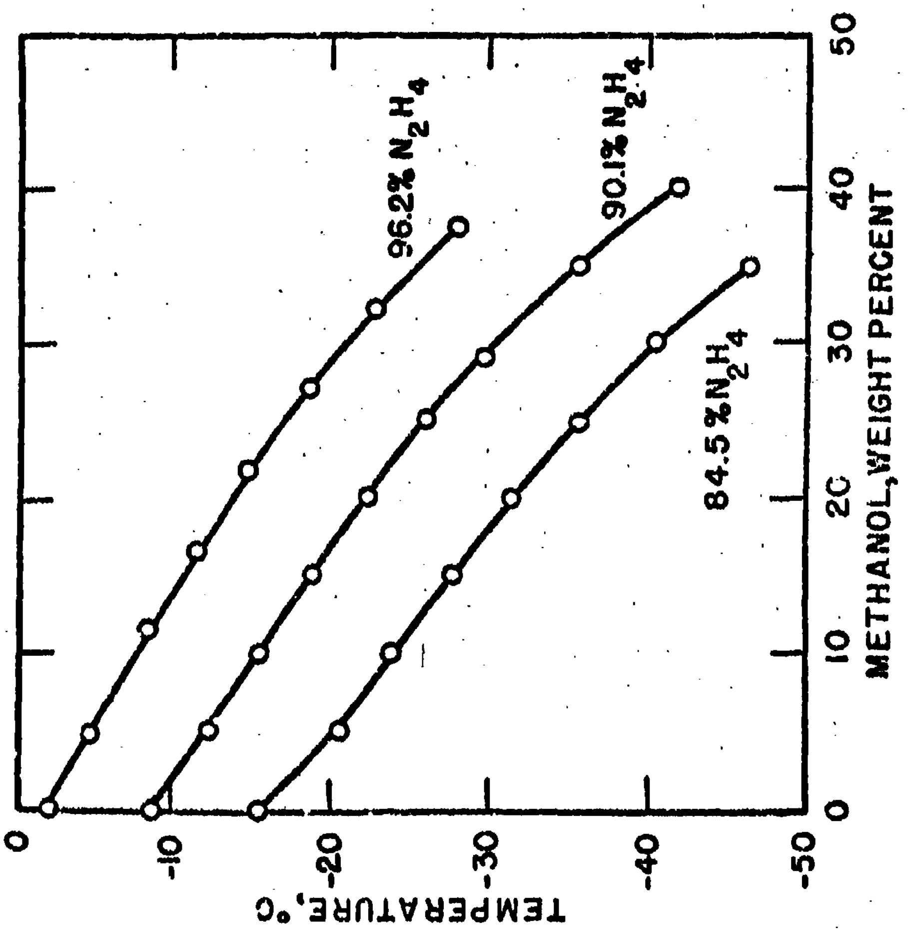
MOLE % ETHANOL

of cooling curves for determination of the solidification point of the eutectic and to the supercooling which was always observed. As the mixtures became richer in hydrazine, very little of the eutectic mixture was left when final solidification took place, and the small thermal effect was insufficient to compensate for the supercooling. For the system hydrazine-methanol, no reliable data could be obtained for the eutectic between the compounds $N_2H_4 \cdot 2CH_3OH$ and $N_2H_4 \cdot 4CH_3OH$.

The work on both of these systems was carried out using substantially anhydrous materials. In actual practice commercial products containing small amounts of water would be employed. For this reason a portion of the ternary system hydrazine-methanol-water was investigated. Three series of experiments were made in which the ratio of hydrazine to water was held constant and the amount of added methanol was varied. The concentrations of aqueous hydrazine solutions employed were 96.2, 90.1, and 84.5 percent. Absolute methanol was added in increments to these solutions and melting points were determined. The data are plotted in Figure 5. Although addition of water gave better freezing-point depression than with methanol alone, excessive dilution of the hydrazine with both water and methanol was required to reach low freezing points.

The system hydrazine-n-propyl alcohol resembles the hydrazine-ethanol system in exhibiting one fairly weak addition compound, $N_2H_4 \cdot 2C_3H_7OH$ (Figure 6). This compound melts at -41.3°C. and the eutectic between hydrazine and the compound melts at -42.4°C. Attempts to freeze mixtures containing more than 94.8 percent n-propyl alcohol were unsuccessful. Glasses were formed in this region and melting points of the mixtures could not be obtained. Investigation of the system hydrazine-isopropyl alcohol also indicated the formation of a 1:2 addition compound. A second inflection in the liquidus curve, however, was observed. It has not yet been determined whether this inflection in the curve represents an inverse peritectic or is due to formation of a second compound. Because of the high viscosity of the mixtures at temperatures in the neighborhood of -75°C., efforts to isolate and analyze the solid phase have not yet been successful.

Hydrazine and allyl alcohol also form a 1:2 addition compound (Figure 7). This compound melts at -68°C. The eutectic mixture of hydrazine and compound contains 62 mole percent allyl alcohol and solidifies at -69°C. At concentrations of more than 90 mole percent allyl alcohol a series of glasses were formed when the mixtures were cooled. These mixtures did not crystallize even on standing for long periods at low temperatures and efforts to


96.2% N_2H_4
90.1% N_2H_4
84.5% N_2H_4
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METHANOL, WEIGHT PERCENT
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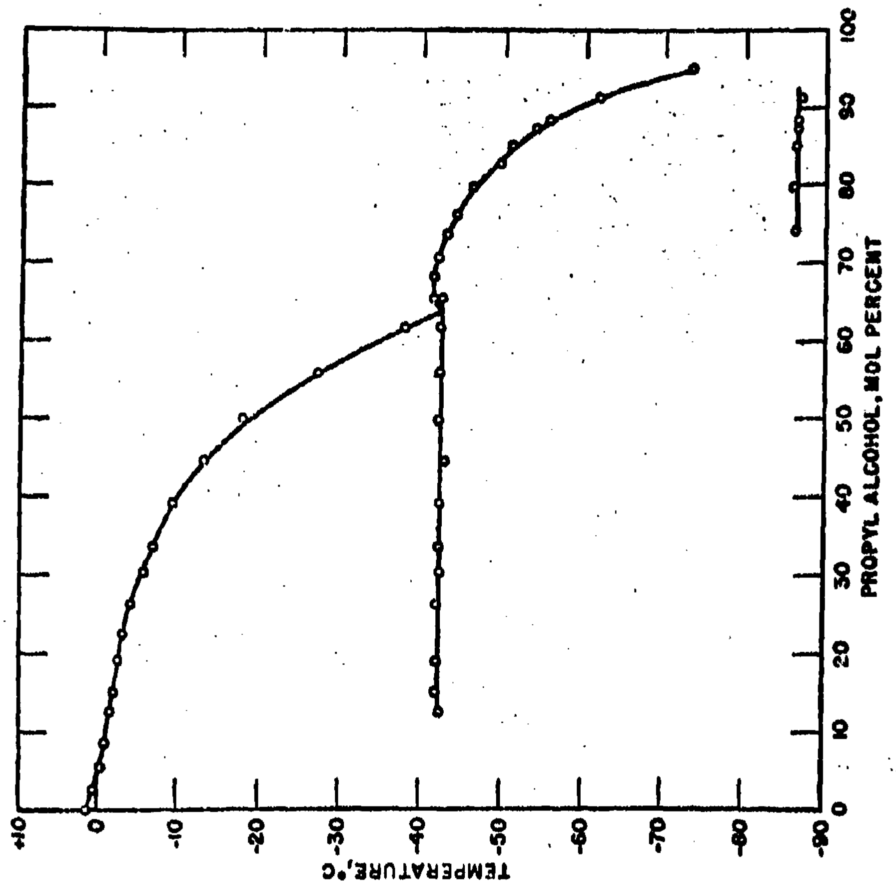
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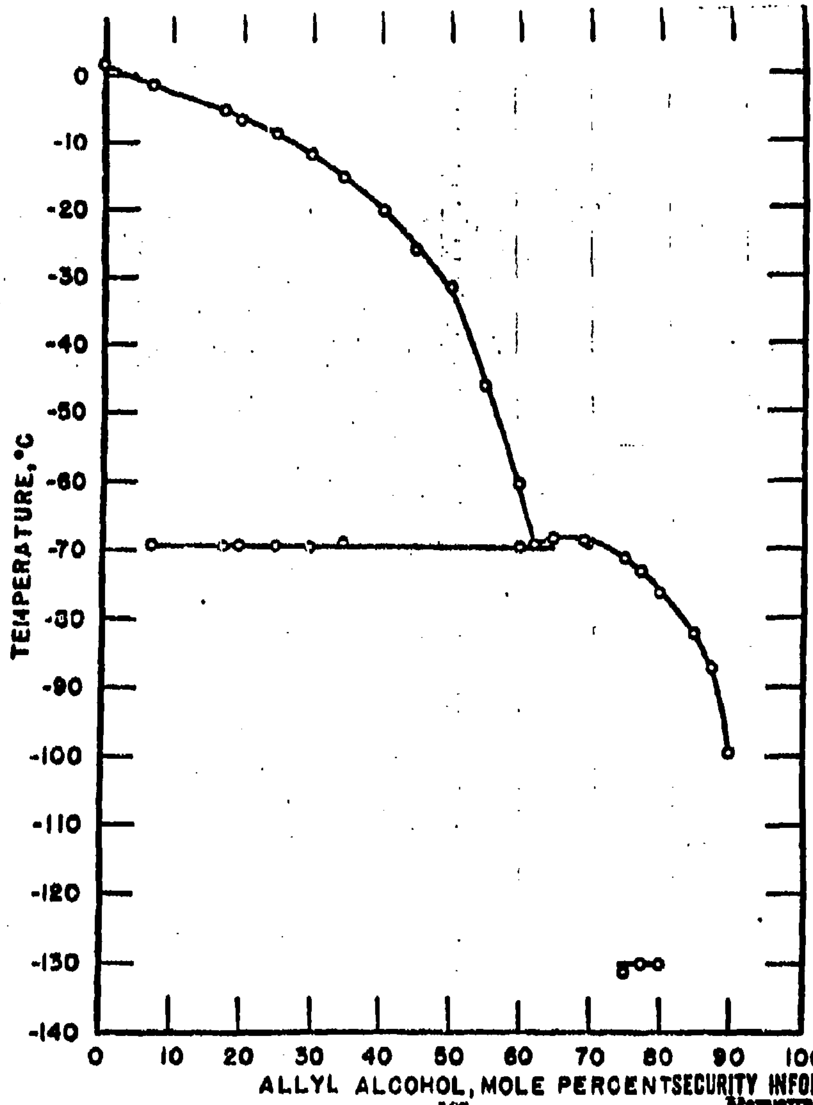
PROPYL ALCOHOL, MOL PERCENT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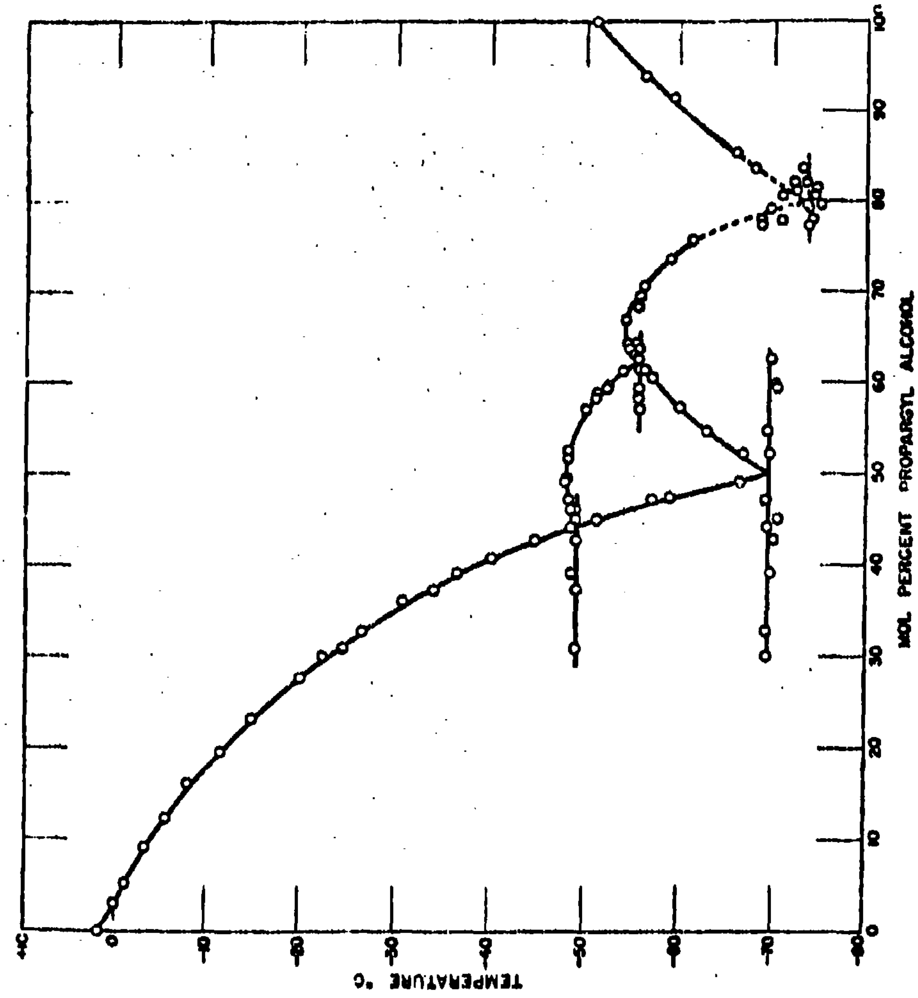
ALLYL ALCOHOL, MOLE PERCENT

in the cooling curves indicated a eutectic between the 1:2 addition compound and allyl alcohol which froze at approximately -130°C. The composition of the eutectic mixture lies between 90 and 100 percent allyl alcohol.

Melting point-composition data for the system hydrazine-propargyl alcohol are plotted in Figure 8. The phase diagram indicates the existence of two addition compounds, $N_2H_4 \cdot HC \equiv C\text{-}CH_2OH$ and $N_2H_4 \cdot 2HC \equiv C\text{-}CH_2OH$, having melting points of -48.0°C. and -54.2°C., respectively. The eutectic between hydrazine and the 1:1 compound melts at -49.2°C., while the eutectic between the two compounds melts at -55.6°C. The third eutectic melts at approximately -73.5°C. In this region a great deal of difficulty was experienced in determining melting points because of the tendency of the mixtures to form glasses. In many cases three to four days of holding the solutions at low temperatures were required to obtain crystallization. When mixtures having compositions in this region were melted, the points did not consistently fall on a smooth curve. The data, therefore, have some degree of uncertainty and part of the curve is indicated with a dotted line. In the area below the 1:1 addition compound a metastable portion of the system was found. The liquidus and eutectic lines for this region which are shown in Figure 8 were obtained when the mixtures were frozen and then melted immediately. If the frozen solutions were allowed to stand for a period of time, warming curves gave points on the upper stable liquidus curve. In a few cases points were found on both the stable and metastable curves. The metastable eutectic between hydrazine and the 1:2 addition compound melts at -69.5°C.

Propargyl alcohol exhibits a stronger combining tendency with hydrazine than any of the other alcohols which have been investigated. A definite, though weak, 1:1 addition compound is formed between hydrazine and propargyl alcohol. Such a compound does not form between hydrazine and ethanol, n-propyl alcohol, isopropyl alcohol, or allyl alcohol. Although with methanol a 1:1 compound is formed, this compound is extremely unstable, and has an incongruent melting point, i.e., the compound decomposes before the melting point is reached. Propargyl alcohol, like the other alcohols studied, also forms a 1:2 addition compound. The maxima in the liquidus curves of this system are sharper, however, indicating greater stability of the addition compounds.



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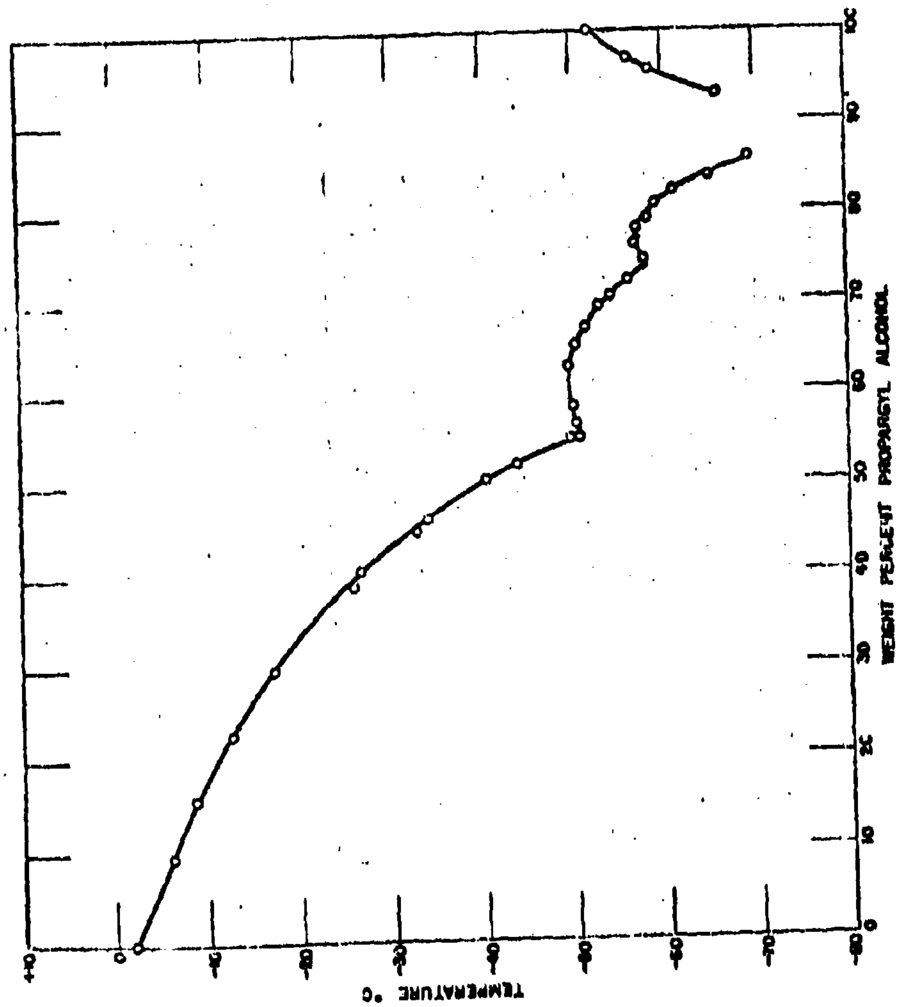
from these experiments are plotted in Figure 9. The shape of the liquidus curve is similar to that obtained with purified materials but melting points are somewhat lower. Thus, the first eutectic melts at -51.0°C. instead of -49.2°C. This mixture contains 55 weight percent propargyl alcohol and the melting point closely approaches the temperature of -65°F. currently specified for rocket applications. Because of compound formation, much larger amounts of the alcohol must be added to depress further the freezing point. In the region of the third eutectic, formation of glasses again took place and data for this part of the curve could not be obtained.

Inasmuch as propargyl alcohol is a potentially useful rocket fuel, further work on other properties of mixtures of this material with hydrazine may prove to be profitable.

Five-aminotetrazole, because of its acidic properties, gave a rapid depression of the freezing point of commercial hydrazine. This system was difficult to study, however, because of the tendency of the mixtures to form glasses. Melting points were determined over the range 0 - 35.0 percent 5-aminotetrazole. The eutectic composed of hydrazine and the hydrazine salt of 5-aminotetrazole melted at -36.8°C. and contained 32.8 percent hydrazine. Because the melting point of the eutectic was not as low as was desired, further work on this system was not carried out. Melting point-composition data (weight percent) for this system are plotted in Figure 10.

A fairly extensive investigation of the system hydrazine nitrate-water-hydrazine was made by thermal analysis methods. In order to plot the complete ternary diagram, thermal analysis data were required on a number of ternary mixtures, and on the three binary systems making up the sides of the triangular diagram. These binary systems were hydrazine nitrate-hydrazine, hydrazine-water, and hydrazine nitrate-water.

Melting point-composition data for the system hydrazine nitrate-hydrazine are shown in Figure 11. The phase diagram indicates the existence of one compound, hydrazine nitrate 1-hydrazinate ($N_2H_5NO_3 \cdot N_2H_4$), melting at 3.0°C. The first eutectic melts at -46°C. and contains 47.5 percent hydrazine nitrate. The eutectic between the compound and pure salt contains 79 percent hydrazine nitrate and solidifies at 2.5°C. The melting point of hydrazine nitrate, as determined in this Laboratory, was 70.7°C.



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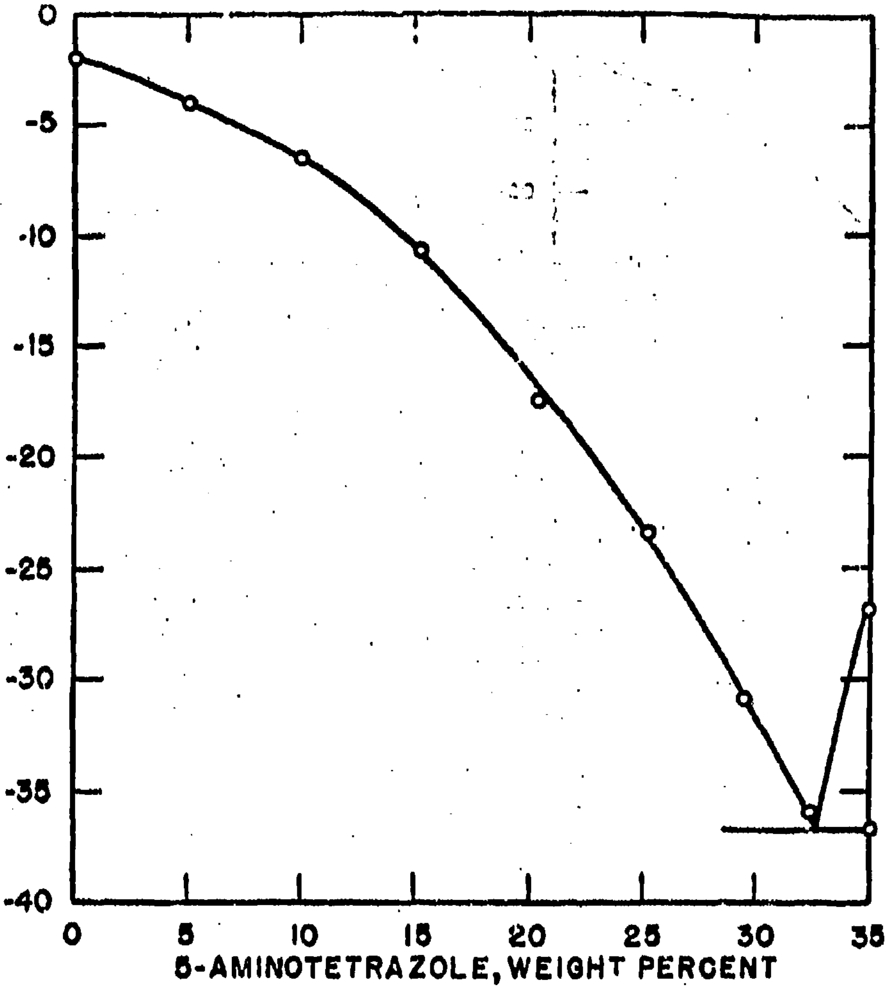
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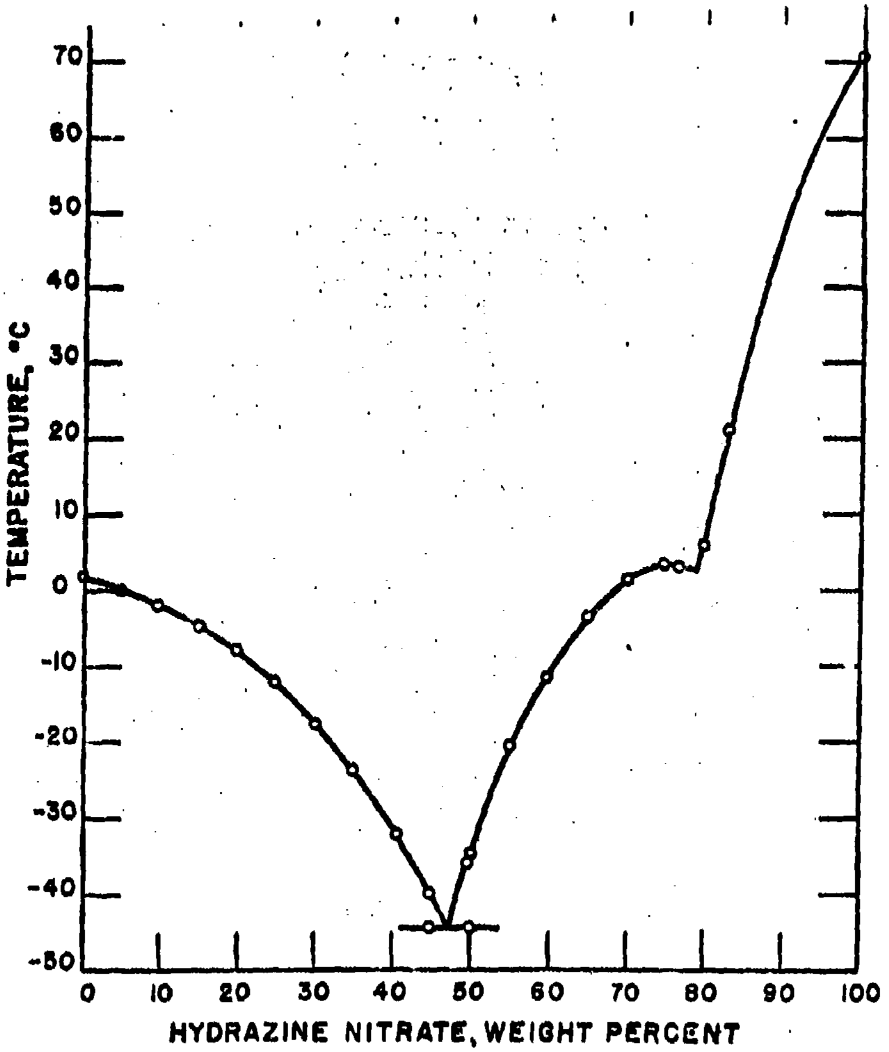
5-AMINOTETRAZOLE, WEIGHT PERCENT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HYDRAZINE NITRATE, WEIGHT PERCENT

good agreement with those of Mohr and Audrieth(4) and Hill and Summer(5). The data given in these papers, therefore, were used in plotting the phase diagram given in this report.

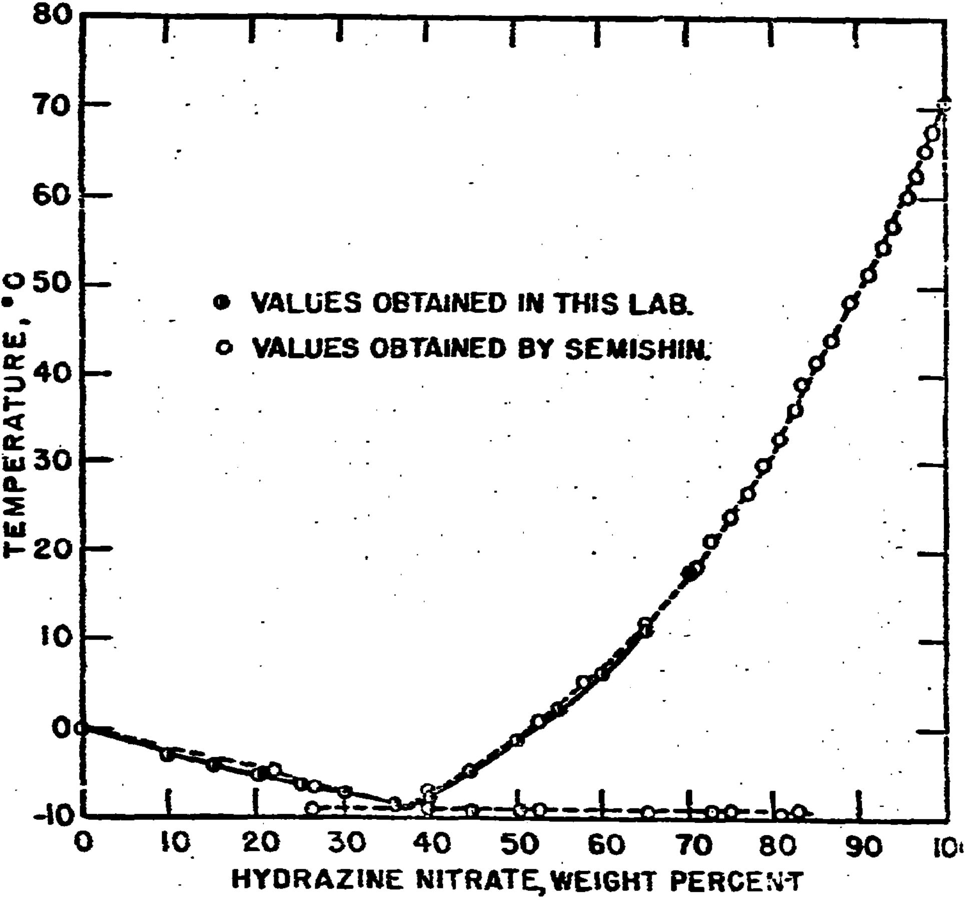
Work on the system hydrazine nitrate-water also has been reported previously. A phase diagram worked out by Semishin(7) indicates that these compounds form a simple eutectic system. Melting point composition data determined during the present investigation differ slightly from those given by Semishin over the range 0 - 70 percent hydrazine nitrate. Data at higher concentrations are in fairly good agreement. Melting point-composition data from both studies are plotted in Figure 12.

Points inside the ternary diagram were obtained from thermal analysis data on three-component mixtures. In most of the work the ratio of hydrazine to water was held constant and the amount of salt was varied. From these results, plane-section diagrams were constructed in which melting points were plotted against percent of hydrazine nitrate. Other plane-section diagrams were constructed from data obtained from a series of mixtures in which the ratio of hydrazine to salt was held constant and the amount of water was varied. In a third series of mixtures the ratio of water to hydrazine nitrate was held constant and the amount of hydrazine was varied. Data for plotting the isotherms on the triangular diagram were taken at five-degree intervals from the plane-section diagrams thus determined. The ternary diagram is shown in Figure 13. A photograph of a three-dimensional model of this system is shown in Figure 14.

The phase diagram shows four invariant points which are two ternary eutectics, a ternary peritectic, and the solidification point of the quasi-binary system hydrazine nitrate 1-hydrazinate-hydrazine hydrate. At the ternary peritectic the reaction

$$\text{Melt} + N_2H_5NO_3 \rightleftarrows N_2H_5NO_3 \cdot N_2H_4 + H_2O$$

takes place. Mixtures having compositions in the partial triangle bounded by hydrazine nitrate 1-hydrazinate, hydrazine nitrate, and water complete their solidification on cooling at the ternary peritectic point (-55°C.). Cooled mixtures having compositions in the triangle bounded by hydrazine nitrate 1-hydrazinate, the peritectic point, and water, have melt remaining when the peritectic temperature is reached. The composition then proceeds down the line to the ternary eutectic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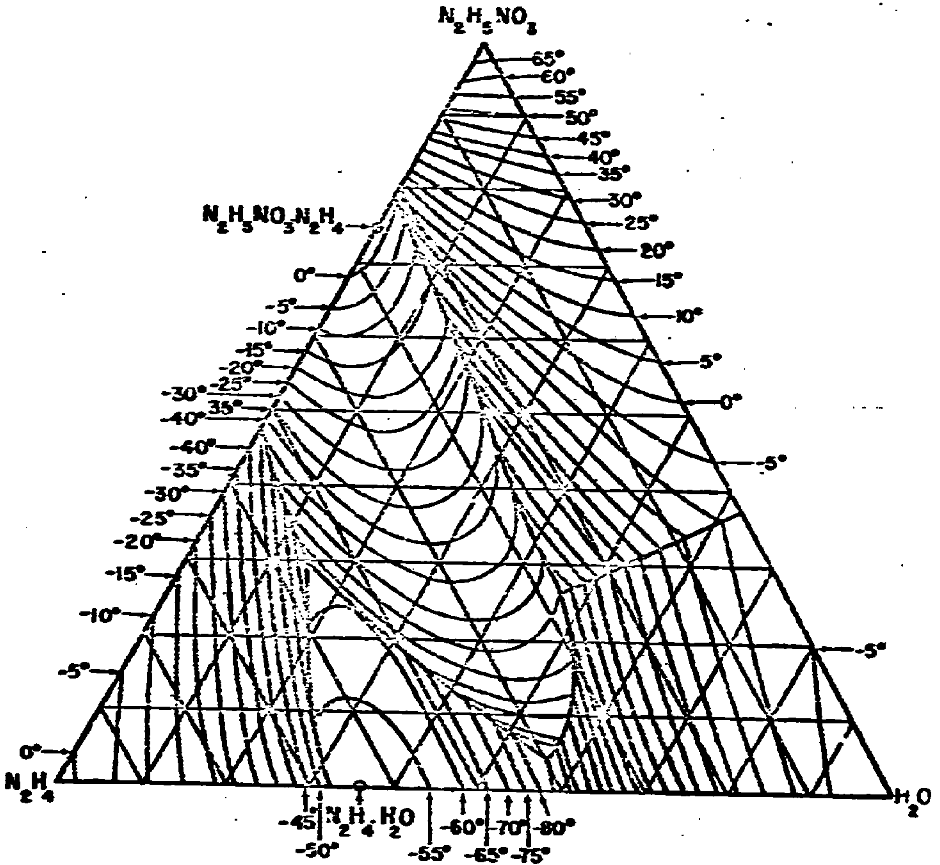
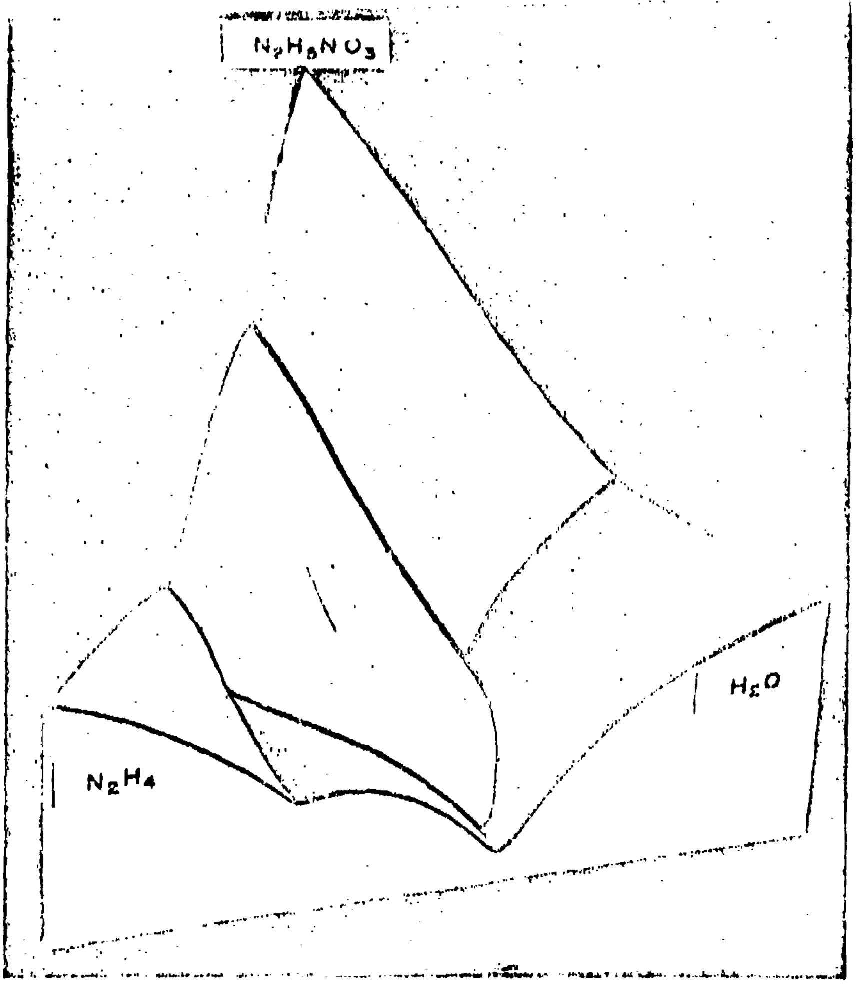
HYDRAZINE NITRATE, WEIGHT PERCENT
● VALUES OBTAINED IN THIS LAB.
○ VALUES OBTAINED BY SEMISHIN.



ISOTHERMS OF THE SYSTEM HYDRAZINE NITRATE-WATER-HYDRAZINE


$N_2H_5NO_3$
N_2H_4
H_2O

composed of hydrazine hydrate, hydrazine nitrate 1-hydrazinate, and water, at which point complete solidification takes place. The temperature of this eutectic is approximately -87°C. Formation of glassy mixtures in this region made the determination of accurate melting points almost impossible. Mixtures in the remainder of the diagram behave in the uncomplicated manner of a simple ternary system.

Compositions in the region of the ternary eutectic composed of hydrazine, hydrazine nitrate 1-hydrazinate, and hydrazine hydrate are of the most interest for fuel applications. The breaks in the warming curves of mixtures near this eutectic indicate a melting point of approximately -64°C. In this region a number of low-freezing mixtures may be formulated which contain appreciable amounts of hydrazine. The hydrazine nitrate concentration may be varied from 15 - 30 percent, and the water content from 10 - 20 percent to give solutions freezing in the neighborhood of -50°C.

SUMMARY

As a part of an investigation of low-freezing fuel mixtures containing hydrazine, phase diagrams were determined for binary systems of hydrazine with aniline, methanol, ethanol, n-propyl alcohol, isopropyl alcohol, allyl alcohol, propargyl alcohol, and 5-aminotetrazole. The ternary system hydrazine nitrate-water-hydrazine also was investigated.

Aniline and hydrazine form a simple eutectic system. The eutectic mixture contains 17.3 weight percent hydrazine and freezes at -35.6°C.

Hydrazine and methanol form three addition compounds, $N_2H_4 \cdot CH_3OH$, $N_2H_4 \cdot 2CH_3OH$, and $N_2H_4 \cdot 4CH_3OH$. The latter two melt at -57.8°C. and -69.5°C., respectively. The compound $N_2H_4 \cdot CH_3OH$ has an incongruent melting point and does not exist above -47.3°C.

A partial investigation of the ternary system hydrazine-methanol-water was carried out in the hydrazine-rich region of this system. Considerable dilution of the hydrazine was required to prepare fuel mixtures having low freezing points.

Ethanol, n-propyl alcohol, isopropyl alcohol and allyl alcohol all formed weak addition compounds with hydrazine containing two moles of alcohol per mole of hydrazine. In all cases the liquidus curve was not steep, and low-freezing compositions contained large amounts of the alcohol.

The system hydrazine-propargyl alcohol was studied using both purified and commercial materials. The phase diagram indicates the formation of 1:1 and 1:2 addition compounds. The optimum fuel mixture for this system from commercial materials appears to be one containing 55 weight percent propargyl alcohol and having a freezing point of -51.0°C. Because the 1:1 addition compound is fairly stable, however, much larger amounts of the alcohol are required to depress further the freezing point of hydrazine.

Stable compound formation occurs between hydrazine and 5-aminotetrazole, and the liquidus curve of the phase diagram, therefore, descends rapidly. The eutectic on the hydrazine side of the system contains 32.8 weight percent 5-aminotetrazole and solidifies at -36.8°C. when the mixture is prepared from commercial materials.

The phase diagram of the ternary system hydrazine nitrate-water-hydrazine shows the existence of two ternary eutectics and one ternary peritectic. In the region of the ternary eutectic composed of hydrazine, hydrazine nitrate-1-hydrazinate, and hydrazine hydrate, low-freezing mixtures (-50°C.) containing appreciable amounts of hydrazine may be formulated.

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PRACTICAL ASPECTS OF THE THERMAL DECOMPOSITION OF LIQUID HYDRAZINE USED AS A REGENERATIVE COOLANT

by

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Abstract

The thermal decomposition of hydrazine restricts the conditions under which this compound can be used as a regenerative coolant. It was necessary to obtain engineering data on the behavior of hydrazine at elevated temperatures so as to find the conditions that minimize this troublesome decomposition. For this purpose a study[1] of the rate of thermal decomposition of commercial liquid hydrazine has been made in the temperature range from 120 to 500°F by a measurement of the rate of pressure rise with time in closed pressure vessels containing hydrazine. There is evidence that both gas- and liquid-phase decomposition occur, although under the conditions of the present tests the rate-controlling reaction appears to be a heterogeneous gas-phase reaction. The mechanism of the decomposition process has not been established in the engineering tests. The catalytic effect on the rate of decomposition of various surfaces likely to be encountered in practical applications was tested. Glass, steels 1020 and 4130, stainless steels 303-A, 304, 347, and 502, iron, copper, and aluminum 2S-0 and 24S-T3, with various surface conditions, were among the materials tested. It was found that cadmium plating of the metal surface, when 0.5 to 1.0 weight per cent of cadmium acetate was dissolved in the liquid hydrazine, has a marked inhibiting effect on the rate of thermal decomposition. Tests of rocket motors employing hydrazine as a regenerative coolant were made with fuming nitric acid as an oxidant.

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[1] This paper presents the results of one phase of research carried out at the Jet Propulsion Laboratory, California Institute of Technology, under Contract No. DA-04-495-Ord 18, sponsored by the Department of the Army, Ordnance Corps.

[illegible]

In rocket motors it is desirable to obtain an increase in thermodynamic efficiency by using the liquid-propellant stream as the coolant which is required for the motor. Where highly corrosive liquids such as fuming nitric acid are employed as oxidants, it may be more practical to use the less corrosive liquid fuel in this process of regenerative cooling. With hydrazine, however, regenerative cooling is subject to limitations due to the inherent thermal instability of this compound. Engineering tests[1] were made of the rate of change of pressure with time in liquid hydrazine contained in closed stainless-steel vessels under isothermal conditions in the temperature range 120 to 500°F; also rocket motors were tested with regenerative cooling using hydrazine. Under these conditions the overall reaction appears to be described by a combination of two separate stoichiometric expressions:

$$3N_2H_4 \longrightarrow 4NH_3 + N_2 \qquad (1)$$

$$N_2H_4 \longrightarrow N_2 + 2H_2 \qquad (2)$$

Combining Equations (1) and (2)

$$(3 + x)\ N_2H_4 \longrightarrow 4NH_3 + (1 + x)\ N_2 + 2xH_2 \qquad (3)$$

where x represents number of moles of hydrazine which decompose according to Equation (2) per 3 moles of hydrazine which decompose according to Equation (1).

Elgin and Taylor (Cf. Ref. 1) and Askey (Cf. Ref. 2) measured the thermal decomposition in the vapor phase in the presence of each of the following materials: Pyrex, platinum, and tungsten, and found that a heterogeneous reaction, first order with respect to N_2H_4, occurred in the presence of glass, giving only NH_3 and N_2 as products according to Equation (1). In the presence of platinum and tungsten, NH_3, N_2, and H_2 were products so that both reactions (1) and (2) occurred to some extent. Szwarc (Cf. Ref. 3) attempted to measure the homogeneous gas-phase, first-order reaction in the presence of toluene vapor and found under these conditions an activation energy of 60 kcal/mol for the reaction. Hanratty et al (Cf. Ref. 4) found that a heterogeneous gas-phase reaction on glass proceeded by a first-order mechanism with an activation energy

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[1] This work was performed at the Jet Propulsion Laboratory by Anthony Briglio, Jr., A. F. Grant, Jr., D. N. Griffin, and D. D. Thomas

of 15.7 and 9.3 kcal/mol for surface-to-volume ratios of 2.5 and 18 cm^{-1}, respectively. Tantar (Cf. Ref. 5), Purgotti (Cf. Ref. 6), and Gutbier (Cf. Ref. 7) studied the decomposition of hydrazine in the liquid phase under various conditions. Kinetic mechanisms for the thermal-decomposition reaction are described in References 1 through 7. An excellent survey of the chemistry of hydrazine is given by Audrieth and Ogg (Cf. Ref. 8).

Equipment and Methods

Stainless steel, type 347 containing approximately 18 per cent by weight chromium and 8 per cent by weight nickel, was used as the material of construction for the cylindrical pressure vessels used in the engineering tests. Cylindrical vessels of two sizes, 20 and 36 ml, were used in the tests. The ratio of the surface of the cylindrical vessel to the volume of liquid contained was about 14 and 10 cm^{-1} for the 20- and 36-ml bombs, respectively. To determine the specific catalytic effect of other solid materials, pieces of the particular material to be tested were added to the bomb. In some cases the material was immersed in the liquid phase; in other cases the material was exposed to the gas phase. Pressure was measured by means of a conventional Bourdon-type gage. Pressure from the test system was transmitted to the pressure gage by capillary tubing filled with mineral oil. A pressure-release disk was provided in the hydraulic system in case an explosive rate of decomposition was encountered. The capillary tubing was joined at the top of the pressure vessel by means of an appropriate fitting. The entire tubing was filled with oil, care being taken to avoid contaminating the vessel with oil.

To keep the vessel and its contents at constant temperature, a bath filled with a low-melting alloy, Cerobend, was used at elevated temperatures, and an oil bath was used at low temperatures. Suitable heaters and control circuits were used to maintain isothermal conditions to within plus or minus 5°F in the bath. A thermocouple was placed in a thermocouple well made of stainless-steel tubing type 347, located inside the pressure vessel for the purpose of measuring the temperature of the contents of the vessel.

The bomb was filled at room temperature to such a level with commercial liquid hydrazine that the desired ullage resulted[1]. The primary impurity of this material was 3 to

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[1] The term ullage refers to the total volume of the gas phase relative to the total volume of the system and in this paper is expressed in per cent.

¼ per cent water with traces of ammonia present. The hydraulic lines were then attached to the vessel at atmospheric pressure. The vessel and its contents were immersed in the preheated constant-temperature bath. Pressure readings were recorded as a function of time, the origin for the time coordinate being taken when the temperature indicated by the thermocouple inside the vessel approached that of the surrounding bath. Pressure measurements with a precision of about 1 per cent were made up to 2000 psia before being discontinued.

The stoichiometry of the reaction was quantitatively tested from the volumetric behavior of the products in the gas phase, and it appears that reaction (2) occurs to some extent under the conditions of the experiments. Only the pressure in the system (not the composition) was measured as a function of time; thus no mechanism for the kinetics can be offered from these experiments without resorting to certain assumptions. Measurements were made over a wide range of temperatures so that an apparent activation energy for the reaction could be obtained. It was assumed that physical equilibrium between the phases was established rapidly with respect to the rate of thermal decomposition. Possible differences in the solubilities of the gaseous products in the liquid phase due to changes in conditions of the experiments were not compensated in the reported rates of pressure rise.

Conventional rocket-motor tests were performed using hydrazine as a regenerative coolant. Fuming nitric acid containing 6½ weight per cent NO_2 was used as an oxidant. Details of the rocket-motor installation are presented in Reference 9.

Results

In Figure 1 are shown typical curves of pressure as a function of time for several temperatures in the range 375 to 490°F for a stainless-steel type 347 bomb with cleaned surface. These measurements were made at an ullage of about 60 per cent. In another set of separate measurements the ullage was varied between 20 and 80 per cent at about 375°F, and there was no measurable change in the rate of initial pressure rise with time. These results suggest that hydrazine decomposition occurs predominantly in gas phase. With physical equilibrium constantly prevailing between the phases, the partial pressure of hydrazine in the gas phase is relatively constant irrespective of ullage. It would, therefore, be expected that the rate of

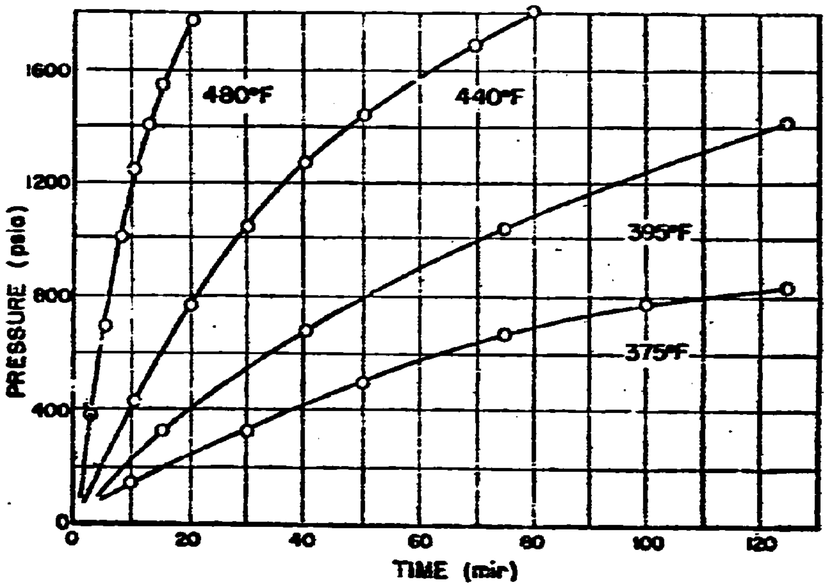

Figure 1. Pressure Rise in Hydrazine Due to Thermal Decomposition at Various Temperatures and 60 per cent Ullage

decomposition in the gas phase would be independent of ullage, as appears to be the case. On the other hand, if decomposition of hydrazine in the liquid phase were predominant, it would be expected that the rate of pressure rise with time in the system would be proportional to the relative amount of liquid phase present and would decrease with an increase in ullage. Such behavior was not measurable, and therefore it appears in the present set of measurements that the gas-phase decomposition is controlling.

In Figure 2 are plotted on a logarithmic scale values of dp/dt, the initial rate of change of pressure with time vs the reciprocal of the absolute temperature over the approximate temperature range 300 to 500°F. One set of these measurements was made in the stainless-steel type 347 vessel. The other set was made in a stainless-steel bomb which was plated with cadmium, and 0.5 weight percent cadmium acetate was added to the hydrazine. These rate data, plotted in Figure 2, are obtained by taking the initial slopes of curves such as those shown in Figure 1. It is evident from the data in Figure 2 that a linear relationship exists between ln(dp/dt) and the reciprocal of the absolute temperature. Such a relationship is in accord with the Arrhenius expression for the effect of temperature on reaction rates and also is in accord with the Clausius-Clapeyron equation for the effect of temperature on vapor pressure. The slopes of the lines in Figure 2 give an energy term which includes the heat of vaporization of hydrazine according to the Clausius-Clapeyron equation if the gas-phase reaction is controlling. From the slope of Figure 2, the energy term has a value of 18.2 kcal/mol for the unplated vessel and 25.5 kcal/mol for the cadmium-plated vessel. Subtracting from these values the latent heat of vaporization for hydrazine at 113.5°C of 10 kcal/mol (Cf. Ref. 8) assumed to be constant over the temperature range covered in Figure 2, one obtains 8.2 and 15.5 kcal/mol for the energy of activation without and with cadmium, respectively. The effect of cadmium on the system thus is to raise the activation energy. These values of the activation energy for a surface-to-volume ratio of 14 cm^{-1} are in the same range as the data of Hanratty et al (Cf. Ref. 4), previously mentioned.

The catalytic effect of various surfaces on the decomposition of hydrazine is depicted in Table I. The initial pressure rise with time dp/dt is given for temperatures in the proximity of 400°F. In the column marked R, values of the relative rate of change of pressure with time per square inch of surface of

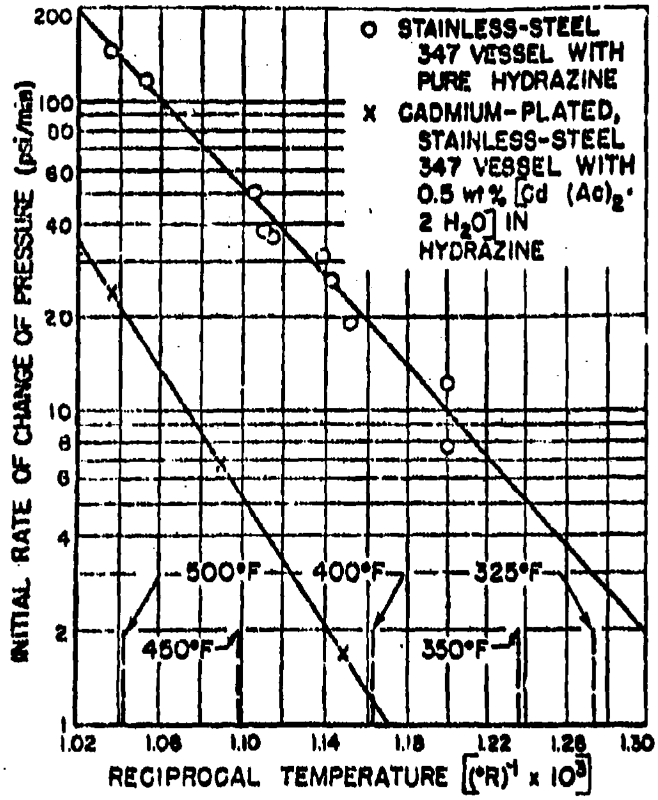

Figure 8. Effect of Temperature on the Rate of Change of Pressure in Hydrazine at 60 per cent Ullage Due to Thermal Decomposition with and without Inhibitor

TABLE I

THERMAL DECOMPOSITION OF HYDRAZINE IN CONTACT WITH VARIOUS MATERIALS AT APPROXIMATELY 400°F and 60 PERCENT ULLAGE

Test		Temp (°F)	dp/dt psi/min)	R (psi/min sq in)	R/R_g	Remarks
1	SS 347 vessel	403	22.9	-	-	-
2	SS 347 vessel	401-405	19.6	-	-	-
3	SS 347 vessel	401	16.2	-	-	-
4	SS 347 vessel + Pyrex glass rod	409	56.3	3.12) } 2.94 av	1.00	-
5	SS 347 vessel + Pyrex glass rod	406	38.0	2.76)	1.00	-
6	SS 347 vessel	401	2.2	-	-	Cadmium-plated vessel
7	SS 347 vessel	407	1.6	-	-	0.25% $Cd(OH)_2$ in hydrazine
8	SS 347 vessel	413	13.3	-	-	0.1% Cd $(Cl)_2$ in hydrazine
9	SS 347 vessel + steel 1020 strip	415	109	11.4	3.88	1020 strip, clean
10	SS 347 vessel + steel 1020 strip	405	81.5	10.2	3.47	1020 strip, clean
11	SS 347 vessel + steel 1020 strip	400	extremely rapid	-	-	1020 strip, highly oxidized
12	SS 347 vessel + steel 4130 strip	398	74.0	15.0	5.1	4130 strip, clean
13	SS 347 vessel + steel 4130 strip	402	94.9	18.4	6.3	4130 strip, clean
14	SS 347 vessel + steel 4130 strip	398	130	68.0	23.1	4130 strip, slightly oxidized

Test		Temp (°F)	dp/dt (psi/min)	R (psi/min sq in)	R/R_s	Remarks
15	SS* 347 vessel + steel 4130 strip	400	extremely rapid	-	-	4130 strip, highly oxidized
16	SS 347 vessel + SS303-A strip	393	23.8	1.40	0.40	303-A strip, clean
17	SS 347 vessel + SS304 strip	404	34.4	1.36	0.46	304 strip, clean
18	SS 347 vessel + SS304 strip	400	39.1	2.14	0.73	304 strip, slightly oxidized
19	SS 347 vessel + SS347 strip	400	59.1	6.02	2.04	347 strip, cleaned
20	SS 347 vessel + SS347 tube	413	95.0	17.8	6.05	347 tube, slightly oxidized
21	SS 347 vessel + SS502 strip	403	102.9	13.0	4.42	502 strip, cleaned
22	SS 347 vessel + SS502 strip	402	212	92.5	31.3	502 strip, highly oxidized
23	SS 347 vessel + iron wire	401	67.8	12.0	4.08	ironwire, cleaned
24	SS 347 vessel + copper strip	403	30.5	2.67	0.91	copper strip, cleaned
25	SS 347 vessel + copper strip	400	28.0	4.92	1.67	copper strip, highly oxidized
26	SS 347 vessel + Al 2S-0	398	38.7	2.92	1.0	Al 2S-0, cleaned
27	SS 347 vessel + Al 24S-T3	403	42.2	2.24	0.74	Al 24S-T3, cleaned

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* Stainless steel

designated material added to the gas phase are tabulated. To calculate values of R the value of dp/dt for hydrazine in the stainless-steel type 347 vessel without added material is subtracted from the overall rate observed in the presence of added material, and the resulting net value of rate of pressure rise is divided by the area of the surface of added material exposed. In the column marked R/R_g, values of the relative pressure rise per unit time per unit area for various materials relative to glass, $R_g = 2.94$ psi/min sq in., are given. It is evident from a comparison of tests 11, 14, 15, 18, 20, 22, and 25 with tests 10, 13, 17, 19, 21, and 24 in Table I that the metals with oxidized surfaces catalyze the decomposition reaction more extensively than do metals with clean unoxidized surfaces. Aluminum alloys and copper appear to catalyze the reaction less than do the steel alloys, except stainless steels types 303-A and 304, which catalyze the reaction to approximately the same degree as do aluminum alloys and copper.

It is evident from tests 6 and 7 in Table I that the rate of thermal decomposition of hydrazine is markedly inhibited either by cadmium plating of the surface of the pressure vessel or by the presence of cadmium hydroxide dissolved in the liquid phase of hydrazine. The effect of cadmium plating of the vessel and of the addition of cadmium acetate to the solution is shown in Figures 2 and 3. In Figure 3 is shown quantitatively the effect of various amounts of $Cd(Ac)_2 \cdot 2H_2O$ as an additive to hydrazine on the rate of pressure rise at 455°F in the stainless-steel type 347 test vessel. It is seen that from 0.5 to 1.0 per cent by weight of cadmium acetate hydrate effectively lowers the initial decomposition rate about twelve fold over the rate when no additive is present. The mechanism by which cadmium, either in solution or plated on the vessel wall, acts as an inhibitor has not been established.

Tetraethyl lead, lead acetate, and liquid mercury were added in quantities of about 25 gm/liter to the liquid phase, and none of these additives measurably affected the decomposition. H_2SO_4 and KOH added to the liquid phase appear to catalyze the decomposition. To lower the freezing point of hydrazine, nitric acid is sometimes added to give hydrazine nitrate. In Figure 4 is shown the decomposition rate as a function of weight per cent HNO_3 for hydrazine containing 0.5 weight per cent cadmium acetate stored at 120°F. The effect of HNO_3 in increasing the decomposition rate precludes the presence of this additive in hydrazine used for regenerative cooling. The effect of added H_2O on the rate of decomposition at 450°F is also shown in

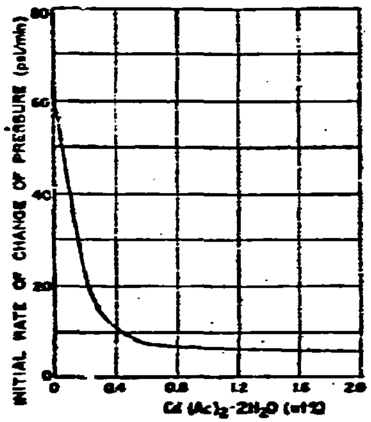

Figure 3. Effect of Dissolved Cd(Ac)$_2$ · 2H$_2$O on the Rate of Change of Pressure in Hydrazine at 455°F 60 per cent Ullage

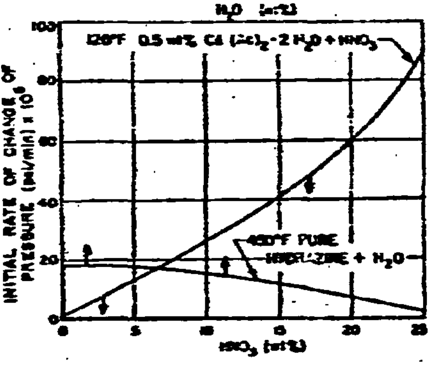

Figure 4. Effect of Dissolved H$_2$O and HNO$_3$ on the Rate of Change of Pressure in Hydrazine at 60 per cent Ullage

Figure 4, and it is evident that H_2O inhibits this rate slightly. HCl is found to catalyze the decomposition more markedly than do the other acids, and this behavior suggests that chloride is a specific catalyst. From test 8 in Table I the ineffectiveness of cadmium chloride in inhibiting the decomposition, compared with the other cadmium salts, may be due to this catalytic effect of chloride.

Rocket motors were regeneratively cooled using hydrazine, and some seventy-five engineering tests were made. Fuming nitric acid containing 6 1/2 weight per cent NO_2 was used as oxidizer. The cooling passages of the motor were made of carefully cleaned stainless-steel 347 tubing for most of the tests, and a limited number of tests was made with copper and steel 1020 as cooling passages. A motor with stainless-steel 347 cooling coils and a characteristic length L* of 31 inches was successfully cooled regeneratively with hydrazine over a range of chamber pressure from 178 to 412 psia, and a motor having a value of L* of 13 inches was operated over a range of chamber pressure from 106 to 430 psia. The maximum bulk temperature of the coolant hydrazine entering the injector was 438°F. When stainless-steel 347 tubing was used in the cooling passages, no explosions occurred during regenerative cooling with hydrazine either with or without a combination of cadmium plating of the steel and the presence of cadmium salts in the hydrazine. However, care had to be taken to eliminate regions in the cooling passages where hydrazine could stagnate and overheat. With copper or steel 1020 cooling passages, failures occurred.

The performance obtained with motors regeneratively cooled with hydrazine was higher than expected, and the gain in performance was greater than could be accounted for by the increase in sensible heat of the incoming hydrazine. This increase in performance is attributed to increased rates of combustion resulting from injection of heated hydrazine into the motor. Complete details of the results of these rocket tests are presented by Briglio (Cf. Ref. 9).

Conclusions

As a regenerative coolant, hydrazine is liable to excessive decomposition on oxidized metallic surfaces. Even on clean metal surfaces the decomposition rate is high enough at elevated temperatures to be intolerable. Aluminum alloys 2S-0 and 24S-T3 and copper are superior to steels 1020 and 4130, stainless steels 347 and 502, and iron. However, stainless steels 303-A and 304 are comparable to the aluminum alloys and copper in this respect. It is recommenced that all metal surfaces exposed to the hydrazine be plated with cadmium and that from 0.5 to 1.0 per cent of $Cd(Ac)_2 \cdot 2H_2O$ be added to the liquid phase to minimize thermal decomposition of hydrazine during the process of regenerative cooling.

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HIGH PRESSURE THERMAL DECOMPOSITION OF HYDRAZINE

by

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Presented by M. N. Olsen

Under sponsorship of the Navy Bureau of Aeronautics, Reaction Motors, Inc. is currently developing a liquid propellant powerplant to operate aircraft catapults. Two model powerplants have thus far been constructed and launching tests with a slotted tube catapult have been successfully completed.

The catapult powerplants rely upon high pressure combustion or decomposition of liquid propellants for the continuous production of large quantities of gas. This gas is then admitted directly into a catapult tube, where it does work against a sliding piston which is connected to the plane or missile to be launched.

Although these powerplants were originally designed for, and are presently successfully operated with gasoline and liquid oxygen, temperature and control problems forced consideration of other propellant combinations. Since these and other problems could be avoided through the use of different reactants, a supplementary catapult propellant investigation was initiated. In this new program high pressure laboratory test apparatus was constructed and combustion and decomposition experiments were made with a variety of propellants. The high pressure apparatus and the decomposition tests with anhydrous hydrazine are the subjects of this presentation.

In order to qualify for catapult use a monopropellant must lend itself to stable, efficient, continuous decomposition without the aid of a catalyst. Therefore, it was necessary to study means of initiating and sustaining controlled thermal decomposition of anhydrous hydrazine over a range of operating pressures. The pressure range selected was 2000 to 10,000 psi.

Absence of a catalyst was specified to avoid the use of a second propellant material which would complicate catapult operation and propellant supply, and also to avoid the accumulation of residue in a catapult tube. Furthermore, previous experiments with other monopropellants, e.g., ethylene oxide and hydrogen peroxide, had already demonstrated the simplicity and efficiency possible with high pressure thermal decomposition reactions.

Although it was hoped that test runs of two to three minutes duration would be possible and in some cases were, all of the hydrazine tests were of approximately one minute duration. The reaction efficiency was to be determined through accurate measurement of propellant flow rate and chamber pressure. Various techniques for starting the decomposition reaction were also to be studied.

Some of the problems peculiar to this high pressure operation were: the design and the fabrication of the chamber, the problem of injecting the propellants against high reaction pressures and the handling of the rather heavy assembly.

After careful study of the propellant injection problem it was decided that the controlled vaporization of liquid nitrogen and liquid oxygen in evaporators was the simplest means of generating the pressurizing gas at the pressures necessary for injecting the propellants. This approach eliminated the need for high pressure sliding seals. Saturable reactors (0-10KVA), visible on the right (Figure I) were procured to provide the electrical power needed for immersion coil heaters. These heaters were placed in the evaporators which were enclosed in the large Dewars seen in the center of the picture. The evaporator pressure was read from the safety of the test instrumentation rooms with the Bourdon Gauges (top center) by means of a telescope. The small container on the left is one of the propellant tanks. These tanks of 1 liter capacity were of stainless steel with a one and one quarter inch wall and a modified high pressure Bridgman seal closure.

In Figure I a portion of a test cart designed to handle the vaporization assembly is visible. This test cart, constructed of one half inch steel plate mounted on heavy duty castors made it possible to easily move the assembly in the laboratory and in the test cell. The evaporators, propellants, tanks, high pressure valves, fittings and tubing, all designed for a 15,000 psi working pressure, and the electrical reactors totalled approximately 2000 lb.

The evaporator vessels (7 liter capacity) in which the electrical heating coils were immersed are shown in Figure II.

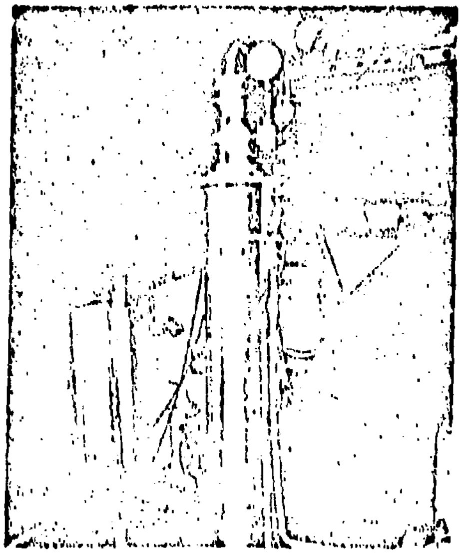

Figure I. High Pressure Propellant Supply

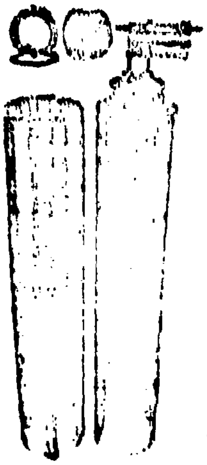

Figure II. Evaporator Vessels

These vessels are also of stainless steel, having the same wall thickness, and a modified Bridgman seal closure. They were purchased from Autoclave Engineering, Inc. of Erie, Pennsylvania. In practice, pressures of from 12,000 to 15,000 psi were generated in these evaporators within five minutes after the power was turned on.

The basic hydrazine decomposition chamber is shown in Figure III. The closures contain threaded steel plugs which were machined to provide various injector and exhaust nozzle configurations depending on the propellant or propellant combination being tested.

Various liners were used in the program but for the hydrazine tests liners of either zirconium dioxide or carbon were used. The liners were used not only to protect the chamber and cut down heat loss but also to eliminate catalytic effects at the steel walls.

As shown in Figure III provision was made for preheating the chamber with an igniter device. Hydrazine was introduced into the chamber only after the chamber temperature reached approximately 1200°F. Precautions were taken to make certain the chamber was sufficiently preheated since in one of the early tests, an overlong induction period caused by nonuniform preheat resulted in a hard start - sufficient to distort the one and one-fourth inch chamber wall.

The following brief discussion of the operating procedures is based on Figure IV (Schematic of High Pressure Supply System). Although both a fuel and oxidizer system are shown, only one half of it is used for tests with monopropellants. The intermediate tank in the fuel system was supplied with liquid nitrogen directly from the liquid nitrogen reservoir. This nitrogen was then forced into the evaporator by gas pressure generated in the intermediate tank through the action of an exchanger coil. When the evaporator was full as evidenced by the escape of liquid nitrogen through the vent valve the system was sealed and personnel were cleared from the test cell. The remainder of the operation was remotely controlled.

The propellant restriction valve (No. 4) was opened which permitted pressurizing of the system to the propellant metering valve (No. 2). At this stage the power switches were closed and the power input to the immersion coil in the evaporator adjusted by means of a variac. Within several minutes a 12,000 to 15,000 psi gas pressure was built up. When the desired pressure was reached, a hydrogen-oxygen igniter was turned on for about 30 seconds, thereby preheating the chamber to 1200°F.

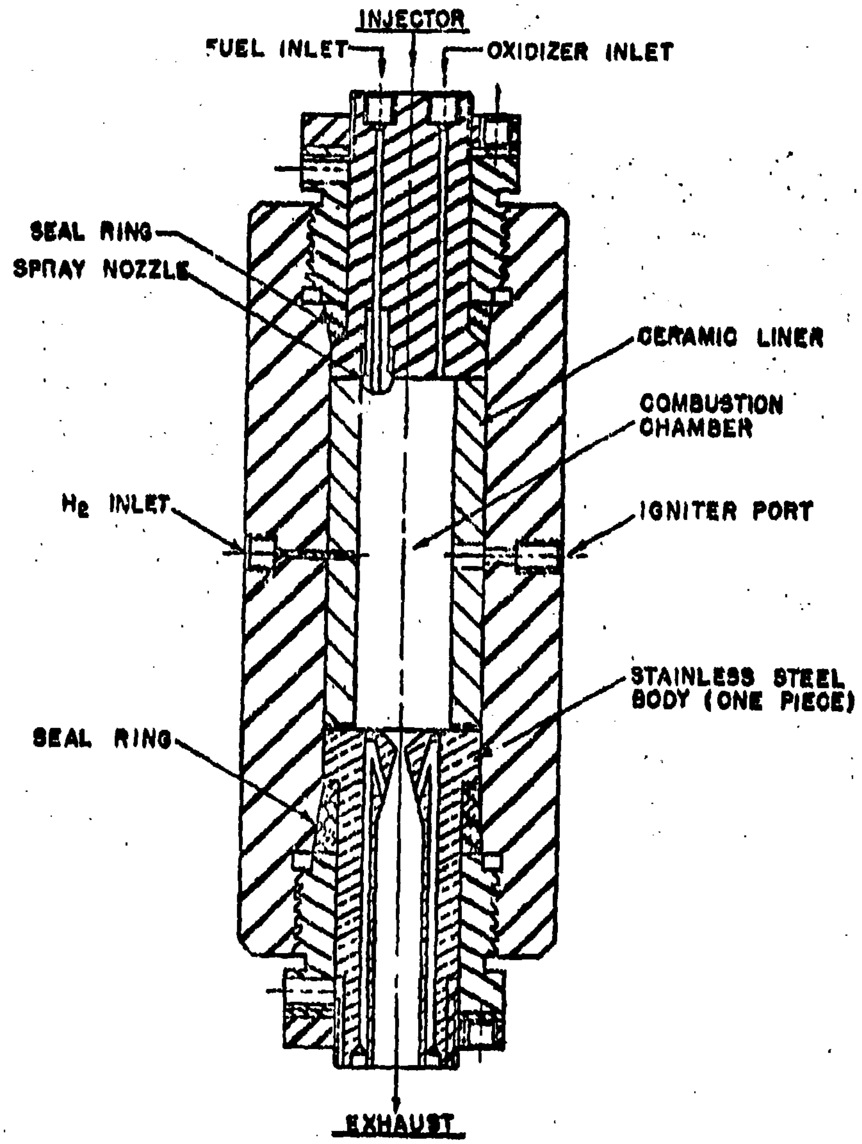

FIGURE III

HIGH PRESSURE COMBUSTION CHAMBER

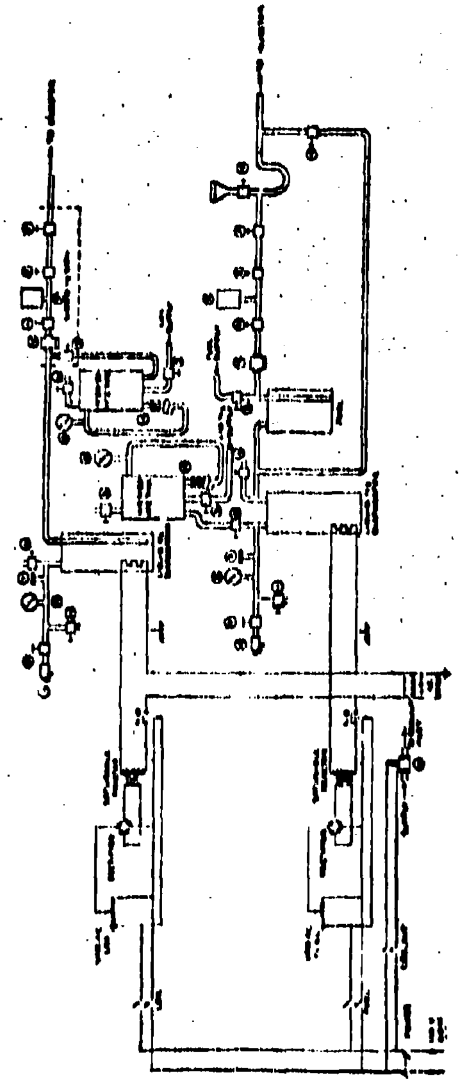

Figure IV. Schematic of High Pressure Supply System

At this point the hydrazine was introduced into the chamber by opening the on-off quick acting valve (No. 1) and metering valve No. 2. The test run continued with the chamber pressure controlled through fuel metering. All of the hydrazine test runs were of about sixty seconds duration, limited both by the fuel supply and evaporator pressure. The run was terminated by closing the quick acting valve (No. 1) and simultaneously opening the blow down valve (No. 13).

A series of twenty-seven test runs were successfully completed with hydrazine in the chamber pressure range of from 2,000 to 10,000 psi. Chamber pressure measurements were made with commercial stain gauge transducers and a self-balancing potentiometer (± 1.5%). In all cases smooth, continous controlled decomposition, thermally initiated, was achieved.

Time versus chamber pressure records of three test runs are shown in Figures V and VI. These typical results illustrate both the rapid chamber pressure build-up and the chamber pressure control achieved by the metered hydrazine flow control. Flows were measured by means of a Potter rotating vane flowmeter and a Brush type Galvanometer recorder. The overall flow measurement accuracy was ± 1.5%. A high pressure housing was devised for the rotating vane element and repeated flow calibration indicated that the volumetric flow measurements were independent of density and pressure.

The intent of this study was not only to maintain decomposition at these high pressures but also to obtain relative performance data. Consequently, the restrictive exhaust orifice was carefully measured and the performance was based on characteristic exhaust velocities, C* defined in the following equation:

$$\overline{C^*} = \frac{P_{ch} A_t g}{W_p}$$

P_{ch} = chamber pressure, psia
g = gravitational constant, 386.4 in/sec^2
A_t = throat area, in^2
W = Total propellant flow lb/sec

Evidently little gas generation performance advantage is gained by operating at pressures above about 6000 psi since a

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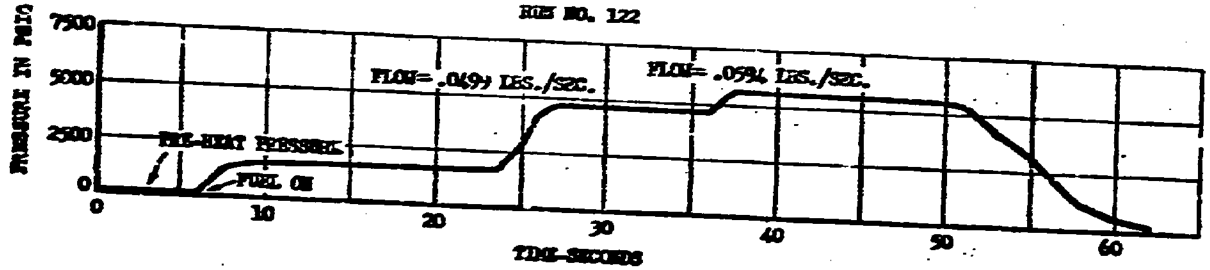
FIGURE V

CONSTANT PRESSURE COMBUSTION TEST
ANHYDROUS HYDRAZINE

RUN NO. 122



RUN NO. 123

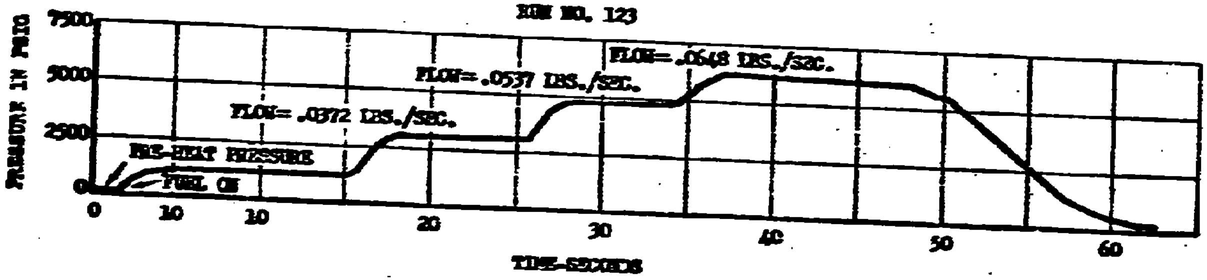


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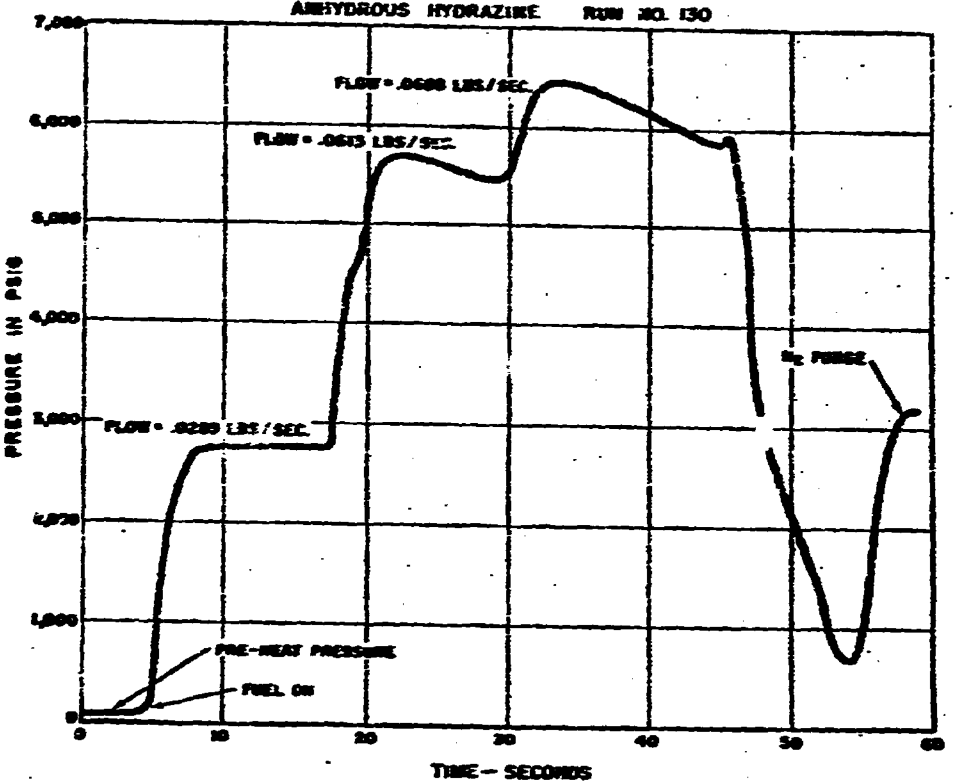
FIGURE VI
CONSTANT PRESSURE COMBUSTION TEST
ANHYDROUS HYDRAZINE RUN NO. 130



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50% increase in chamber pressure at this point results in only a 3% increase in C*. The particular value of these data lies in their use for comparative purposes with other propellants. For example, data collected in the investigation show that C* for ethylene oxide under the same conditions is about 6% higher than that for hydrazine.

In conclusion, it should be emphasized:

(1) That controlled thermal decomposition of hydrazine has been demonstrated in the pressure range 1600 to 10,000 psi. Decomposition below 1500 psi becomes more critical. No apparent serious problems confront sustained thermal decomposition at even higher pressures.

(2) Chamber preheating, either by electrical resistance elements or with a gas torch is extremely dependable for initiating the decomposition of anhyrous hydrazine. Many tests characterized by smooth starts and good control demonstrated this.

(3) At elevated pressures, chamber and injector configurations become less critical and consequently good performance can be achieved with very simple devices.

In the opinion of the authors, operation in the high pressure realm offers many advantages in miniaturization of otherwise heavy duty equipment. Because of the development of high pressure sliding seals present high pressure apparatus can be greatly simplified by substituting piston feed units for evaporators. The authors believe that valuable information has been obtained and techniques acquired through these studies in this relatively unexamined area. However, additional studies should be conducted, particularly on fast starting techniques and catalytic effects in the higher pressure ranges.

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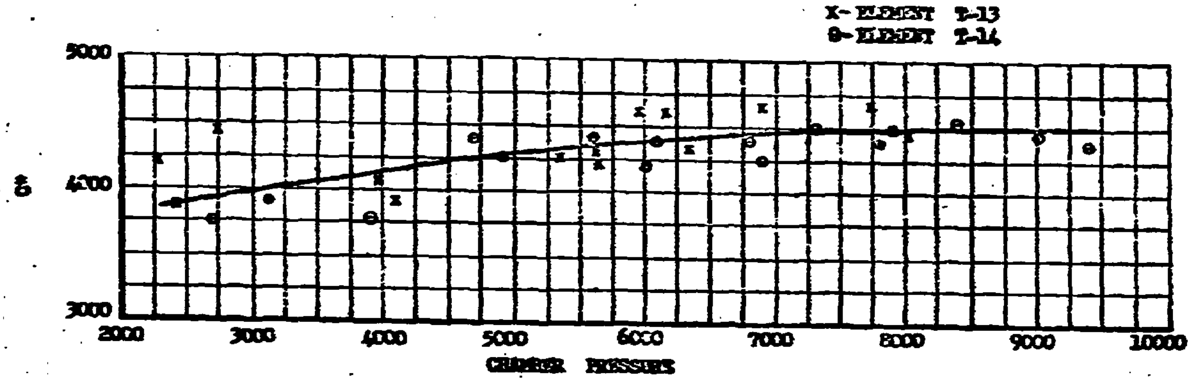
FIGURE VII

C* vs. CHAMBER PRESSURE
ANHYDROUS HYDRAZINE



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DECOMPOSITION RATES OF HYDRAZINE AND HYDRAZINE NITRATE SOLUTIONS AT HIGH PRESSURES

by

T. L. Thompson
Redel Incorporated

The employment of hydrazine as a propellant in liquid propellant guns is an important factor in the consideration of this chemical. Potentially, large tonnages of hydrazine may be consumed in this manner and in the present development phase of the liquid propellant gun program, many facets of knowledge of hydrazine, its properties, and its reactions are being brought to light. The Services have a well integrated plan of research and development which is being carried on at various universities, Service laboratories, and private firms. As a part of this effort, Redel Incorporated is investigating the variation of reaction rates of hydrazine propellant solutions with wide differences of conditions such as pressure and temperature. The knowledge of these reaction rates is important in the design and development of the guns as it will allow maximum energy release for propulsion without exceeding the strength limits of the barrel and will allow rapid cycling of propellant loading without cartridge cases. The full advantage of liquid propellants can not be utilized unless the reaction in the chamber is under control at all times.

The program of investigation initially calls for the determination of reaction rates for pressure variations from atmospheric to 30,000 psi, for solutions of hydrazine - hydrazine nitrate - water. The compositions under test at present range from straight commercial hydrazine to a solution of hydrazine saturated with hydrazine nitrate - approximately 85% hydrazine nitrate by weight.

The apparatus in which the rate determinations are made consists of a glass tube with fine burnout wires sealed in at inch intervals. The propellant is ignited by an electrical squib. As the reaction of the propellant proceeds, the reacting level drops, the fine wires burn out and cause a step in an oscilloscope sweep to indicate the time at which each wire breaks. The apparatus is positioned in a 200 cc bomb and pressurized with nitrogen to the desired pressure.

Ignition could not be attained with the squib with hydrazine alone or the usual gun propellant compositions at pressures up to 2000 psi. Tests were then started with solutions very rich in hydrazine nitrate. It was found that liquid monopropellants were like solid powders in that below some "critical" pressure for each composition, the reaction ceased.

The Figure illustrates the relationship between reaction rates and pressure for a number of propellant compositions. This graph is plotted as the log of rate in inches per second against the log of pressure in pounds per square inch. The slope of the lines is therefore the exponent "n" in the expression $r = aP^n$. This expression is the simplified work-horse relationship used in burning rate calculations for solid propellants.

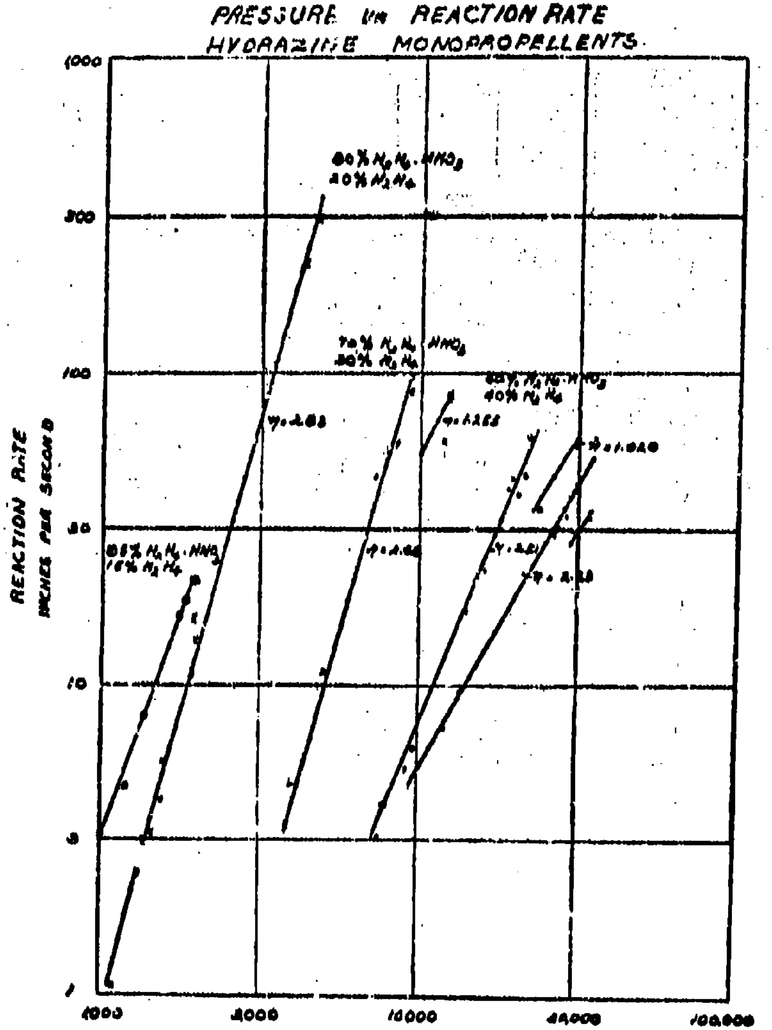
It is of interest to note that "n" for solid rocket propellants is in the range of 0.70 to 0.85 and for solid gun propellants in the range of 0.70 to 1.11.

Values of "n" for the hydrazine compositions have been measured as follows:

$N_2H_4HNO_3$	N_2H_4	n
85	15	2.36
80	20	2.83
70	30	2.68
60	40	2.51
50	50	2.23

The breaks in the curves are of great interest. Breaks are noticeable in the 70-30 curve, the 60-40 and the 50-50 percent curves. When the break occurs, the exponent "n" or the slope drops from 2.68 to 1.26 for the 70-30 curve and from 2.51 to 1.02 for the 60-40 curve. The breaks occur at decreasing rate values for the decreasing nitrate percentage solutions. There would seem to be a correlation between composition and the occurrence of the break. Tests will be made above 30,000 psi in the future to determine if other breaks occur in the curves. Future tests will also be made at other temperatures.

The 80% nitrate - 20% hydrazine solution does not exhibit a break at the high end of the curve. It runs up to a rate of 300 inches per second at 5000 psi, enters a region of poor


PRESSURE vs REACTION RATE
HYDRAZINE MONOPROPELLENTS
REACTION RATE INCHES PER SECOND
1000
300
100
30
10
3
1
1000
3000
10000
30000
100000
PRESSURE - PSI
60% $N_2H_4 \cdot HNO_3$ 40% N_2H_4
70% $N_2H_4 \cdot HNO_3$ 30% N_2H_4
60% $N_2H_4 \cdot HNO_3$ 40% N_2H_4
85% $N_2H_4 \cdot HNO_3$ 15% N_2H_4

reproducibility and above 8000 psi, detonations occur. With the 80% nitrate solution a break does occur at the lower end of the curve. The slope of the displaced segment is almost the same as the main curve. Below the rate of 1.15 inches per second at 1100 psi, the reaction will not continue. This break is believed to correspond to breaks in reaction rate - pressure curves of other monopropellants found by Whittaker and others at the Naval Ordnance Test Station. Their work showed a number of monopropellant compositions; for example, a mixture of 2 nitropropane and nitric acid, had breaks in the region of 0.3 to 1.5 inches per second. These breaks are believed to be mainly chemical in nature, probably the evidence of a change of reaction mechanisms or processes. Physical parameters such as the tube diameter, tube composition, fluid viscosity, may vary the location of the break but are not responsible for its existence. The other solutions on the graph do not react in this rate range and so the possible breaks are masked.

In discussing changes in reaction mechanisms it would be well to examine the work of Dr. Adams of Waltham Abbey, England. Dr. Adams ignited commercial hydrazine in a glass tube by means of a hot wire. The tests were conducted in equipment wherein the pressure could be varied. Dr. Adams determined reaction rate - pressure relations for several compositions of hydrazine and water. These rates were 0.004 to 0.05 inches per second, a very low range when compared to the rate of 2 to 300 inches per second of the high nitrate solutions.

Dr. Adams reported that as the pressure was increased, the reaction rate increased towards a maximum limit but above 10 atm (150 psi) or up to 30 atm for some compositions, the reproducibility got bad, the reaction rate was no longer proportional to pressure and above a critical pressure, the reaction was extinguished. Our laboratory ran similar tests and obtained results identical with Dr. Adams.

It is of interest that Dr. Adams got successful tests from atmospheric pressure to a maximum of 450 psi giving very low reaction rates whereas our laboratory started with higher pressures working down to 1050 psi for one solution with other compositions having much higher critical pressures. In between these regions of successful testing is an area where the reactions have not yielded to study. This presents a field for future research in the study of hydrazine.

At atmospheric pressure, the overall decomposition reaction of hydrazine is N_2H_4 ---NH_3 + $\frac{1}{2}$ H_2 + $\frac{1}{2}$ N_2, H = 23 K Cal.
However, at higher pressures the predominant reaction is:
N_2H_4 --- N_2 + $2H_2$ H + -12 K Cal.

Neither of these reactions represents the actual process of the decomposition of hydrazine at low pressures. The actual process may be represented by the equations:

N_2H_4 ---- $2NH_2$

$N_2H_4 + NH_2$ ---- $NH_3 + N_2H_3$

N_2H_3 ---- $N_2 + H_2 + H$

or N_2H_3 ---- $N_2H_4 + NH_2$

$H + N_2H_4$ ---- $NH + NH_2$

with termination reactions

$H + N_2H_3$ ---- $N_2 + 2H_2$

$NH_2 + N_2H_3$ ---- $NH_3 + N_2 + H_2$

Hall and Murray presumed that the reaction N_2H_4 -- $2NH_2$ was the rate determining step. It is a first order decomposition with an activation energy of 60 K cal/mole. However, this would limit the linear rate of burning with respect to the unburned gas to 30 centimeters per second. This is greatly exceeded and thus the decomposition reaction is not to be considered as the rate determining step. NH_2 is formed by several of the reactions as well as the initial decomposition.

The above reactions are those of the decomposition of hydrazine only. Add to these, the reactions of nitric acid, the complexities of the nitrogen oxides, the oxidation processes, and one realizes the difficulties in mapping the reaction process of the monopropellant solution. The predominance of particular end products, - ammonia or nitrogen and hydrogen - depends on the equilibrium constants and reaction rate variations of these reactions under varying conditions of pressure and temperature. The regions of unstable reactions, discontinuities in the rate - pressure curves, and points of "critical" pressures undoubtedly represent sets of conditions wherein the chain of reaction is changing.

It may be of interest to note that all investigations of chamber pressure in guns using the hydrazine monopropellant have shown rough combustion or pressure surges as compared to the burning of solid propellants. It is thus indicated that the reaction process may be more sensitive to pressure or temperature changes than conventional propellants. Tests with a small caliber rifle indicate phenomena in the gun that might be explained by the breaks in the curves previously discussed. A correlation between the ballistics of this propellant system and the theoretical analysis of the hydrazine reactions is beginning to form. It may take several years to attain a clear picture but a start is being made.

DISCUSSION ON PAPERS BY
DR. HOWARD W. KRUSE, DR. D. M. MASON, MR. M. N. OLSEN, AND MR. THOMAS L. THOMPSON

THE CHAIRMAN: Thank you, Mr. Thompson.

The first four papers are now open for discussion and please announce your name clearly, your affiliation, and your discussion clearly so we may take it down, and do not be afraid to use the blackboard if you have any facts and figures you would like to present.

MR. D. N. GRIFFIN (Mathieson Chemical Corporation): I have two comments to add to Dr. Mason's paper on thermal decomposition bomb studies. Since leaving the ivied walls, we have continued with similar bomb studies in connection with the liquid propellant gun development program for the Navy Bureau of Ordnance. Just by chance I happened to bring a slide along with me.

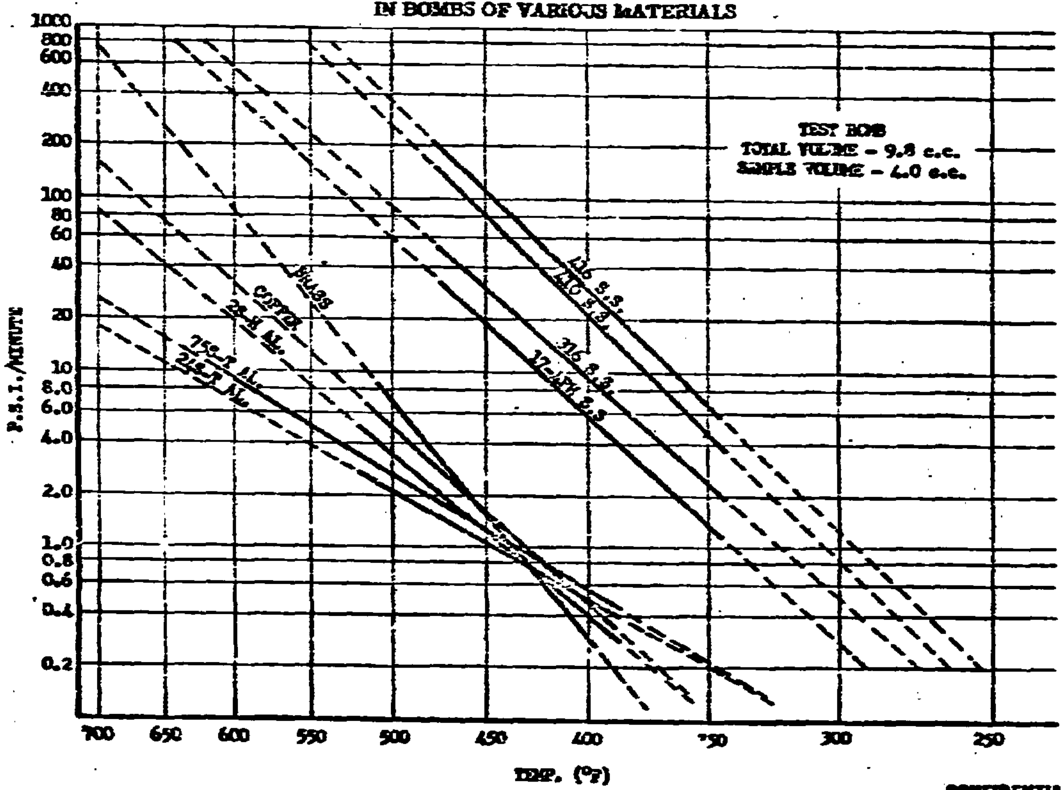
I might say first that in this work we have been interested in studying the effect of various materials on the decomposition rate of hydrazine. Therefore, we have used bombs which were made exclusively of the material to be studied so that only that material would come in contact with the hydrazine or hydrazine vapors. In past work quite often decomposition rates have been measured in a bomb of a given material such as stainless steel, but one in which was present weld material, silver solder, other metal gaskets, and so on. We have tried to be a little more consistent by keeping the hydrazine completely isolated from anything but the one material in question.

(Slide) (See page 148)

Shown here are the results of some tests in bombs of different materials and with anhydrous hydrazine only. We are also conducting studies of the hydrazine - hydrazine nitrate - water mixtures; however, this work is not complete enough to be reported on at this time.

Each material indicated in the figure represents a different bomb; however, the dimensions are the same in all cases. Internal dimensions are in the same order of magnitude as in the JPL tests.

COMPARISON OF RATES OF DECOMPOSITION OF HYDRAZINE IN BOMBS OF VARIOUS MATERIALS



The results falls into two distinct classes. Relatively high decomposition rates occurred in all of the steel bombs; whereas copper, brass, and several aluminum alloys gave rates approximately two per cent of that obtained with stainless steel.

At JPL it was observed that 1/2 per cent cadmium acetate reduced the decomposition rate of hydrazine in a stainless steel bomb to one-tenth of its normal rate. Now we observe that the rate for anhydrous hydrazine in an aluminum bomb, for example, is in the order of about one-fourth or one-fifth the rate in steel with cadmium added.

Therefore, we recently made some brief tests to determine the effect of cadmium on the decomposition rate in an aluminum bomb. Although the results are not shown in the figure, the addition of cadmium acetate had no appreciable effect. Apparently materials in the class of aluminum, and possibly copper, are essentially inert towards the thermal decomposition reaction of hydrazine, hence a surface poison is not required. This is in contrast to steel surfaces which are apparently active, and therefore can be inhibited by the addition of cadmium.

The results with aluminum are of particular interest since this appears to be one of the most compatible of the common metals with hydrazine. In the past, if I am correct, hydrazine has not been heated above 500-525°F., without explosive decomposition rates occurring. As shown on the slide, we have heated hydrazine to 600°F. in a 75-ST aluminum bomb, at which temperature the decomposition rate was only 10 psi/min. which corresponds to an absolute decomposition rate of approximately 2-1/2 per cent per hour.

These results, particularly with the aluminum alloys, should be of value both to people concerned with regenerative cooling in propellant applications and those engaged in hydrazine manufacture and storage. Hence I consider it appropriate to offer this material at this time.

THE CHAIRMAN: Thank you.

Any further discussion?

MR. PAUL M. ORDIN (NACA, LFPL, Cleveland): Dr. Mason, do you recall the heat transfer values in your rocket engine tests?

DR. MASON: Off-hand, I don't know. Mr. Grant, of JPL, who is present, perhaps can answer your question.

MR. A. F. GRANT (Jet Propulsion Laboratory): Two B.T.U. per square inch per second.

THE CHAIRMAN: Dr. Haller, you have been very quiet. Do you want to say a few words about cadmium?

DR. HALLER: I don't think it is quite appropriate. I would rather wait until after Dr. Dexter presents his paper; it's very pertinent.

MR. TROYAN: I would like to make one comment.

There was some comment made about the effect of vapor exposure to the metal surface as contrasted to liquid. According to your statement you saw no concrete effect but there was indication of possibly more decomposition occurring in the vapor stage.

DR. MASON: I would not categorically state that decomposition in the liquid phase does not occur. The results we reported are those that were observed under the conditions of our measurements. By the nature of our measurements some gas phase is always present. No tests were made where this phase was completely excluded. My guess is, without experimental verification that there may possibly be concurrent decomposition in the liquid phase; although the gas phase reaction is more rapid according to our experiments.

MR. TROYAN: I seem to recall that you said that regardless of the ullage you got no significant difference.

We have some work which will be reported tomorrow that indicates very definite effects -- a large difference in decomposition. However, the work was done at 50 degrees Centigrade where possibly there isn't as much inert gas evolved by decomposition and there is more hydrasine available in the gas phase, let's say, than there is when you are decomposing at much higher rates where in the gas phase you have less hydrasine. I don't know whether that is a vualitative viewpoint or not.

DR. MASON: The partial pressure of hydrasine over liquid hydrasine should not be markedly dependent on the pressure of inert gases in the system. Our observation was that the initial rate of pressure rise in the system with time was independent of ullage, which suggests that a gas phase reaction is controlling at the elevated temperatures of our measurements.

MR. ERNEST D. CAMPBELL (U.S. Naval Ordnance Test Station): I would like to ask Dr. Mason, what was in the ullage - was it nitrogen?

DR. MASON: That is a point which was not brought out in the talk but is mentioned in the paper. The initial gas phase contained air. Thus, when the temperature of the system was raised, reaction between hydrazine vapor and oxygen of the air might be expected to occur.

MR. CAMPBELL: You didn't distinguish between the oxidative decomposition and thermal decomposition?

DR. MASON (Interposing): Of course the total number of moles of oxygen initially present are small compared to the total number of moles of hydrazine which decompose to give large pressures.

MR. GRIFFIN: You might also add that by the time you attained the temperature at which the measurements were made probably all of the oxygen of the air had reacted, leaving essentially only nitrogen plus hydrazine vapor and hydrazine decomposition products.

THE CHAIRMAN: I would like to have Dr. Kruse of NOTS just briefly outline the work in progress at our laboratories on the thermal decomposition of liquid hydrazine.

DR. KRUSE: We are starting to make some measurements at 75 degrees C. That temperature is very close to a figure we got from the Bureau as the upper temperature limit that a propellant should withstand.

Thus far we have found that hydrazine decomposition in glass containers at 75 degrees Centigrade proceeds so slowly as to be almost immeasurable, that is, on the order of less than one per cent per year.

At present we are trying to find out whether decomposition is taking place in the liquid phase or in the vapor phase, or both. If decomposition occurs in the vapor phase, we shall attempt to find out whether it takes place on the walls of the container or in the free space.

Thus far we have only a little data. These data indicate that hydrazine is very stable. In the absence of air or catalysts, decomposition is extremely slow.

THE CHAIRMAN: Thank you, Dr. Kruse.

Professor Waring, do you have any comment to make on this decomposition work that has been presented?

PROFESSOR C. E. WARING (University of Connecticut): We have been investigating the decomposition of hydrazine vapor at elevated temperatures, that is, around 200 to 400 degrees Centigrade. All I can say now is that it is heterogeneous, which agrees with previous reports on its behavior.

I would like, if I may, to add another comment about burning rate studies at high pressures.

THE CHAIRMAN: Surely.

PROFESSOR WARING: If I understand it correctly, the last speaker seems to feel that the breaks one gets in the curves when measuring liquid burning rates at elevated pressures are apparently due to a change in the chemistry of the system.

We went along with that at the University of Connecticut until recently where we have been measuring the burning rates of propane and nitric acid systems. We began to suspect that these characteristic breaks might be due to physical effects.

Some of you may be aware that as you increase the pressure on liquid systems the vapor pressure increases. This is the Poynting Effect. While we are not prepared to state this finally, maybe we never can, we began to suspect there may be vapor pressure relationships operative at this very high pressure.

THE CHAIRMAN: Thank you.

DETERMINATION OF THE PROPERTIES OF HYDRAZINE NITRATE

by

J. N. Mandas and D. W. Ryker
Olin Industries, Inc.
Presented by J. N. Mandas

INTRODUCTION

At the request of the Navy Bureau of Ordnance, Olin Industries undertook a study of hydrazine nitrate in September 1951. This paper summarizes these studies to date.

In this study, we were concerned with the physical, chemical and explosive properties of hydrazine nitrate. The stability and compatibility of the salt with common materials of construction were also studied.

This work quite naturally led to a consideration of methods for large-scale manufacture. The work now in progress is directed to this problem.

PREPARATION

In the early stages of the work, the method chosen to prepare hydrazine nitrate was the neutralization of 85% hydrazine hydrate to a methyl red end point with dilute (54%) decolorized nitric acid. The reaction was maintained below 30°C and in each instance consumed the calculated amounts of reagent indicating at least a 99% yield of the salt in solution. The salt was separated from solution with a modified flash evaporator or by boiling off the water in a round bottom flask under reduced pressure. All hydrazine nitrate used for experimental purposes throughout this work was prepared in this manner from redistilled hydrazine hydrate and C.P. nitric acid decolorized with urea.

ANALYSIS

The chemistry of hydrazine is new and reveals but a few properties usable as vehicles for quantitative methods of analysis. The reducing action of hydrazine and its salts has been the most widely studied to date and was therefore considered to be the best approach in the search for a method of analysis.

An iodometric method was found which involved the use of standard laboratory equipment and had the simplicity of technique necessary for a general method of analysis.

The work reported by McBride and coworkers(1) on the direct titration of hydrazine with potassium iodate recommends it as a suitable iodometric method of analysis. The method adopted for study was the direct titration of hydrazine nitrate with potassium iodate to the iodine monochloride end point using a solvent indicator. The equivalence point occurs when the last of the I_2 formed in the early stages of the titration is converted to ICl on the continued addition of the potassium iodate solution. The end point is detected by the disappearance of the iodine color in carbon tetrachloride which forms a second phase in the titrating flask. The method was chosen for two reasons: (1) Only one titration is executed, (2) potassium iodate is a primary standard(2).

It was found in accordance with McBride et. al. that the excess of chloride ion must be kept high to obtain an accurate end point. With the chloride ion concentration adjusted above six molar and the hydrogen ion concentration approximately four molar, the end point was sharp if stirring was efficient. One tenth of a drop was sufficient to cause the change in color of the carbon tetrachloride phase from an extremely pale pink to colorless at the end point. The tendency to over-titrate is inherent in the technique due to the rate at which the system attains equilibrium; the rate of attaining equilibrium is proportional to the chloride ion concentration. By allowing at least thirty seconds between each drop as the end point is reached, a reliable result is obtained.

To check the standard potassium iodate solution, three samples of recrystallized hydrazine sulfate were weighed out and dissolved in a little hot water, sufficient concentrated acid was added to give a six molar hydrochloric acid solution at the end point and the resulting solution titrated with the standard potassium iodate solution using carbon tetrachloride as an internal indicator. The average of the three titrations gave 0.110 as the molarity of the potassium iodate solution. This compares with the weighed value of 0.1107M.

Crystals of hydrazine nitrate separated from a saturated solution were dried in vacuo over anhydrous calcium sulfate for 18 hours at room temperature. Three samples were quickly and accurately weighed out, 65 mls of concentrated hydrochloric acid and a few drops of CCl_4 were added and the resulting mixture titrated with standard KIO_3 . Results, which are listed in

Table I, show an acceptable order of precision, i.e., ± 0.3%.

A saturated solution of hydrazine nitrate standing at room temperature was used for the determination of the salt in solution. A sample of the solution (3.934 grams) was diluted to 250 mls and aliquots were delivered from a 50 ml burette and titrated in the following manner. 50-55 mls of concentrated HCl and 14-16 grams of NaCl were added to over 40 mls of measured solution. Two to three drops of CCl_4 were added and the mixture titrated with the standard KIO_3. Results which show a precision of ± 0.1% are listed in Table II.

PHYSICAL PROPERTIES

Crystal Density. The uncertainty as to the hydroscopicity of hydrazine nitrate at the time of the determination of crystal density required the method of displacement of an inert liquid in a pycnometer be used because the sample of salt could be dried before weighing and kept dry while weighing. Special care was given to the determination of the density of the sample of diethyl phthalate used as the inert liquid. Hydrazine nitrate was fused in vacuo to remove all traces of occluded water and to ensure the absence of voids in the crystals. The data obtained gave a value of 1.685 ± 0.005 gm/ml as the absolute density of the crystalline salt.

Melting Point. The melting point of hydrazine nitrate was determined by noting the temperature at which the salt absorbed its heat of fusion as indicated on a time-temperature curve. Hydrazine nitrate, twice recrystallized from distilled water, was fused in vacuo for two hours at about 110°C to remove all water. The data for the highest melting point obtained gave a value of 70.7 ± 0.1°C. As a measure of purity, the melting point of a sample of hydrazine nitrate separated from a saturated solution and dried in vacuo over "Drierite" for three days was determined and found to be 69.7 ± 0.1°C. An analysis of these crystals showed them to be 99.3 ± 0.2% in hydrazine nitrate.

Hygroscopicity. The hygroscopicity of pure hydrazine nitrate was determined by noting the change in weight of samples stored under selected conditions of relative humidity. Hydrazine nitrate was fused in vacuo to insure the complete absence of water. A series of desiccators was arranged with relative humidities of 20, 43, 55, 60, 65, 70 and 90 per cent and samples of the salt were weighed out and introduced into each of the desiccators. The samples remained in the desiccators until they came to constant weight which was considered to be the equilibrium hygroscopicity of the salt. A plot of the values obtained (Figure 1) indicates that at relative humidities

TABLE I

ANALYSIS OF CRYSTALLINE HYDRAZINE NITRATE

$N_2H_4HNO_3$ Taken (gm.)	0.110 M KIO_3 (ml.)	$N_2H_4HNO_3$ (%)
0.5210	49.00	98.32
0.7261	68.80	98.48
0.3929	36.85	98.06
	Mean	98.3
	Std. Dev.	0.2

TABLE II

ANALYSIS OF HYDRAZINE NITRATE IN SOLUTION

$N_2H_4HNO_3$ Solution (ml.)	0.110 M KIO_3 Solution (ml.)	Wt. $N_2H_4HNO_3$ per 3.934 grams of Saturated Solution (gm.)
40.45	41.95	2.715
44.10	45.90	2.720
45.10	46.90	2.718
47.60	49.60	2.724
46.20	48.10	2.723
44.80	46.60	2.718
47.50	49.47	2.718
	Mean	2.719
	Std. Dev.	0.003

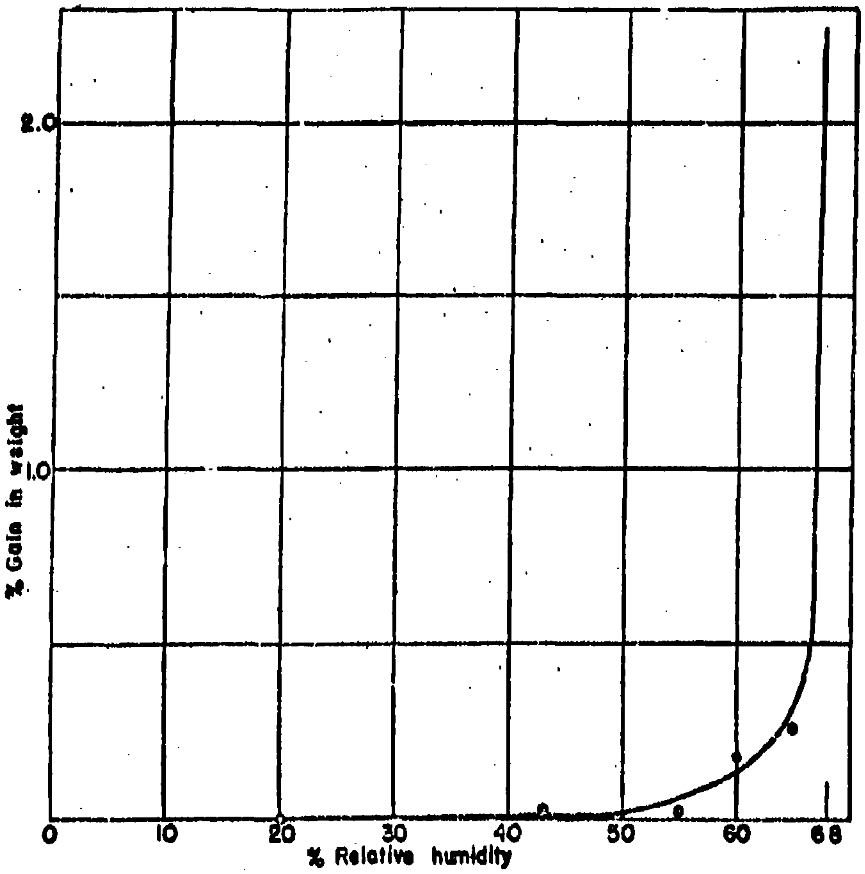


FIG. 1 HYGROSCOPICITY OF HYDRAZINE NITRATE

greater than 68% the salt deliquesces. It is to be noted, however, that an appreciable amount of water is picked up at relative humidities of sixty and sixty-five per cent.

STABILITY

The stability of hydrazine nitrate was considered in three ways: the stability of the pure salt, the stability of impure salt, and the stability of a saturated solution of the salt.

The Stability of Pure Hydrazine Nitrate was determined via the vacuum stability test on the pure fused salt and by storing a sample of the pure fused salt at 50°C.

The vacuum stability of hydrazine nitrate was determined at 68.3°C by the Western Cartridge Company technique used in determining the vacuum stability of tetryl. One-gram samples of fused salt were placed in the sample container of the apparatus which was placed under a vacuum and brought to temperature in an oil bath. The internal pressure of the system was read with a mercury manometer calibrated in milliliters. After forty hours the mercury level was noted and corrected for any change in barometric pressure that might have occurred during the test. An increase in volume was taken as evidence of the evolution of a gaseous product resulting from decomposition of the salt. One-gram samples evolved up to 0.06 ml. of gas in forty hours. In the same test, but at 120°C, RDX evolved 0.90 ml. of gas per gram, and tetryl evolved 1.00 ml. of gas per gram. The RDX and tetryl were production samples.

A four-gram sample of the salt was stored for four weeks at 50°C in a glass vial stoppered with a rubber stopper. A daily check was made of the salt and the vacuum stability test was made on portions of the sample at the end of two and four weeks. The salt did not alter in appearance over the four-week period with the exception of a tendency to cake. The salt evolved 0.07 ml. of gas in the vacuum stability test after being stored for one week at 50°C and 0.09 ml. of gas after being stored for four weeks.

The above results suggest that hydrazine nitrate is stable and may be capable of being stored over long periods of time.

The Stability of Impure Hydrazine Nitrate was determined by noting the reactivity of the salt with materials representing the most common substances with which the salt might come into contact in its industrial preparation and commercial use. The chosen substances were introduced into samples of the salt and tested for their reactivity at elevated temperatures (110 to 120°C), at elevated temperatures in vacuo (vacuum stability test at 68°C), and at elevated temperatures for long periods of time (surveillance at 50°C).

Each of the chosen materials was introduced into a porcelain crucible containing hydrazine nitrate and heated electrically to a temperature between 100° and 120°C. Any reaction (evolution of gas, change in color, foaming, etc.) noted was considered an indication that the two materials would be incompatible under any set of conditions of preparation, storage, or shipping. The results are tabulated in the first column of Table III. Brass, copper, lead, copper oxide, hydrazine dinitrate and lead monoxide reacted with the fused salt.

The materials found to be compatible with fused hydrazine nitrate at elevated temperatures were considered with respect to any catalytic action, or reactivity which would tend to decompose the hydrazine salt over a long period of time. The vacuum stability test was chosen to test samples of hydrazine nitrate contaminated with the filings or dust of materials found to be compatible with the fused salt. The results are tabulated in the second column of Table III. Ferric oxide contaminated salt evolved 3.0 ml. of gas.

New samples of the mixtures found to be stable in the two foregoing tests and samples prepared with large pieces of the contaminants whenever possible, were placed under surveillance for four weeks at a temperature of 50°C and daily inspection made. The results are tabulated in the third column of Table III. Cadmium, copper, magnesium and zinc were readily attacked. The stainless steels all developed rust spots on their rough edges only. The woods were all discolored.

<u>Stability of Hydrazine Nitrate Solutions</u>. The foregoing tests ruled out materials that are incompatible with hydrazine nitrate in the dry state. In the event the material deliquesces due to storage under high humidity, any reaction would be that of a saturated solution of hydrazine nitrate and the material. Such a condition also exists in preparing the salt in that it is generally prepared and concentrated in an aqueous medium.

A series of saturated solutions was prepared containing pieces of the several materials (the metallic compounds being excluded) and stored at room temperature. The materials were inspected for chemical attack, weighed to detect any loss due to corrosion and washed down with distilled water and the washings from the metals tested for the respective ion.

The results of this study are listed in Table III. All metals (with the exception of zirconium) and woods tested were attacked by the solution. The solid magnesium bar decrepitated to a sludge in the bottom of the vial. Brass, cadmium, copper, lead and zinc bars all developed heavy coatings. The steels were spotted slightly with rust.

The Materials Which Can be Considered Most Compatible with hydrazine nitrate under general conditions of preparation, shipping and storage as determined by the foregoing work are listed as follows:

Metals
- Aluminum
- Silver
- Polished stainless steels
  - #309
  - #317
  - #321
  - #304 ELC
  - #347
- Tin
- Zirconium

Packaging Materials
- Asbestos
- Pyrex glass
- Polyethylene
- Polystyrene
- Rubber, red
- Rubber, gum
- Soda glass
- Teflon

TABLE III

RESULTS OF FUSION, VACUUM STABILITY, SURVEILLANCE AND CORROSION TESTS OF HYDRAZINE NITRATE

Material	Fusion Test	Vacuum Stability Test	Surveillance Test	Corrosion Test
	R = Reaction - = No reaction	(ml.)	R = Reaction - = No reaction	
Metals				
Aluminum A-1	-	0.5	-	R
Brass	R			R
Cadmium	-	0.0	R	R
Copper	R		R	R
Lead	R			R
Magnesium	-		R	R
Silver	-		-	R
Steel				
#309	-	0.0	R	R
#317	-	0.0	R	R
#321	-	0.0	R	R
#304 ELC	-	0.0	R	R
#347	-	0.5	R	R
Tin	-	0.0	R	R
Zinc	-	0.1	R	R
Zirconium	-	0.0	-	-
Woods				
Oak	-	0.0	R	R
Sugar Pine	-	0.0	R	R
Hard Maple	-	0.0	R	R
Metallic Compounds				
Aluminum Hydroxide	-	0.0	-	
Aluminum Oxide	-	0.0	-	
Copper Oxide	R			
Ferric Oxide	-	3.0		
Hydrazine Dinitrate	R			
Lead Monoxide	R	0.0		
Lead Sulfide	-	0.0	-	
Magnesium Oxide	-		R	
Silver Sulfide	-	0.0	-	
Tin Oxide	-	0.0	-	
Zinc Sulfide	-	0.0	-	

TABLE III (Continued)

Material	Fusion Test R = Reaction - = No reaction	Vacuum Stability Test (ml.)	Surveillance Test R = Reaction - = No reaction	Corrosion Test
Packaging Materials				
Asbestos	-	0.0	-	
Paper (waterproof)	-	0.0	R	
Pyrex glass	-	0.0	-	
Polyethylene	-	0.0	-	
Polystyrene	-	0.0	-	-
Rubber, gum	-	0.0	-	-
Rubber, rod	-	0.0	-	-
Soda glass	-	0.0	-	-
Teflon	-	0.0	-	-
Hydrazine Nitrate	-	0.0	-	

PHYSICAL PROPERTIES OF THE WATER-HYDRAZINE NITRATE SYSTEM

Hydrazine nitrate prepared in this laboratory was recrystallized from distilled water once and used to make up a series of aqueous solutions. Each solution was analyzed using the potassium iodate direct titration method. The density, refractive index, freezing point, and boiling points at various pressures of each of the solutions were determined.

Three sources of data were utilized in preparing the phase diagram of the water-hydrazine nitrate system. Solubility data found in the literature were used as points at which a second phase appeared. The melting point of the pure salt was used as the 100% point and solubility of the salt at 21.0°C as determined in this laboratory was used as another point at which a second phase appears. Freezing point data obtained with freezing point equipment in this laboratory was used to complete the diagram. The data obtained were plotted (Figure 2) and the point at which the two curves met at the eutectic temperature (-9.2°C) gave the eutectic composition as 42.5% in hydrazine nitrate.

The densities of the various solutions were determined with the pycnometers calibrated for use in the determination of the crystal density. The solutions were cooled well below the temperature of the initial weighing and introduced into the pycnometers. The pycnometers were then set in a controlled air bath and allowed to rise in temperature very slowly until they reached the desired temperature and weighed. The density values calculated from the data taken are tabulated in Table IV. All values were corrected to vacuum.

The refractive index was measured with a Bausch and Lomb type 33-45-56 Abbe' Refractometer supplied with a flow of constant temperature water around the prisms. Solutions ranging in concentration from eight to seventy-three per cent hydrazine nitrate were prepared from distilled water and the refractive index measured. The values obtained are plotted in Figure 3. The plot of the values from 0.00% to 51.6% hydrazine nitrate is a straight line and is suitable as an analytical tool. The curve beyond 51.6% becomes steeper and if used for analysis will yield values having an accuracy dependent on the number of points plotted.

The method of Menzie was used in determining the vapor pressure of hydrazine nitrate solutions varying in concentration from six to seventy-four per cent. This consisted in isolating the solution and its vapor in the reservoir bulb of an isoteniscope by introducing a liquid having a very low vapor pressure into the U of the isoteniscope after the atmosphere over the solution had been swept clear of other gases. The pressure of the water vapor over the solutions at various temperatures was measured with an open end mercury manometer. Smooth curves (Figure 4) were obtained from 30°C to the atmospheric pressure boiling points of the solutions which ranged from 101°C for the 6% solution to 117°C for the 74.5% solution.

TABLE IV

DENSITY OF AQUEOUS HYDRAZINE NITRATE SOLUTIONS AT VARIOUS TEMPERATURES

Solution	Per Cent Hydrazine Nitrate	10°C	15°C	20°C	25°C	30°C
I	5.54%		1.0242*	1.0225	1.0211	1.0191
II	10.0	1.0464	1.0444	1.0432	1.0414	1.0393
III	21.7	1.1048	1.1025	1.0998	1.0963	1.0931
IV	45.9	1.2262	1.2234	1.2204	1.2173	1.2139
V	54.1	1.2842	1.2809	1.2773	1.2735	1.2705
VI	73.5	-	-	1.3941**	1.3839	1.3797

* Density at 14°C
** Density at 21°C

All values have a standard deviation of ± 0.0001 except 73.5% at 21°C (± 0.0009) and at 30°C (± 0.0002) and that of the 21.7% at 20°C (± 0.0002).

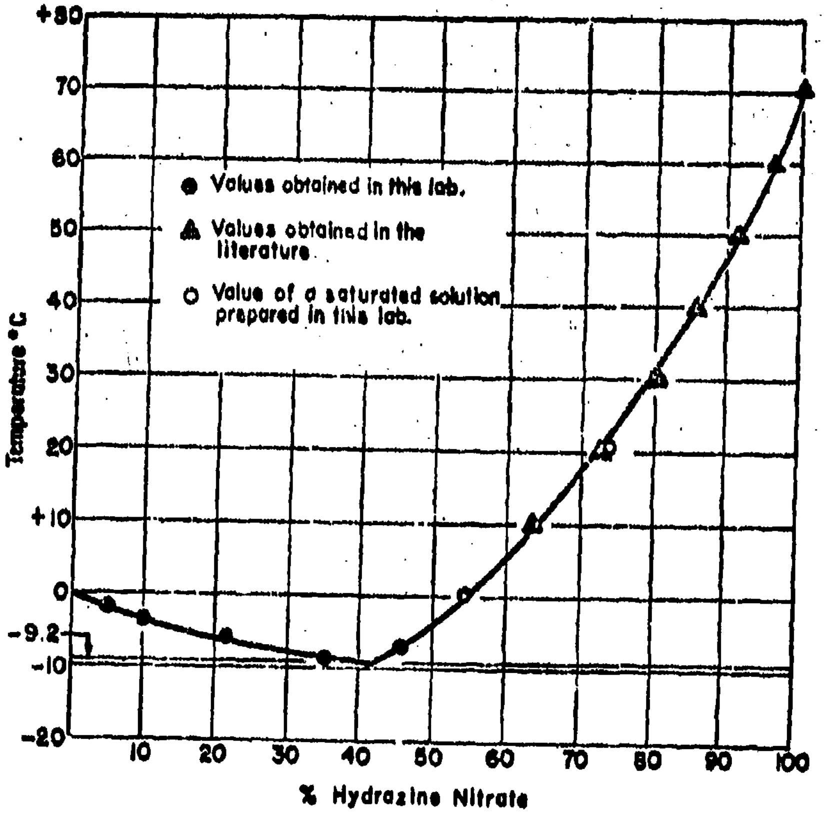


FIG 2 PHASE DIAGRAM OF THE WATER-HYDRAZINE NITRATE SYSTEM AT CONSTANT PRESSURE

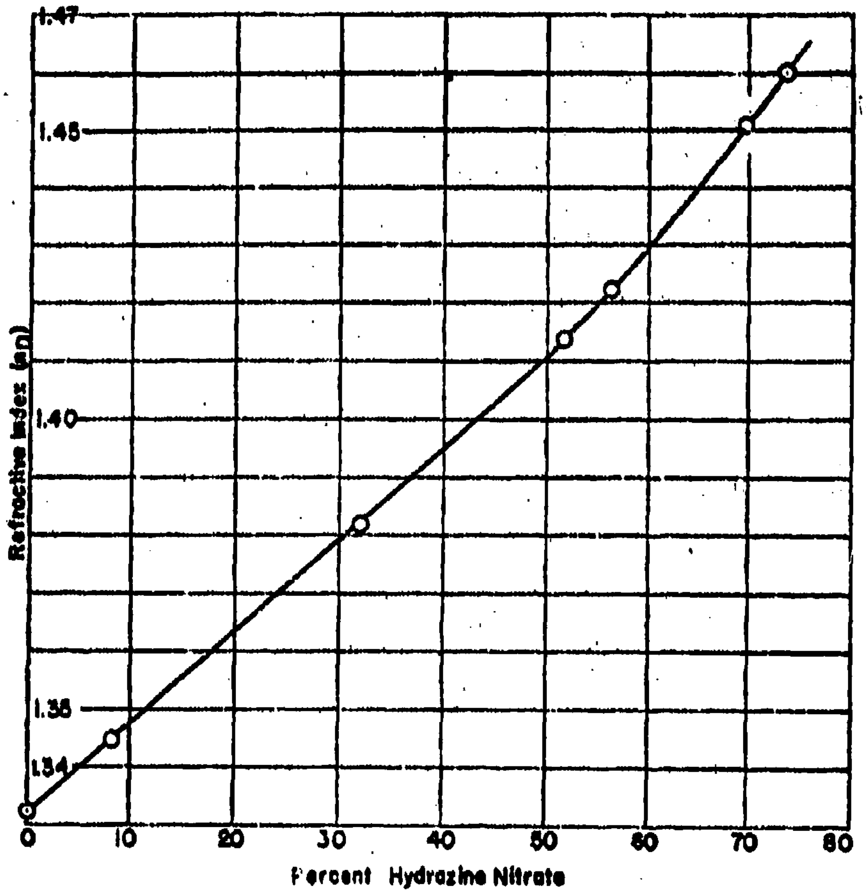
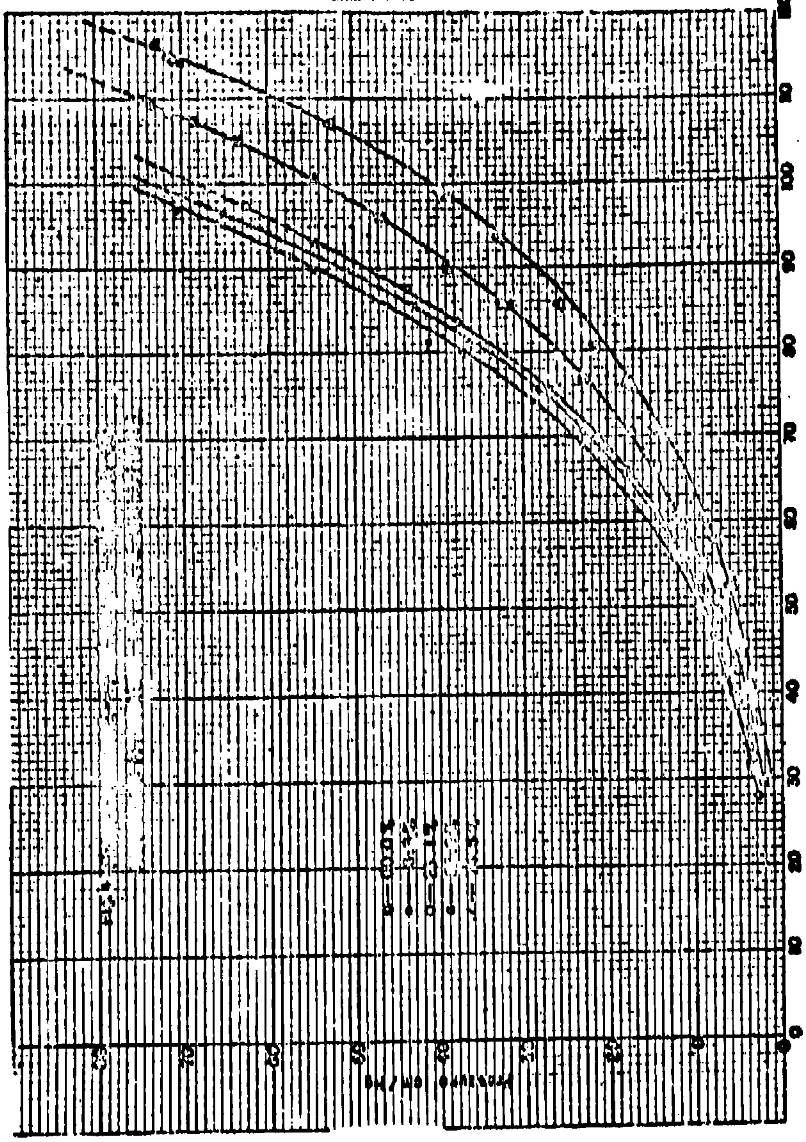


FIG. 3 REFRACTIVE INDEX OF AQUEOUS HYDRAZINE NITRATE SOLUTION AT 25° C


Temperature °C
Pressure cm/Hg
0
10
20
30
40
50
60
70
80
90
100
110
120
5
10
15
20
25
30
35
40
45
○—0.1%

EXPLOSIVE PROPERTIES

Samples of pure hydrazine nitrate and hydrazine nitrate contaminated with sand, steel filings, hydrazine nitrite and hydrazine dinitrate were tested for impact, friction and detonation sensitivity.

Sample Preparation. Hydrazine nitrate was fused in vacuo to remove all water. Ottawa sand crushed to pass a 100 mesh screen and filings from #304 stainless steel were used as fine particle contaminants. A standard hydrazine nitrite solution, freshly prepared from dihydrazine sulfate and barium nitrite, was added to a weighed amount of solid hydrazine nitrate via burette. The resulting solution was evaporated and dried in vacuo at room temperature and used as the hydrazine nitrate sample contaminated with hydrazine nitrite. Standard nitric acid solution was added to solid hydrazine nitrate and the resulting solution treated as above to give a sample contaminated with hydrazine dinitrate.

Impact Sensitivity. Sensitivity to impact was determined using a modified Bureau of Mines Impact Machine (cup method). The fire-no fire point was determined and used for comparison purposes. The impact sensitivity of standard samples of tetryl and cyclonite were determined at the time the hydrazine nitrate samples were tested.

The impact sensitivity of pure fused hydrazine nitrate was found to be a function of the average particle size (Table V). The sensitivity ranges from that tetryl (Western Cartridge Lot No. 280-6300, Impact Sens. 80 cm no fire, 82 cm two fires out of ten trials) to that of cyclonite (Western Cartridge Lot No. 278-15, Impact Sens. 48 cm no fire, 50 cm one fire out of five trials). Thirteen to twenty-six per cent sand increased the sensitivity of the salt to that comparable to fine mercury fulminate (8 cm) and four per cent steel filings increased it to a point comparable with dextrinated lead azide (19 cm). Hydrazine dinitrate and hydrazine nitrite increased the sensitivity only slightly.

Detonation Sensitivity. The detonation sensitivity was determined by the use of a sand bomb. Varying amounts of mercury fulminate were used to detonate four tenths of a gram of hydrazine nitrate, the amount of sand crushed indicating the absence or completeness of detonation.

Pure hydrazine nitrate was found to be slightly more sensitive to detonation than tetryl with respect to mercury fulminate as an initiator but the power of hydrazine nitrate to be less than that of tetryl. Each of the contaminated samples except the sample containing hydrazine nitrite was as sensitive to mercury fulminate as the pure salt. As expected, the samples containing sand (13%) and steel filings (4%) were not as powerful as the original salt on a weight for weight basis. The sand and steel contaminants did not alter the propagation of the detonation through the salt. One per cent hydrazine nitrite contamination gave a material less sensitive to mercury fulminate and slightly less powerful than the pure salt. One per cent hydrazine dinitrate contamination did not alter the sensitivity, but the resulting material was slightly less powerful than the pure salt. The dinitrate salt interfered in the propagation as a partial detonation occurred for one set of loadings.

TABLE V

IMPACT SENSITIVITY OF PURE HYDRAZINE NITRATE OF CONTROLLED PARTICLE SIZE

	Sieve Size			
Sample	Passes Through (μ)	Held By (μ)	Height at which no fires occurred out of ten trials (cm)	Number of fires at a point two cm above the no-fire point (Fires/Trials)
1	-	840	80	1/10
2	840	590	78	1/4
3	590	297	70	1/8
4	297	125	62	1/7
5	125	pan	48	1/10

Friction Sensitivity. The sensitivity of hydrazine nitrate to friction was determined using the Bureau of Mines Type A and Type B Pendulum Friction Devices.

The Type B Friction Pendulum Machine would not fire any of the samples of the salt using a steel shoe as the bob on the pendulum and a steel anvil.

With the Type A Pendulum Friction Machine, a local crackling was heard in five out of ten trials using five grams of tetryl on the steel anvil and using a steel shoe as the bob on the pendulum. Using the same setting of the machine, hydrazine nitrate detonated twice out of five trials and local crackling was heard each of the five times. The steel shoe was replaced by a fibre shoe and using the same setting of the machine, hydrazine nitrate did not fire ten out of the ten trials.

Pure hydrazine nitrate is more sensitive to friction than tetryl when tested on the Bureau of Mines Type A Pendulum Friction Machine.

POLYMORPHISM OF HYDRAZINE NITRATE

The study of the polymorphism of hydrazine nitrate was approached using microscopic techniques.

Two polymorphic modifications of hydrazine nitrate were found to exist between -70°C and +70.7°C at atmospheric pressure. The forms constitute a Form I melting at 70.7°C and a Form II melting at 62.5°C. The system is monotropic at atmospheric pressure, i.e., Form II is unstable and reverts to Form I, the reverse not being true.

The hydrazine nitrate melt invariably super cooled independent of how rapidly or how low the temperature was dropped. The solid, therefore, passed through the unstable Form II modification on cooling unless seeded between 62.5°C and 70.7°C. The transformation from II to I results in numerous irregularly spaced shrinkage cracks indicating the density of Form I to be greater than that of Form II. Hydrazine nitrate I prepared from a fusion preparation without going through the Form II modification, appeared as rods and elongated plates.

Hydrazine nitrate II crystallized from the melt as feathery rods and broad plates. On transformation to Form I, the general outline of this crystal formation was retained in outline with the new form constituting the structure inside these outlines, thus exhibiting pseudomorphism. Investigation of any given salt sample under a microscope will divulge the crystal history to the extent of indicating whether or not it passed through the unstable Form II in its preparation.

Forms I and II were found to coexist at temperatures below -30°C. A fusion preparation crystallized as Form II was seeded with Form I. When the transformation front had reached the center of the field, the slide was cooled rapidly on a brass cooling bar. By repeating this operation and cooling to lower and lower temperatures, it was found that the rate of transformation as seen under the microscope approached zero at -30 ± 5°C. At temperatures below -30°C the (two) forms existed side by side without any visible transformation.

LARGE-SCALE MANUFACTURE

The laboratory preparations of hydrazine nitrate by the neutralization of hydrazine with dilute nitric acid indicated that the reaction was quantitative and easily carried out. The experience gained in making laboratory batches of hydrazine nitrate was used in developing a method believed to be applicable to large-scale manufacture.

Pilot Plant Operation. A pilot plant run of the neutralization reaction was made in a small steam-heated, stainless steel kettle at atmospheric pressure in order to obtain data that would be useful in the design of a large-scale operation. The pilot plant run indicated that the neutralization reaction was an acceptable one, but that more information as to the effect of reaction temperature and feed concentrations was necessary. Other information obtained from the pilot plant run showed that in the engineering design of a large-scale plant the main problem would be to separate the salt from the water.

Reaction Temperature Feed Concentration Studies. In order to determine the temperature limitations for producing hydrazine nitrate, studies were made of (1) the decomposition of the salt in aqueous solution at various temperatures and (2) the percentage yield at various reaction temperatures.

Samples of 54% aqueous hydrazine nitrate solution were prepared with C.P. salt prepared in this laboratory. These samples were refluxed at various temperatures for ninety hours. There was no loss of material in these samples.

Solutions of 85% hydrazine nitrate were neutralized with 70% nitric acid at a fairly rapid rate. The heat of the reaction raised the solution temperature to over 130°C. The yield of salt was found to be 100%.

Engineering Study. A series of calculations were made to determine the cheapest method of evaporation on the basis of initial cost, cost of operation, and overall safety. Methods considered included atmospheric evaporation, triple effect evaporation, vacuum evaporation, spray drying, prilling, film flashing, and salting out with a water miscible solvent. The single stage vacuum evaporation method was selected for further study.

The vacuum evaporation method has a low equipment cost, is simple to design, and can be operated at a low temperature. The low temperature is desirable from a safety standpoint.

Bench scale operation of this method is contemplated.

REFERENCES

(1) McBride, Henry and Skolnick, Anal. Chem., 23, 890-2 (1951).

(2) Kothlogg and Sandell, "Textbook of Quantitative Inorganic Analysis," Revised Edition, McMillan Company, New York, N. Y., 1946, p. 623.

THE ANALYSIS OF HYDRAZINE

by

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Various methods of analyzing hydrazine are discussed, and some of their shortcomings are pointed out. The method used at the U. S. Naval Air Rocket Test Station, based on the quantitative oxidation of hydrazine by Chloramine T, is described.

There is no need, at a symposium on hydrazine, to point out the importance of an accurate method of analysis of the material. I intend merely to describe the method used, as a routine procedure, by the Propellants Laboratory of the U. S. Naval Air Rocket Test Station, and to indicate the results which may be obtained by the use of this procedure.

Hydrazine is to be assayed for its probable major constituents ---NH_3, water and the material itself. Hydrazine is both a base (a little weaker than ammonia) and a reducing substance, and the assay may involve either or both properties.

If it is to be assayed as a base, the simplest method is a back titration with a strong base, such as NaOH, after the sample is diluted with a known quantity of a strong acid. This method is preferable to a forward titration of the material after dilution with water, since accidental oxidation and evaporation of the hydrazine is prevented. The end point may be found either with a pH meter, or with an indicator such as Brom Cresol Green. The pH of the end point, with a total weight of hydrazine of 40 mg in a final titration volume of 250 cc, has been calculated to be 5.12. The method has been adapted from a routine procedure used by the RAF (Ref 1) and by many other activities. It is perfectly straightforward, and gives excellent results. The obvious disadvantage is that it does not distinguish between hydrazine and ammonia, and some other procedure is necessary to make that distinction.

The direct titration of hydrazine with iodine has been suggested as an analytical method, (Ref 2) and has been tried at NARTS with completely unsatisfactory results. The main disadvantage is that when hydrazine is oxidized, nitrogen is evolved, which sweeps out some of the volatile iodine, leading to an error of unknown size. Several variations on the method have been tried, with no success whatever.

Another procedure has been recommended by the Naval Research Laboratory (Ref 3) as an "Umpire" method. Here the hydrazine is oxidised with iodate or bromate in a strong HCl solution, using as an indicator either a chloroform layer or an internal oxidation-reduction indicator. The total reaction is

$$N_2H + KIO_3 + 2\ HCl = KCl + ICl + N_2 + 3H_2O$$

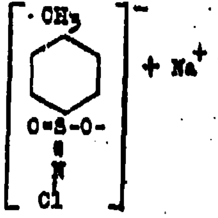
$$5e^- + IO_3^- + 6H^+ = 3H_2O + \tfrac{1}{2}I_2$$

$$\tfrac{1}{2}I_2 + Cl = ICl + e^-$$

As may be seen, free I_2 is present at one stage of the reaction. A test with starch paper showed that the I_2 is swept out with the evolved N_2, just as in the direct I_2 titration, with a similar inherent error. Various agencies, however, use the method, with reportedly satisfactory results. The usual expedient is to ice the titrated solution in order to reduce the vapor pressure of the iodine, but we at NARTS considered the expedient to be a nuisance and no guarantee of the complete elimination of iodine losses.

A procedure using ceric sulfate and dichromate has been employed by Kellogg with excellent results (Ref 3 and 4) but when it was tried at NARTS we found that the end point was so hard to see that we did not consider the method suitable for routine work.

A German method (Ref 6) involved the titration of N_2H_4 with Chloramine-T, but no details of the procedure were given. However, a satisfactory analysis has been worked out at our Propellants Laboratory, and has been used with excellent results. Chloramine-T has the following structural formula:



which may be abbreviated as follows:

$$R = NCl^- + Na^+$$

It reacts with hydrazine according to the following equation:

$$2R = N\text{-}Cl^- + N_2H_4 = 2R = NH^- + 2H^+ + 2Cl^- + N_2$$

A potassium iodide-starch indicator is used to show the end point, and the titration is run in the presence of bicarbonate in order to neutralize the HCl formed and to accelerate the reaction.

Our complete procedure is then the following:

Reagents

Prepare 1-N H_2SO_4 according to accepted procedures, and standardize against Na_2CO_3 primary standard (Ref 7).

Prepare 0.1 N NaOH by diluting a saturated solution of NaOH (15 N) 150 times with distilled water. Then standardize the solution against potassium acid phthalate primary standard (Ref 8).

Prepare 0.1 N Chloramine T solution by dissolving 1/20 gm molecular weight (M.W. = 281.17) in distilled water and diluting to 1000 ml. Scrupulously clean glassware must be used and the solution must be protected from dust, grease, and organic matter in general.

To standardize the Chloramine T solution, add with stirring exactly 50 ml of the 0.1 N Chloramine T solution to be standardized, to a solution containing 50 ml 0.5 N KI solution and 20 ml glacial acetic acid.

Titrate with 0.1 thiosulfate solution to the disappearance of the I_2 color. Starch solution may be used if desired.

Normality of Chloramine T =

$$\frac{\text{ml of thiosulfate x normality of thiosulfate}}{50}$$

An indicator solution for hydrazine is prepared by dissolving 60 gm $NaHCO_3$ and 40 gm KI per liter of distilled water.

Procedure

The percentage of total base as N_2H_4 may be determined as follows:

a. Draw into a 1 cc tuberculin syringe about 0.8 gm (0.8 ml) of hydrazine, and weight to 0.1 mgm.

b. Empty the contents of syringe, without washing, into a 200 ml volumetric flask which contains 30 ml of 1-N H_2SO_4 and boiled distilled water to within one inch of the dilution mark on the flask. Quickly stopper and invert the flask to mix the contents, and dilute to the mark.

c. Weigh the empty syringe. The difference of the two weighings is the weight of the sample taken.

d. Bring the volume of the flask up to 200 ml with boiled distilled water and shake to ensure homogeneity of the solution.

e. Pipette a 10 ml aliquot into a 600 ml beaker and add about 200 ml of boiled distilled water.

f. Titrate the solution with 0.1 N NaOH to a pH of 5.12 with the final volume of solution about 250 ml Brom cresol green (pH range 4.0 - 5.6) indicator may be used in place of the pH meter, but if the pH meter is employed, the same sample may be used for the determination of N_2H_4.

g. Calculate:

Percent total base N_2H_4 =

$$\frac{\left(\frac{\text{ml } H_2SO_4 \times N\ H_2SO_4}{20\ (=\text{dilution factor})} - \text{Ml NaOH} \times N\ \text{NaOH}\right) \times \frac{32.048}{1000}}{\frac{\text{wt sample}}{20}} \times 100$$

or, =

$$\frac{(\text{ml } H_2SO_4 \times N\ H_2SO_4 - 20 \times \text{ml NaOH} \times N\ \text{NaOH}) \times 3.2048}{\text{wt sample}}$$

The percentage of hydrazine is now determined by the following steps:

a. After the acid-base titration add 25 ml of indicator solution for hydrazine to the contents of the beaker.

b. Titrate the solution with 0.1 N Chloramine T to an iodine end point, using starch solution if desired.

c. Calculate percent hydrazine:

$$\%\ N_2H_4 = \frac{\text{ml Chloramine T} \times N\ \text{Chloramine T} \times \frac{8.012}{1000}}{\frac{\text{wt sample}}{20}} \times 100$$

Or,

$$\% \; N_2H_4 = \frac{\text{ml Chloramine T} \times \text{N Chloramine T} \times 16.024}{\text{wt sample}}$$

Calculate percent NH_3:

$$\% \; NH_3 = \frac{17}{32} (\% \text{ total base} - \% \text{ hydrazine})$$

The percentage of H_2O may then be determined:

$$\% \; H_2O = 100 - \% \; N_2H_4 - \% \; NH_3$$

Results

In practice, the procedure described has turned out to be completely satisfactory, rapid in operation, and precise to 0.1 percent. The Chloramine-T titrant appears to be quite passably stable, and a weekly standardization is all that is necessary. It must be emphasized, however, that completely clean glassware must be used to make and to store it. A trace of stopcock grease will apparently catalyze the decomposition of the material, and the solution will froth so violently as to spray itself all over the laboratory.

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ANALYSIS OF HYDRAZINE MIXTURES

by

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Introduction

In the search for materials that might improve the performance of hydrazine as a liquid-fuel component for use in liquid-propellant aircraft rockets, ammonium thiocyanate was added to hydrazine with certain desirable results. One of the most important features of this additive was its effectiveness in lowering the freezing point of hydrazine. It was soon apparent that an extensive investigation of hydrazine-thiocyanate mixtures would require careful analytical control. The nature of this mixture required that existing methods for analyzing hydrazine and thiocyanate be modified and that a new method for ammonia be developed. This study has resulted in the development of two methods, which are described in this report. The first portion of the report contains a description of the method for analyzing ammonia in hydrazine; the second, a description of the method for analyzing hydrazine-ammonium thiocyanate mixtures.

Procedure for Determination of Ammonia In Hydrazine-Ammonium Thiocyanate Mixtures

Existing methods (Ref. 1 and 2) for determining ammonia in hydrazine were not satisfactory when ammonium thiocyanate was present. The Andrews-Jamieson method (Ref. 3) for determining hydrazine and thiocyanate has been used as a titrimetric method of analysis for these materials, as described later in this report. Since oxidation with iodate yields nitrogen in the case of hydrazine and hydrocyanic acid in the case of thiocyanate, it appeared feasible to determine ammonia by use of such an oxidation as a preliminary step. The two oxidations are represented by the following equations:

$$N_2H_4 + IO_3^- + 2Cl^- + 2H^+ \rightarrow N_2 + ICl + Cl^- + 3H_2O$$

$$4SCN^- + 6IO_3^- + 6Cl^- + 8H^+ \rightarrow 4SO_4^{--} + 6ICl + 4HCN + 2H_2O$$

By purging the system with air following the quantitative titration with iodate, it is seen that all nitrogenous compounds other than ammonia are removable. A simple additional step was found necessary for removal of the iodine monochloride and excess iodate. This was conveniently accomplished by adding crystals of sodium sulfite until the solution was colorless. An ordinary Kjeldahl distillation of ammonia was used to complete the determination.

Reagents. In the determination of ammonia in hydrazine-ammonium thiocyanate mixtures by the method described in the preceding paragraphs, the following reagents are used:

Hydrochloric acid, concentrated, c.p.

Potassium iodate solution, 0.1N

Amaranth indicator, 0.2-percent aqueous solution

Sodium sulfite, c.p.

Potassium hydroxide solution, 10N

Hydrochloric acid, 0.1N

Sodium Hydroxide, 0.05N

Methyl red indicator

Apparatus. The following items of apparatus are required to determine ammonia in hydrazine-ammonium thiocyanate mixtures by this method:

Glass tubing with fritted-glass tip

Gas bubbler

Kjeldahl distillation apparatus, using 500-ml Kjeldahl flask

Burets, 50-ml

Pipets

Procedure. Select a sample of such a size that an aliquot will furnish a maximum of about 0.5 milliequivalents (meq) of ammonia (10 mg of NH_3). Pipet this quantity into a flask containing 25 ml of 12N hydrochloric acid plus enough water so that the final volume (acid plus water plus sample) will be 70 ml. Immediately add from a buret approximately 0.1N potassium iodate solution until the color of the solution has progressed through a deep brown (iodine) to a light yellow hue. Then add two drops of amaranth indicator and complete the titration to the disappearance of the pink color. Begin bubbling air through the solution at once[1]. After 15 minutes add sodium sulfite crystals until the solution becomes colorless. Continue the air purge for an additional 15 minutes. Transfer the solution to a Kjeldahl flask; rinse several times with distilled water; and add 50 ml of 10N potassium hydroxide. Complete the usual Kjeldahl distillation, receiving the distillate in 20 ml of 0.1N acid[2]. Conclude the determination by titrating the standard acid plus distillate with 0.05N alkali, using methyl red indicator.

The acidity must be carefully controlled for best results in the Andrews-Jamieson procedure. If the above titration requires more than 40 ml of iodate solution, an additional 5 ml of hydrochloric acid should be added (at that point in the titration). The final acid normality should be 2.5 to 5 (Ref. 1 and 4) to ensure quantitative reaction and a sharp end point.

Results. The results of the analyses of several synthetic samples are shown in Table 1. The analyses of the samples in Group 1 were made using 5 ml aliquots from a standard ammonium thiocyanate solution for which the ammonia content had been determined both by the Kjeldahl procedure and by titration with standard silver nitrate. Hydrazine was added to those samples by direct addition of weighed amounts of hydrazine sulfate. The hydrazine sulfate alone had been analyzed by this same procedure for ammonia with no ammonia being found. Smaller amounts of ammonia were determined, as indicated in Groups 2 and 3, with very little sacrifice in precision. Samples containing more than 3.0 meq (redox) of ammonium thiocyanate (38.06 mg of NH_4SCN) could not be analyzed by this procedure.

In all cases attempted with higher amounts of thiocyanate, results were high by as much as 0.03 to 0.05 meq. It was found in these cases that ammonia was being generated in the oxidation medium, either through oxidation or hydrolysis of the hydrocyanic acid. It appears that above a certain level of concentration the hydrogen cyanide cannot be removed rapidly enough to escape partial change to ammonia.

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[1] Glass tubing with a fritted-glass tip is recommended as a bubbler. The air should be passed through a prescrubber containing dil. HCl.

[2] "Fisheyes" were used as boiling chips. They were washed and dried in the oven for reuse.

TABLE 1

ANALYSIS OF SYNTHETIC SAMPLES CONTAINING HYDRAZINE SULFATE AND AMMONIUM THIOCYANATE BY THE IODATE-KJELDAHL METHOD

Sample No.	Volume of NH_3 found		
	meq	mg	%
Group 1. Samples containing 0.1 g of $N_2H_4 \cdot H_2SO_4$ and 36.84 mg of NH_4SCN (0.484 meq; 8.24 mg of NH_3; and 6.02% of NH_3)[a]			
1[b]	0.482	8.21	6.00
2[b]	0.487	8.29	6.06
3[b]	0.485	8.26	6.04
4	0.489	8.33	6.09
5	0.487	8.29	6.06
6	0.489	8.33	6.09
7	0.484	8.24	6.03
Group 2. Samples containing 0.1 g of $N_2H_4 \cdot H_2SO_4$ and 7.37 mg of NH_4SCN (0.0967 meq; 1.65 mg of NH_3; and 1.54% of NH_3)			
1	0.096	1.63	1.52
2	0.097	1.65	1.54
3	0.098	1.67	1.56
Group 3. Samples containing 0.1 g of $N_2H_4 \cdot H_2SO_4$ and 3.68 mg of NH_4SCN (0.0484 meq; 0.82 mg of NH_3; and 0.79% of NH_3)			
1	0.044	0.75	0.72
2	0.046	0.78	0.75
3	0.047	0.80	0.77

[a] Characteristics of the samples in Group 1 were as follows:

Average NH_3 found, %	6.05
Standard deviation	0.032
Standard deviation of mean, s_m	0.012
Confidence limits at 95% level	6.05 ± 0.03

Confidence limits = $\bar{x} \pm ts_m$, $t = 2.447$ for 6 degrees of freedom

[b] Hydrazine sulfate not added to these samples, percentages are expressed on basis that 0.1 g hydrazine sulfate is present.

Procedure for Determination of Hydrazine and Ammonium Thiocyanate

The Volhard method for determination of halides served, with minor variations, for the determination of thiocyanate. The presence of hydrazine requires a strongly acidic solution to prevent hydrazine from acting as a reducing agent. Where reduction occurred, nitric acid could be added to cause the return of the silver to solution without any error.

The Andrews-Jamieson method for the titrimetric determination of hydrazine is widely used, but the reaction of iodate with thiocyanate is less well known.

The reaction is as follows:

$$4SCN^- + 6IO_3^- + 6Cl^- + 8H^+ \rightarrow 4SO_4^{--} + 6ICl + 4HCN + 2H_2O$$

The identical conditions can be used for titrating both hydrazine and thiocyanate; so a simultaneous determination of these two constituents appears feasible.

Reagents. The reagents used in the method developed for the determination of hydrazine and ammonium thiocyanate are as follows:

Silver nitrate, 0.1N

Nitric acid, concentrated, c.p.

Ferric alum indicator solution, saturated
$Fe_2(SO_4)_3 \cdot (NH_4)_2SO_4 \cdot 12H_2O$

Ammonium thiocyanate, 0.1N

Hydrochloric acid, concentrated, c.p.

Potassium iodate solution, 0.1N

Amaranth indicator, 0.2-percent aqueous solution

Carbon tetrachloride or chloroform

Apparatus. The following items of apparatus are required for the determination of hydrazine and ammonium thiocyanate:

Burets, 50 ml and 10 m.

Pipets

Iodine flasks, 250 ml capacity

Procedure for Determining Thiocyanate in Presence of Hydrazine (Volhard). Select a sample of such a size that a convenient aliquot will furnish approximately 2.0 meq (150 mg) of ammonium thiocyanate. Pipet this quantity into an iodine flask containing 25 ml of 0.1N silver nitrate, 10 ml of 6N nitric acid, and 2 ml of ferric alum indicator. Immediately titrate with 0.1N ammonium thiocyanate, using a 10 ml buret. A fleeting end point appears approximately 1 percent before the equivalence point. Make sure that the final end point color is permanent and does not disappear even after strong shaking. Use precaution in removing the stopper from the iodine flask; apply a liberal stream of water as the stopper is removed.

Procedure for Simultaneous Determination of Hydrazine and Thiocyanate (Andrews-Jamieson). Pipet an aliquot of the ammonium thiocyanate-hydrazine mixture (a maximum of 5 meq on a redox basis) into a glass-stoppered flask containing 25 ml of 12N hydrochloric acid and enough water so that the final volume is 70 ml. Add 5-10 ml of chloroform (or carbon tetrachloride). Immediately begin titrating with 0.1N potassium iodate and continue until the aqueous layer begins to change from a dark brown to a light yellow hue. At this point add the iodate dropwise and shake the solution vigorously after each addition. The end point is indicated by disappearance of color from the solvent layer. The stopper should be rinsed with a small amount of water each time it is removed.

An internal indicator is equally suitable for this titration. Four drops of amaranth indicator (0.2 percent aqueous solution) is used instead of the organic solvent indicated above. If this same solution is to be used subsequently for the determination of ammonia, the use of organic solvent as indicator is to be avoided.

Results. In the Andrews-Jamieson method for the determination of total hydrazine and thiocyanate it is recommended that a maximum of 5 meq be titrated. An aliquot containing 5 meq of a 1:1 (by weight) sample of hydrazine and ammonium thiocyanate would contain approximately 2 meq of ammonium thiocyanate on a redox basis (i.e., 0.3 meq on a neutralization basis), which is suitable for subsequent ammonia determination. Thus one aliquot serves for the Andrews-Jamieson titrimetric determination of hydrazine-thiocyanate as well as for the later determination of ammonia.

To check the accuracy of the method, standard solutions of ammonium thiocyanate and of hydrazine sulfate were titrated individually and in combination. These data are shown in Tables 2 and 3 where a comparison of titration volumes shows agreement

TABLE 2

TITRATION DATA FOR MIXTURES OF AMMONIUM THIOCYANATE AND HYDRAZINE BY JAMIESON METHOD

Values in milliliters

Sample No.	Mixture		
	A. 4 ml of Standard NH_4SCN solution	B. 10 ml of Standard $N_2H_4 \cdot H_2SO_4$ solution	C. 10 ml of $N_2H_4 \cdot H_2SO_4$ solution plus 4 ml of NH_4SCN solution
1	18.74	10.68	29.53
2	18.80	10.76	29.58
3	18.72	10.73	29.53
4	18.80	10.75	29.57
Av.[a]	18.77	10.73	29.55
Std. Dev.	0.041	0.032	0.045

[a] Titration A + titration B = 18.77 + 10.73 = 29.50

Titration C (combined A and B) = 29.55

TABLE 3

TITRATION OF THIOCYANATE BY VOLHARD METHOD[a]

Sample No.	Standard thiocyanate required, ml	
	A. 10 ml standard thiocyanate solution	B. 10 ml thiocyanate solution plus 0.4 g hydrazine
1	12.72	12.76
2	12.76	12.76
3	12.73	12.73
4	12.69	12.70
Av.[b]	12.73	12.74
Std. Dev.	0.029	0.026

[a] 15.00 ml of silver nitrate added to each sample

[b] Titration A = 12.73 + 10.00 (originally added)
= 22.73 total

Titration B = 12.74 + 10.00 (originally added)
= 22.74 total

within a few parts per thousand in all cases. Additional reliability is provided in the comparison of normalities of the thiocyanate solution as established argentometrically and iodometrically.

The normality of the ammonium thiocyanate solution based on the data shown in Table 3 (argentometric) is 0.0773. The normality based on data shown in Table 2 (oxidimetric) is 0.46314, which converted to argentometric basis (factor is 1/6) is 0.0772. The normalities based on these two methods are seen to agree within two parts per thousand.

Calculations. In computing the amount of hydrazine and ammonium thiocyanate as determined in the combined Volhard and Andrews-Jamieson procedures, the following equations are used:

Volhard Method

$$\text{Mg of } NH_4SCN \text{ in original sample} = \left[(\text{ml of } AgNO_3 \times N) - (\text{ml of } NH_4SCN \times N)\right] \times (\text{mol. wt. of } NH_4SCN) \times \frac{1}{\text{Dilution factor}}$$

Jamieson Method

$$\text{Mg of } N_2H_4 \text{ in original sample} = \left[(\text{ml of } KIO_3 \times N) - \frac{(\text{mg of } NH_4SCN \text{ found previously})}{\text{mol. wt. of } NH_4SCN/6}\right] \times \frac{\text{mol. wt. of } N_2H_4}{4} \times \frac{1}{\text{Dilution factor}}$$

The milligrams of NH_4SCN entered into this equation must be carefully considered. The number must be the number of grams of NH_4SCN in the original sample multiplied by the dilution factor for the sample in the Andrews-Jamieson method; i.e., it is the number of milligrams of thiocyanate actually present in the aliquot being titrated.

Ammonia Method. In computing the amount of ammonia in a sample of hydrazine, the following equation is used:

$$\text{Mg of } NH_3 \text{ in original sample} = \left[(\text{ml of acid} \times N) - (\text{ml of base} \times N)\right] \times \frac{17.03}{\text{Dilution factor}}$$

A sample calculation is given below based on the following data:

Original weight of sample: 0.5000 g; diluted to 250 ml

Volhard titration: 50 ml aliquot used; 15.00 ml of $AgNO_3$ added: standard thiocyanate required, 8.43 ml

Jamieson titration: 25 ml aliquot used; iodate required, 50.90

Ammonia determination: sample used as obtained from Jamieson titration: standard acid, 20.00 ml: standard base, 26.86 ml

All standard solutions are assumed to be 0.1N except the base, which is 0.05N.

Volhard Method

NH_4SCN in original sample

$$= \left[(15.00 \times 0.1000) - (8.43 \times 0.1000)\right] \times 76.12 \times \frac{1}{50/250} = 250 \text{ mg}$$

Jamieson Method

Hydrazine in original sample

$$= \left[(50.90 \times 0.1000) - \frac{25.000}{76.12/6}\right] \times \frac{32.04}{4} \times \frac{1}{25/250} = 250 \text{ mg}$$

Ammonia Method

NH_3 in original sample

$$= \left[(20 \times 0.1000) - (26.86 \times 0.05)\right] \times 17.03 \times \frac{1}{50/250} = 55.94 \text{ mg}$$

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ANALYTICAL METHOD FOR HYDRAZINE, HYDRAZINE NITRATE, WATER MIXTURES

by

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Presented by
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The Naval Ordnance Laboratory was assigned the task of investigating mixtures of hydrazine, hydrazine nitrate, and water for use as a liquid monopropellant for guns. The physical, chemical, and explosive properties of a series of mixtures were to be determined. Consequently, there was a need for rapid, yet reliable, methods for chemical analysis of these solutions. The method developed is, essentially, a series of acidimetric titrations on a single sample. Free hydrazine, by razonium ion and ammonia may be determined.

Reagents

Nitric Acid, HNO_3, 0.15N, Standardize against standard sodium hydroxide solution.

Sodium Hydroxide, NaOH, 0.15N, CO_2 -free, Standardize against Bureau of Standards potassium acid phthalate.

Indicator Solution, 0.08% bromocresol green, 0.05% methyl red, 0.05% bromothymol blue, and 0.05% phenol red, all dissolved in 95% ethyl alcohol. Neutralize to pH8 with sodium hydroxide.

Acetone, reagent grade.

Formaldehyde Solution, 37%, reagent grade.

Procedure

1. Prepare a small, thin-walled bulb with a column of 1-2 c.c. and having a long, thin drawn capillary stem. Heat the tared bulb gently over a small flame to expel part of the air. Submerge the open end of the capillary in the solution to be sampled. Allow about 0.2 gm of sample to be drawn into the bulb. Remove the bulb from the solution and seal the tip of the capillary stem in a small hot flame. After thermal equilibrium is reached, weigh the bulb and contents.

2. Place the bulb in a 250 ml beaker and cover with a 2-5 ml excess of standard nitric acid. Crush the glass bulb with a stirring rod, making sure the capillary stem is also crushed.

3. Add three drops of indicator solution. The color should be pink, indicating a pH less than 4.5.

4. Stir the solution mechanically, and back-titrate with standard sodium hydroxide until the color changes from pink to orange-yellow, indicating a pH of 4.7. Record the milliliters of sodium hydroxide required.

5. Add 10 ml of acetone and continue adding sodium hydroxide solution, rapidly at first, to neutralize the acid liberated by the formation of dimethylamine. When the color of the solution changes from yellow to green, stop the addition of base for about one minute. Resume the titration dropwise until the first appearance of blue in the green solution. This indicates a pH of 7.6. Take the buret reading and subtract the previous buret reading to obtain the milliliters of base used after addition of acetone.

6. Add 10 ml of 37% formaldehyde solution to the beaker and continue the addition of standard sodium hydroxide, dropwise, until the color of the solution changes from green to purple. This indicates a pH of 7.9. Be sure the purple color is permanent before recording the buret reading. Subtract the milliliter values for the two previous titrations from the buret reading. This represents the milliliters of standard sodium hydroxide required after addition of formaldehyde.

7. Since formaldehyde solution is slightly acid, it is necessary to make a blank correction. This is determined by repeating step No. 6 on a few representative samples and averaging the values for the milliliters of standard sodium hydroxide required.

__Calculations__

Let V_N = milliliters of standard nitric acid.

V_{bk} = milliliters of standard sodium hydroxide used for the back-titration.

V_a = milliliters of standard sodium hydroxide used after the addition of acetone.

V_f = milliliters of sodium hydroxide used after the addition of formaldehyde.

V_{bl} = milliliters of sodium hydroxide used for the formaldehyde blank.

N_b = normality of sodium hydroxide.

N_a = normality of nitric acid.

The grams of hydrazine equivalent to one milliliter of 1.0 N acid or base may be calculated as follows:

1 ml of 1.0 N acid or base = 0.03205 gm N_2H_4

Similarly for Ammonia,

1 ml of 1.0 N acid or base = 0.01703 gm NH_3

Then,

gms of NH_3 = $(N_b)\ (0.01703)\ (V_r - V_{bl})$

gms of free N_2H_4 = $(N_a)\ (0.03205)\ (V_h) - N_b\ (0.03205)\ (V_{bk} + V_r - V_{bl})$

gms of total N_2H_4 = $N_b\ (0.03205)\ (V_a)$

gms of $N_2H_5NO_3$ = (gms of total N_2H_4 - gms free N_2H_4) $\frac{95.05}{32.05}$

Discussion

The first step in this procedure converts all the free hydrazine and free ammonia (or their hydroxides) into the nitrate salts. The acid consumed in this reaction is a measure of the free hydrazine plus ammonia. Acetone reacts with hydrazonium ion forming dimethylazine and liberating a hydrogen ion for each hydrazonium ion. Titration of these hydrogen ions, then, provides a measure of the total N_2H_4 present in the sample. Formaldehyde reacts with ammonium ion to similarly release a hydrogen ion. Titration of this acidity gives a measure of the ammonia present.

Results of evaluation tests indicate that free hydrazine alone can be determined with an approximate error of -0.6% with a standard deviation of 0.4%. These figures were determined using samples containing about 0.15 grams total hydrazine and acid-base solutions about 0.15 normal.

Figures for hydrazine salts alone, with no free hydrazine, would be the same. Accuracy and precision values for mixtures of hydrazine and hydrazine salts would be less favorable since the sample size is determined by the sum of the free and combined hydrazine.

Table 1 presents some data obtained in the evaluation of the methods. Table 2 presents figures showing the estimated accuracy for various ratios of hydrazine to hydrazine nitrate. The values for Table 2 are estimated as follows:

Error for free N_2H_4 = $\frac{A}{B}$ X C

Error for $N_2H_5NO_3$ = $\frac{A}{D}$ X C X $\frac{E}{F}$

Where,

A = gms total N_2H_4 in sample

B = gms free N_2H_4 in sample

C = average error for free N_2H_4 from Table 1

D = gms N_2H_4 combined as $N_2H_5NO_3$

E = molecular weight of $N_2H_5NO_3$

F = molecular weight of N_2H_4

When water is present, the sample weight is increased so that all samples contain about 0.15 grams of total hydrazine.

TABLE 1

TITRATIONS OF HYDRAZINE-AMMONIA MIXTURES

Sample, gms		Recovery, gms Free N_2H_4	Total N_2H_4	NH_3	Percent Error Free N_2H_4	Total N_2H_4	NH_3
0.1401	---	0.1387	0.1395	---	-1.00	-0.43	---
0.1401	---	0.1387	0.1392	---	-1.00	-0.64	---
0.1391	---	0.1380	0.1386	---	-0.79	-0.36	---
0.1391	---	0.1378	0.1383	---	-0.93	-0.57	---
0.1391	0.0052	0.1383	0.1386	0.0052	-0.57	-0.36	0.0
0.1391	0.0052	0.1381	0.1386	0.0055	-0.71	-0.36	-6.0
0.1391	0.0052	0.1385	0.1385	0.0050	-0.43	-0.43	-3.8
0.1406	0.0177	0.1406	0.1405	0.0177	0.00	-0.07	0.0
0.1406	0.0177	0.1399	0.1400	0.0175	-0.50	-0.43	-1.1
	Average % Error				-0.66	-0.41	-2.2
	Standard Deviation				0.32	0.16	2.9

TABLE 2

ESTIMATED ACCURACY FOR ANALYSIS OF MIXTURES CONTAINING HYDRAZINE, HYDRAZINE NITRATE AND WATER

Ratio % Hydrazine to % Hydrazine Nitrate	Sample Weight, Grams Hydrazine Plus Hydrazine Nitrate	Percent Error	
		Hydrazine	Hydrazine Nitrate
1:0	0.15	-0.6	--
7:1	0.16	-0.6	-7.2
3:1	0.18	-0.7	-3.6
5:3	0.20	-0.8	-2.4
1:1	0.22	-0.9	-1.8
3:5	0.26	-1.0	-1.4
1:3	0.30	-1.2	-1.2
1:7	0.36	-2.4	-0.8
0:1	0.45	--	-0.6

THE TOXICITY OF HYDRAZINE AND EXPERIMENTAL THERAPY OF HYDRAZINE POISONING(1)

by

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Death from acute hydrazine poisoning when untreated occurs early and is due to convulsions. Convulsions may be prevented by the use of barbiturates but animals receiving the large doses of hydrazine die later despite the treatment. The late deaths from hydrazine are associated with and apparently due to liver damage. With low dose chronic toxicity there is a loss of appetite which is sufficient to cause some animals to starve unless they are carefully watched and force fed or otherwise encouraged to eat. For inhalation toxicity studies the amount of hydrazine dispersed can not be used as a measure of concentration in air. McGrath et al. has shown that the determined values average only 2% of the nominal values when there were animals present in the chamber. Exposure levels of 300 mg./M^3, 76 mg./M^3 or 26 mg./M^3 5 days per week, 6 hours per day gave LD_{50}'s in rats of 27, 50, and 144 hours of exposure. An exposure level of 6 mg./M^3 on the same schedule was apparently harmless to rats and dogs for six months and had no effect except on appetite and food consumption. The intravenous LD_{50}'s are reported as about 25 mg./kgm. in the dog and 25 or 30 mg./kgm. in the rabbit. Intraperitoneal LD_{50}'s are about 100 mg./kgm. in the rat and the pigeon, and 60 mg./kgm. in the mouse. The oral LD_{50} is reported as about 150 mg./kgm. in the rat.

The development of the treatment of hydrazine poisoning was based on the idea of preventing convulsions with a barbiturate while materials from the intermediate metabolism of glucose were used to attempt to counteract the later toxic effects. Each intermediate was tried once on a group of mice treated with glucose 250 mg./mouse subcutaneously and once on an untreated group of mice. If either group gave a longer survival than those which received a barbiturate alone, the experiment was repeated. The results on these experiments are seen in Tables 1 and 2. It can be seen that Na succinate and Na oxaloacetate give increased survival time when the mice received dextrose and that Na pyruvate and Na fumarate gave increased survival when the mice did not receive dextrose. Those which had no effect were Na citrate, lactate, glutamate, and malate. Table 3 shows the reason for selecting Na pyruvate as the material with which to develop a treatment. It alone was as good or better on survival time than any of the combinations and when Na pyruvate was added with another material the combination seemed better than the other material alone. Table 4 shows the use of the combination of thiopental Na and Na pyruvate which was able to change 100 mg./kgm. of hydrazine from fatal to all mice to non-fatal for all mice and 125 mg./kgm. from all fatalities to 2/3 survivors. The effects of Na pyruvate are apparently not limited to one species since guinea pigs showed the same general effects. It is perhaps important to note here that Na pyruvate alone is without effect on the survival time of hydrazine poisoning in the presence of barbiturates. Presumably any other anti-convulsant might replace the barbiturates in the therapy with pyruvate. The mechanism of action of the pyruvate is unknown but at least the fatal liver damage was prevented.

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(1) In recognition of health hazards to personnel engaged in development, production, handling, and using a wide variety of chemicals of military importance, aside from CW materials, the technical services of the Army, Navy and Air Force support a project entitled, "Health Hazards of Military Chemicals." U. S. Army Chemical Corps Medical Laboratories, Army Chemical Center, Maryland, have been given responsibility for conducting investigations under the project and are guided by the Research and Development Board. Investigations on specific chemicals are initiated upon request of agencies involved in development, production, handling and using such chemicals. Chemicals intended for use as fuels, propellants, oxidizers, lubricants, fire extinguishers, explosives, combustion products and others, fall within the scope of the project. The project is a continuing one, the "end-items" being (a) adequate toxicity and mechanism of action data on which medical and safety personnel may base safety, protective and treatment recommendations in the case of hazardous chemicals for which safer substitutes are not available, and (b) "screening" toxicity data, enabling developmental agencies to select the least toxic from among a number of candidate chemicals otherwise equally satisfactory for a given application.

This communication is based on studies conducted under this project.

TABLE 1

MINUTES OF SURVIVAL AFTER HYDRAZINE
(Average of 4 mice for each figure)

	No Dextrose	Dextrose		
Control	49	79	53	69
Citrate	61	30		
Lactate	43	79		
Succinate	68		85	128

TABLE 2

MINUTES OF SURVIVAL AFTER HYDRAZINE
(Average of 4 mice for each figure)

	No Dextrose			Dextrose		
Control	64	51	67	48	45	62
Glutamate	45			57		
Pyruvate	122	119		51		
Fumarate	91	86		50		
Oxaloacetate			60		91	88

TABLE 3

MINUTES OF SURVIVAL AFTER HYDRAZINE
(Average of 4 mice for each figure)

Control	43	67	50	45
Pyruvate	275	329		
Pyruvate +	152*	154*		
Fumarate			182	
Fumarate +			150*	
Succinate				117
Succinate+				157**

* 4% Na fumarate and 4% succinic acid
** 4% Na pyruvate

TABLE 4

Dose of Hydrazine I.P. mg./kgm.	(4 mice each test) Number Surviving Control	Treated
100	0	4
100	0	4
100	0	4
125	0	4
125	0	1
125	0	3

DISCUSSION ON PAPERS BY
MR. J. N. MANDAS, DR. JOHN D. CLARK, MR. JOHN E. DE VRIES, MR. B. F. LARRICK, AND DR. VERSA V. COLE.

THE CHAIRMAN: Thank you, Dr. Cole.

Our papers are now open for discussion. If you like, we can take all the papers of the afternoon group.

MR. GALE: I would like to direct a question to Dr. Cole.

We have been concerned with the detection in the early stages of hydrazine poisoning. We have found that there are abnormalities in the blood known as Heinz bodies which are created as a result of the hydrazine poisoning.

I was wondering if your group has done any work or made any study on the possibility of detecting hydrazine poisoning in the early stages by blood sampling? In the event of hydrazine poisoning, has your group formulated the dosages for human beings of the pyruvate or barbiturate treatment?

DR. COLE: We have made no observations on the Heinz bodies. My own particular work has been confined to treatment of acute poisoning.

As far as the dosage goes, it so far is partly guess work. The sodium pyruvate, for example, is not exceedingly toxic although you can kill an animal with it. If you give a mouse one gram per kilogram by vein instead of subcutaneously you can kill him with it. You are fairly safe with the barbiturate if you keep the individual at a level that he does not convulse and use sodium pyruvate one gram at a time with fluid.

I hope that Dr. Pfeiffer's work with atrolactamide on semi-carbazide poisoning will turn out to be also effective in hydrazine poisoning. If that is true, the doses are established.

MR. GALE: Would you give that name again?

DR. COLE: Alpha phenyl lactic acid amide.

THE CHAIRMAN: Dr. Lewis?

DR. BERNARD LEWIS (Bureau of Mines, Pittsburgh): I would like to take this opportunity to commend Doctors Haller and Dexter for their very beautiful paper.

I wish to ask Mr. Mandas whether he found a break in the vapor pressure curve of mixtures of hydrazine and hydrazine nitrate at 51 per cent hydrazine nitrate similar to the abrupt change in index of refraction at this percentage.

MR. MANDAS: No, the abrupt change did not reflect itself in the vapor pressure.

DR. STEPHEN KROP (Army Chemical Center): I would like to add to what Dr. Cole said about our guess work in searching for a therapeutic agent for intoxication by hydrazine.

Our guess work was fortified somewhat by the statements in the literature that hydrazine is known as a "carbonyl trapping" agent, so we settled upon trials of physiologically occurring carbonyl compounds; obviously one such is a metabolic decomposition product of glucose, viz., pyruvate.

In regard to toxicity for man, we can't get figures on that very well because we are hampered by the lack of volunteers! (Laughter). The practical rule of thumb the one might use for toxicity of hydrazine vapor is that it is in a class with phosgene or cyanide.

In the booklet, which I scanned hurriedly, prepared by the Mathieson people and distributed here, there are some estimated figures on oral toxicity for man. According to some of our most recent data, which have not yet been published, I think that those figures may be on the high side. By that I mean that they may be too optimistic. Hydrazine, I think, is more toxic by inhalation than those figures might lead one to infer.

MR. E. MILTON WILSON (Aerojet Engineering Corp.): If I may add a qualitative statement as to toxicity studies, having handled both hydrazine and methyl hydrazine, I would say the latter is far more toxic. Do not handle methyl hydrazine outside of a good fume hood; it can give a very serious headache.

DR. KRUSE: (To Dr. Krop) I should like to ask if you are referring to inhalation or skin-contact poisoning?

DR. KROP: The former.

I think that the discussion of toxicity in the Mathieson booklet is a very good one, as a matter of fact. The information essential for preventing intoxication is all there, namely, adequate protective equipment, adequate ventilation, and the use of water - plenty of it and fast - after skin contact.

THE CHAIRMAN: Dr. Gantz, would you like to comment on Dr. J. D. Clark's observation on the liberation of iodine on the oxidation of hydrazine?

DR. E. ST. CLAIR GANTZ (U.S. Naval Ordnance Test Station): One thing that occurred to me is how rapidly he added iodate in those titrations and whether the level of the hydrochloric acid was as high as most people recommend.

Although we didn't show them, we have slides with us which show that recovery data starting with hydrazine sulfate rather than liquid hydrazine is about as high as you can ever expect from good analytical titrations and we should have had low results according to his statements.

I wondered about what hydrochloric solution you need.

DR. CLARK: It was quite a strong solution but I am not sure of its exact strength. We had no guarantee that the iodine loss was significant, but we were scared of it. When we found out that there was any loss at all we weren't happy with iodate, and didn't want to have anything more to do with it.

DR. GANTZ: One advantage with iodate is that it is an extremely stable substance. You hardly need to check it more than once a month at the most.

DR. CLARK: That is quite true, but we found chloramine quite satisfactory, too.

MR. MANDAS: We have found the same thing. We also found, according to McBride, that a 6 molar concentration of chloride ion at the end point is absolutely necessary. Our experience has shown that three titrations are usually necessary. The first titration is run hurriedly to roughly locate the end point. The succeeding titrations are carried out by rapidly adding the standard solution until two or three milliliters from the end point, thus permitting the necessary cautious approach of the end point. We have had very good results with it using primary standard hydrazine sulfate. I don't doubt Dr. Clark's findings as iodine vapors can be seen over the solution if it becomes warm enough during the titration. However, our experience has shown that any loss does not decrease the accuracy of the titration, which is from two to three parts per thousand.

DR. KRUSE: I am wondering if some error could be introduced by titrating in an open vessel. It is conceivable that the evolution of nitrogen could carry out some iodine. We have always stoppered the flask and shaken the solution thoroughly between additions of the standard iodate solution.

THE CHAIRMAN: Dr. Clark, do you want to comment on that?

DR. CLARK: I have no comment on that.

MR. MANDAS: We have successfully titrated in both open and closed vessels.

THE CHAIRMAN: Professor Gilbert, would you like to comment?

PROFESSOR E. C. GILBERT (Oregon State College): It is probably unnecessary. My only comment is that my favorite titration is the iodate titration using the glass stoppered flask for titrating hydrazine sulfate. I think that is a better method as far as I am concerned after ten or fifteen years of experience. Quantitatively, if you use the glass stoppered flask, it is possible to get the correct results within a few hundredths of one per cent.

THE CHAIRMAN: Thank you, Dr. Gilbert.

Professor Schlesinger, would you like to comment on some of the papers?

PROFESSOR H. I. SCHLESINGER (University of Chicago): No, thank you.

THE CHAIRMAN: Professor Urry?

PROFESSOR URRY (University of Chicago): I have no comment.

THE CHAIRMAN: Well, if there is no further discussion, we will recess the meeting until tomorrow morning.

MORNING SESSION
3 February 1953

CHAIRMAN, DR. HOWARD W. KRUSE
U. S. NAVAL ORDNANCE TEST STATION, INYOKERN

Mr. J. E. Troyan, Mathieson Chemical Corporation, presented his paper entitled, "Safety in the Handling of Hydrazine."

SAFETY IN THE HANDLING OF HYDRAZINE

by

J. E. Troyan
Mathieson Chemical Corporation

Abstract

Hydrazine is recognized as a versatile, reactive chemical, which though potentially hazardous, can be handled safely if treated with proper precaution. Problems of explosion, fire, and toxicity are of primary concern to personnel working with hydrazine. Information pertinent to these subjects is summarized and evaluated as an approach to defining safe practices. It is shown that stability of hydrazine is influenced by temperature and materials of construction. Decomposition may be catalyzed in certain cases to the point of explosion.

Introduction

Hydrazine is a new industrial chemical, whose present and projected uses are based to a large extent upon its high degree of reactivity. This same property, however, has in the past given hydrazine the reputation of being an unstable and hazardous compound.

Misapprehension concerning the nature of hazards involved in handling hydrazine started before the compound was isolated, and has continued for more than fifty years. Curtius (Ref. 1), who first prepared hydrazine in solution, expressed the conjecture that "the free base is so unstable that it can not exist in the free state." The prediction of Curtius was later proved erroneous by Labry de Bruyn (Ref. 2), who isolated the anhydrous free base, and reported that "it is a very stable compound, and in contrast to hydrogen peroxide, not explosive. It can be heated above 300°C without being decomposed." Despite this observation, and in spite of other experimental evidence to the contrary, the idea of inherent instability continued to persist.

In more recent years, miscellaneous reports of fires and explosions involving hydrazine have sustained the impression that hydrazine was dangerously unstable. Such incidents, in which exact causes have not been obvious, stimulate the kind of fear commonly associated with unknown risks. Only by increasing our knowledge of the behavior of hydrazine under all conceivable conditions can fact be separated from conjecture.

An attempt is made in this report to summarize much of the available information pertinent to the subject, to define the known areas of safety and danger, and to describe general safety rules which have been used by Mathieson Chemical Corporation. Physiological hazards, in addition to those related to decomposition, fire and explosion, are included in the discussion.

Properties

Physical, chemical, and thermodynamic properties of hydrazine have been covered in considerable detail in the excellent book by Audrieth and Ogg (Ref. 3). As background for a discussion of the hazards involved in handling hydrazine, certain of the pertinent properties listed in this book are summarized herewith. Supplementary data, taken from other literature sources or developed in the Mathieson laboratories, are also recorded.

Physical. Anhydrous hydrazine (N_2H_4) is a highly polar, hygroscopic liquid which will absorb CO_2 or oxygen from the atmosphere. It melts at 2.0°C, and boils at 113.5°C (760 mm Hg). Since its density as a solid (1.146/-5°C) is higher than as a liquid (1.024/20°C), there is no danger of rupturing containers under freezing conditions.

Vapor pressures are represented by the following empirical equation:

$$\log_{10} P \text{(mm Hg)} = 7.80687 - 1680.745/(t + 227.74)$$

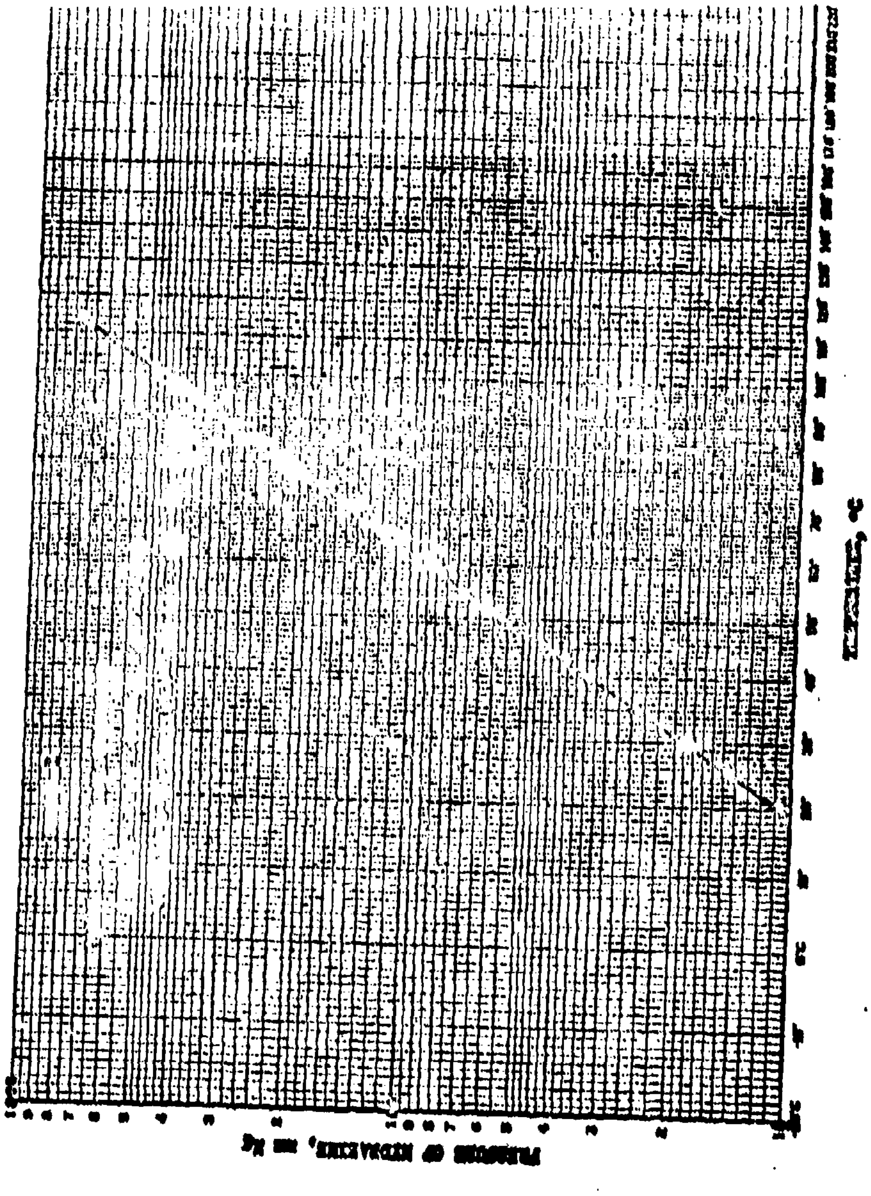
Values are plotted for reference in Figure 1. Above the atmospheric boiling point, data are said to be less reliable due to thermal decomposition. For most engineering purposes, the results of Lobry de Bruyn (Ref. 4) given in Table I are sufficiently accurate.

TABLE I

VAPOR PRESSURE OF ANHYDROUS HYDRAZINE

Temp. °C:	113.5,	140,	170,	200,	250,	300,	350,	380 (T_c)
Press., Atm.:	1.0,	2.3,	5	10,	26,	56,	104,	145

According to the literature, hydrazine and water form an azeotrope mixture which boils at 120.3°C (760 mm Hg) and which contains 58.5 mol % N_2H_4. More recent work reported by Dunnam (Reference 5) and Burtle (Reference 6), and verified independently by our laboratories indicate that the azeotrope composition is closer to 55 mol % N_2H_4 (68.5% wt).


PRESSURE OF HYDRAZINE, mm Hg
TEMPERATURE, °C

Freezing point data on the N_2H_4-H_2O system show the compound $N_2H_4 \cdot H_2O$ to be a stable solid phase melting at -51.7°C. Eutectics exist at 29.5 mol % (-88°C m.p.) and at 56 mol % (-53.5°C m.p.).

Chemical. From a strictly chemical standpoint, hydrazine is classified as a very strong reducing agent, and a mildly alkaline base. It reacts readily and exothermically with most oxidizing agents, the speed of reaction depending upon concentration, temperature, catalytic conditions, and the specific oxidizing agent.

Examples of oxidizing agents include not only the electronegative elements, and highly oxidized compounds, but also lower oxides of some metals and even certain metal ions. Hydrazine may be liquid or vapor, concentrated or dilute, free or in combined form. Principal products are usually N_2 and H_2O, but in some cases substantial amounts of NH_3 are produced. Typical reactions include reduction of salts or oxides of copper, iron, silver, mercury, and many other similar metals. Reaction with MoO_3, Fe_2O_3, MnO_2, HgO, CuO, PbO_2, CrO_3, $AgNO_3$, and $Cu(NO_3)_2$ may be particularly violent. This marked activity has accelerated decomposition and even caused fires during use and storage of hydrazine.

Atmospheric oxidation of hydrazine will occur if care is not taken to exclude air. It has been reported (Ref. 7) that 85% $N_2H_4 \cdot H_2O$ is oxidized roughly 5% per hour when violently agitated at room temperature. When not agitated, oxidation rate is only 0.01%/hour. Rates are greatly accelerated as temperature is raised.

Even when oxygen is absent, hydrazine is capable of self-oxidation and reduction, forming nitrogen and ammonia. The latter reaction proceeds at a negligible rate at ambient temperatures and under ordinary circumstances. In the presence of certain catalysts or catalytic surfaces or at higher temperatures, decomposition rate increases.

Ignition, Combustion, and Explosive. Combustion of hydrazine as a liquid is, strangely enough, difficult to initiate when the material is cold. Ignition will occur only when temperature has been raised above roughly 100°F. When burning freely in air, hydrazine behaves much like gasoline. However, as heat raises its temperature to boiling, hydrazine burns fiercely.

Flash and fire points (open-cup) for hydrazine-water mixtures were determined recently in Mathieson's laboratory. Data were obtained using regular ASTM techniques (D92-46), except that a glass cup was substituted for the metal to obviate any catalytic effects. Results are plotted in Figure 2. Flash points of 100% N_2H_4 and 85% hydrate (54.4% N_2H_4) were 125°F and 193°F, respectively.

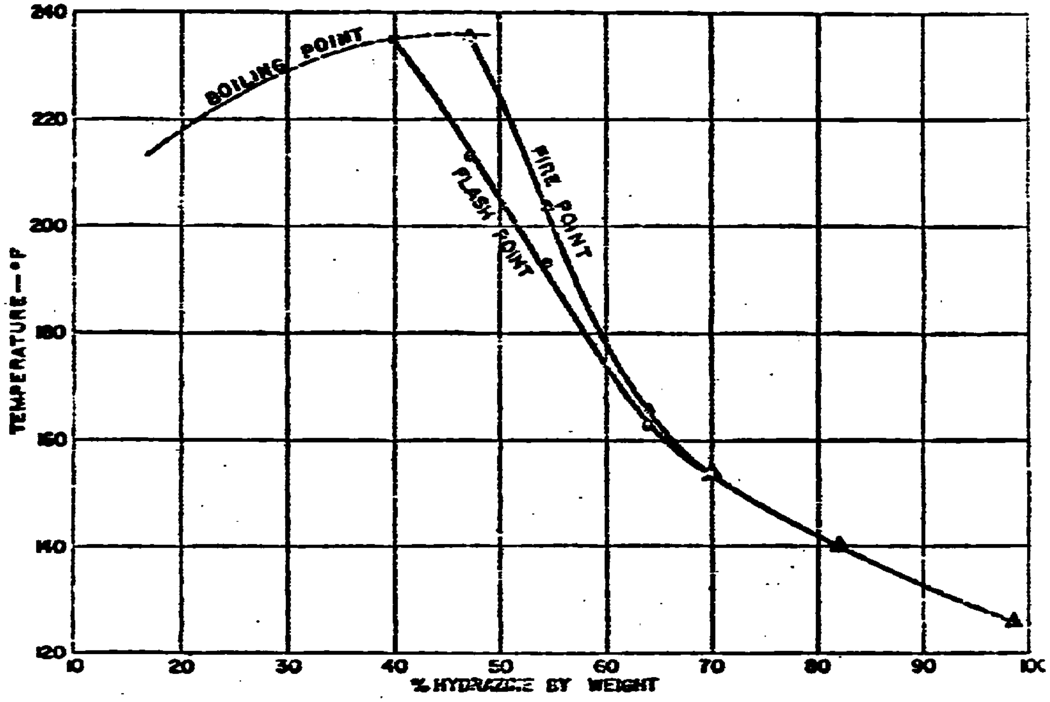


FIGURE 2

OPEN CUP FLASH & FIRE POINTS FOR AQUEOUS HYDRAZINE SOLUTIONS

USING ASTM OPEN CUP METHOD (D92-46) WITH A GLASS CUP

It is assumed that the closed cup flash point for 100% N_2H_4 would approach 104°F, which is the temperature at which liquid hydrazine has sufficient vapor pressure (35 mm Hg) to give an explosive mixture with air. This lower explosive limit, corresponding to 4.7% by volume in air, was reported by Scott, et al (Ref. 8). Table II shows comparable data for other fuels at one atmosphere, 100°C, and with downward propagation of the flame.

TABLE II

LOWER LIMITS OF EXPLOSIVE CONCENTRATION OF FLAMMABLE VAPORS IN AIR

Compound	Volume %
Acetylene	2.7
Methane	3.2
Hydrazine	4.7
Ethane	6.0
Hydrogen	9.0
Carbon Monoxide	15.0

In contrast to most other fuels, hydrazine has no upper limit to the range of explosive concentrations. Although unusual, this behavior is not unique. At slightly elevated pressures (4.9 psig or more), the same behavior is exhibited by acetylene.

In contact with catalytic surfaces, ignition of hydrazine occurs spontaneously at a temperature dependent upon composition and condition of surface, and on the composition of the vapor mixture. Data on spontaneous ignition temperatures cover a wide range -- from less than 30°C (for liquid N_2H_4 in contact with platinum in O_2 atmosphere) to more than 415°C (for non-catalytic surface in absence of oxidants). Reactions between liquid hydrazine and stronger oxidizing agents may be initiated at even lower temperatures. Results of ignition tests carried out by the Bureau of Mines (Ref. 8) are shown in Table III.

TABLE III

MINIMUM IGNITION TEMPERATURES OF HYDRAZINE

Surface	Atmosphere	Ignition Temp., °C	Ignit. Lag, Seconds
Pyrex glass	air	270	3.9
Pyrex glass	O_2	204	4.9
Platinum	air	226	3.0
Platinum	O_2	30	6.0
Ferric oxide[a]	air	23	-
Ferric oxide[a]	N_2	23[b]	-
Black iron	air	132	instantaneous
Black iron	N_2	131	instantaneous
Stainless steel	air	160	2.0
Stainless steel	air	156	0.9
Stainless steel	N_2	[c]	-

[a] Powdered Fe_2O_3 spread over bottom of flask.
[b] Sparking, then red heat. Flame after air entered flask.
[c] No ignition up to 415°C.

Similar data were obtained by Picatinny Arsenal (Ref. 9) for ignition of hydrazine in air. Temperatures of ignition were 220°C on clean iron, 135°C on iron containing a film of Fe_2O_3, 110°C on oxidized Woods Metal (50% Bi, 25% Pb, 12.5% Sn, 12.5% Ca) and 220°C on porcelain.

It is noteworthy that even in the presence of air, the minimum observed ignition temperature over non-porous, non-oxidizing solids is well above the boiling point of hydrazine. The ignition temperature of 270°C for hydrazine in air over Pyrex glass is comparable with values for some of the lower paraffin hydrocarbons, ranging from 218°C for n-octane to 462°C for isobutane, measured in the same apparatus (Ref. 10).

Qualitative data on spontaneous ignition of hydrazine in air indicate that the presence of oxidizing solids is not a necessary condition for spontaneous ignition at room temperature or below. Such ignition was observed at Mathieson when asbestos, expanded vermiculite, kieselguhr, sawdust, and some metal powders were moistened with hydrazine and exposed to the atmosphere at room temperature. The phenomenon is similar to the spontaneous ignition of drying oils, starting with slow oxidation under conditions that prevent the dissipation of the heat as fast as it is liberated, and proceeding faster as the temperature rises until the ignition temperature is reached. The effect of the porous solid may be either catalytic or simply that of a barrier to dissipation of heat.

From the previously noted fact that hydrazine vapor has no upper limit of explosive concentration, it is obvious that the presence of an oxidizing agent is not a necessary condition for decomposition of hydrazine vapor. The energy liberated by decomposition of hydrazine vapor alone under suitable conditions of temperature and concentration is sufficient to propagate the reaction as an explosive wave.

Because of the low vapor density at pressure of 1 atm or less, the explosion is not violent at temperatures up to the normal boiling point of hydrazine (113.5°C). At temperatures below 100°C, the saturated vapor in contact with excess liquid phase has been exploded in glass vessels without rupturing them (Ref. 8). Pure hydrazine vapor (without oxidant or diluent) will propagate an explosion initiated by an electric spark at any pressure above about 12 mm Hg, corresponding to saturation at about 22°C.

Non-oxidizing gases mixed with hydrazine vapor tend to increase the partial pressure of hydrazine required to propagate an explosion. Table IV summarizes data (Ref. 8) on explosive limits of hydrazine vapor in mixtures with several inert diluents. In general, the minimum explosive concentration decreases as the total pressure and temperature increase; but these factors are of less importance than the nature and proportion of the diluent in the mixture. It is to be noted that ammonia is more effective than water vapor, helium, or nitrogen in repressing the propagation of explosions in hydrazine vapor. The difference between NH_3 and N_2 in changing the explosive limit was also shown by Bamford (Ref. 11).

With N_2 padding, an explosive mixture will not exist below 87°C, which is the temperature corresponding to the vapor pressure giving the lower explosive limit concentration.

[illegible] WITH INERT DILUENTS

Diluent	Vol % N_2H_4	Pressure, mm Hg Total	Pressure, mm Hg N_2H_4	Temp °C
None	100	12	12	29
Nitrogen	38.0	754	286	109-112
"	48.6	185	90	100
Helium	37.0	757	280	105-118
Water Vapor	30.9	789-889	244-275	130-135
" "	37.1	251-265	93-98	100
n-heptane	85.6	695-714	587-611	115
Ammonia	61.2	147	90	100

Stability

Probably the most important, yet often the least desirable chemical reaction which hydrazine undergoes is decomposition. This may proceed according to all or any of the equations listed below:

$$3N_2H_4 \rightarrow N_2 + 4NH_3 \qquad (1)$$

$$2N_2H_4 \rightarrow N_2 + H_2 + 2NH_3 \qquad (2)$$

$$N_2H_4 \rightarrow N_2 + 2H_2 \qquad (3)$$

It is generally conceded that ammonia produced in the first two equations is dissociated to the elements when temperatures are sufficiently elevated. Many mechanisms for the chain of reactions involved have already been described (Ref. 3), so the topic will not be discussed further in this report.

The rate at which hydrazine decomposition proceeds and the relative quantities of the end products (N_2, H_2, and NH_3) are influenced by temperature and by the presence of catalytic surfaces or materials. These two factors are considered below:

Thermal Decomposition. In spite of its thermodynamic instability, hydrazine's rate of decomposition under suitable conditions of storage is so low that ordinary handling presents no serious problem. For example, in the range of 20-40°C hydrazine has been stored for many months with no indication of pressure rise due to gas evolution. Mathieson's experience has been confirmed by many others using hydrazine. Containers of glass, aluminum and 304 or 347 stainless steels have been involved.

Decomposition of hydrazine was studied in our laboratories at the boiling point and at room temperature. Gas which was evolved closely approached the theoretical composition expressed by equation (1). The percent of hydrazine decomposed per day was calculated from the moles of gas liberated. Control tests in Pyrex glass at 113-114°C indicated that rate of decomposition of 95% N_2H_4 decreased with time of contact. The highest rate occurred in the first few hours as surface was apparently being deactivated. Decomposition values after several hours were .1-.2% per day and after two hundred hours, 0.01% per day.

Considerable work on thermal stability at temperatures above the boiling point has been done by Jet Propulsion Laboratories (Ref. 12). Studies of decomposition at temperatures up to 265°C (500°F) led to the following conclusions:

1. Gaseous hydrazine in the presence of an excess of liquid at 500°F or lower decomposes at a predictable rate which is a function of temperature. Products are NH_3 and N_2.

2. Above 500°F some of the ammonia decomposes into the elements.

3. The reaction is wall catalyzed and rate is independent of the amount of liquid in the test chamber.

4. Certain materials significantly increase decomposition rates and are usually more important than surface catalysis.

Catalytic Decomposition. Catalytic surfaces or materials have a more pronounced effect on the stability of hydrazine than does temperature. The catalytic activity of certain metals is discussed in the following sections.

a. Dissolved Ions. Laboratory tests were carried out in a glass apparatus in which 96.8% N_2H_4 was refluxed under a nitrogen blanket (Ref. 13). Various ions were checked at 20 ppm concentration, measuring decomposition rate by the gas evolved. Whereas the control showed 0.14% N_2H_4 decomposed per day, samples containing chromic, ferric, and cupric ions showed 0.3%, 0.24%, and 0.17%/day, respectively. Samples containing aluminum, nickel, sulfate, and acetate ions, were equal to or more stable than the control.

In studies conducted in the presence of atmospheric oxygen, Audrieth & Mohr (Ref. 14) found that traces of dissolved copper strongly catalyzed autoxidation of hydrazine. Iron, cobalt, chromium, and nickel were not catalytic.

Although hydrazine is produced and stored in stainless steel equipment, ions of iron, chromium, nickel, etc. will not be present unless there has been salt or acid contamination. Under such circumstances, corrosion of the metal may occur. Observed decomposition is then usually due to the metallic ions resulting from corrosion (solution) of the metal.

b. Metal Surfaces. In finely divided form, metals such as molybdenum, Raney nickel, iron, cobalt, or stainless steels have been found by Mathieson and others (Ref. 13) to catalyze hydrazine decomposition. The effect is assumed to be due to both extended surface area and the specific material involved.

Of more practical interest, however, is the influence on hydrazine stability of various metals when utilized in sheet, plate, or other massive forms. On the basis of a large number of tests conducted by Mathieson, it has been established that stainless steel (type 304 or 347) is the preferred material of construction. Molybdenum stabilized stainless (type 316) is to be avoided because of the fact that the molybdenum present catalyses decomposition. Aluminum may also be suitable for use with anhydrous, but there is some evidence of corrosion by hydrate at the boiling point. Plain steel appears almost equivalent to stainless steel under controlled test conditions. However, since the steel oxidizes readily, and iron oxide is well recognized as a decomposition catalyst, the use of steel in plant installations is not considered a safe practice.

Copper, like steel, may perform satisfactorily as a material of construction for hydrazine if oxygen is avoided; that is, if equipment is not allowed to become oxidized during use. On the basis of preliminary tests of corrosion resistance and decomposition effects in 1947, copper was actually selected over stainless steel for fabrication of a flash distillation unit. The choice appeared satisfactory for almost two years, since relatively trouble-free operation was experienced. Oxide film and/or oxide welding slag inclusions, later recognized as decomposition catalysts, eventually caused an explosion in the copper still. Use of copper was therefore discontinued.

Decomposition tests conducted at 50°C in small cylinders of 347 stainless steel showed that (1) 95.5% N_2H_4 decomposed to NH_3 and N_2; (2) rate of decomposition decreased linearly with time (0.08%/day at 2 hours; 0.002%/day at 293 hours); and (3) decomposition was greater when more vapor phase was exposed to the metal (see Table V).

TABLE V

HYDRAZINE DECOMPOSITION IN 347 STAINLESS STEEL BOMBS AT 50°C. EFFECT OF VAPOR/LIQUID RATIO

	% Decomposed/day	
Time, hrs.	15 cc liq. + 100 cc vap. Ratio = 6.7/1	85 cc liq. + 30 cc vap. Ratio = .35/1
2	-	.082
4	.33	-
24	.14	.011
72	.069	.0044
150	.047	.0026
250	.036	.0020

Data are plotted in Figure 3 along with other decomposition results obtained in Mathieson laboratories. Selected data reported by Battelle (Ref. 15) are also shown for comparison. Values are summarized in Table VI.

In a 55 gallon drum, the surface/volume ratio would be 3.5/1. In our laboratory runs, using 24 cm² samples in about 150 cc of hydrazine, the ratio is 0.167/1. The stainless bombs had a 0.9/1 ratio. Battelle data shown in the figure were based on experiments using a 43/1 ratio. This may explain the higher decomposition even though runs were made at 60°C rather than at boiling point.

Molybdenum metal has been observed to be a specific and potent catalyst for the decomposition of liquid hydrazine as well as fused dihydrazine sulfate. There are several standard types of stainless steel which contain from 0.6% up to 4% Mo. Average content of other stainless steels is about 0.15% with 0.5% frequently noted. Evidence is not sufficient at present to warrant setting a Mo tolerance on steel for hydrazine

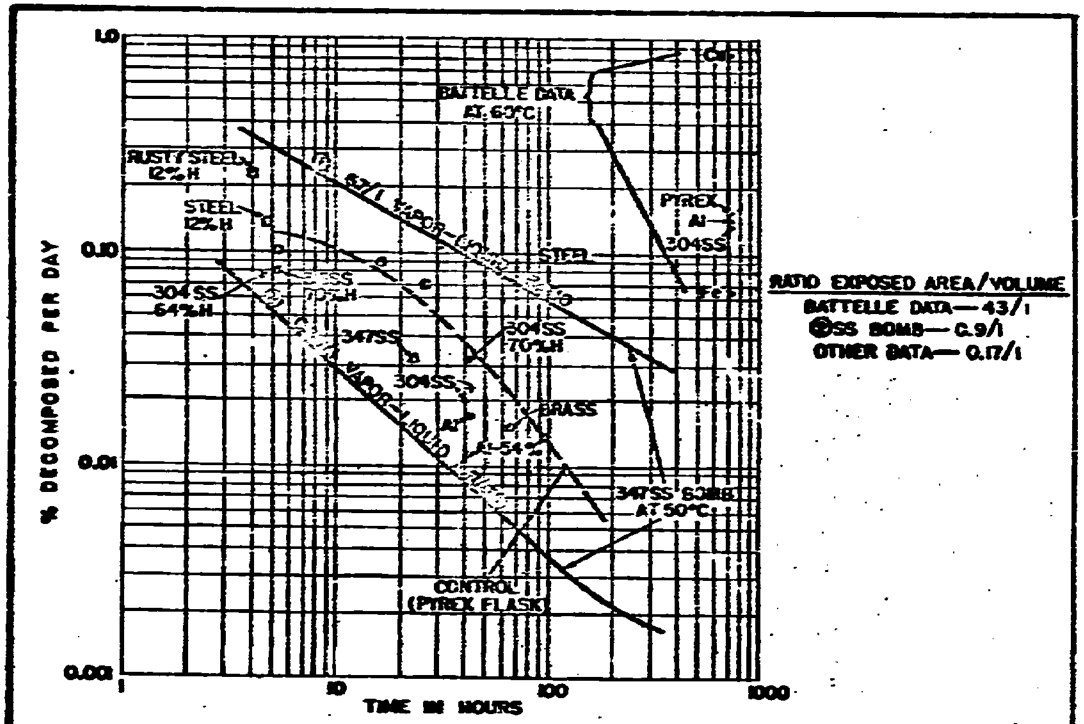


FIGURE 3 DECOMPOSITION OF BOILING HYDRAZINE

(95% N_2H_4 UNLESS OTHERWISE INDICATED)

HYDRAZINE DECOMPOSITION RATES

Metal	Hydrazine	Temperature °C	Time, Hrs.	% Decomposition per day
Mathieson Data				
Control in Pyrex	95%	114	5.5	.103
Control in Pyrex	95%	114	16	.090
Control in Pyrex	95%	114	26	.068
Control in Pyrex	95%	114	95	.014
304 ss	64%	120	4.5	.078
304 ss	95%	114	40	.02
304 ss (welded)	95%	114	44	.023
304 ss	70%	114	40.5	.033
321 ss	95%	114	25.3	.015
347 ss	95%	114	24	.032
316 ss	70%	114	5.2	.08
Aluminum 2S	95%	114	40.5	.018
Aluminum 2S	54%	119	37.5	.01
Brass (Red)	95%	114	63	.015
Steel	95%	114	65	.079
Steel	12%	102	4.7	.133
Steel (rusty)	12%	102	4.0	.233
Battelle Data (Ref. 15)				
Aluminum 2S	95%	60	720	.134
Copper	95%	60	720	.896
Iron	95%	60	720	.063
Pyrex	95%	60	720	.151
304 ss	95%	60	720	.135

equipment below 0.5%, but it clearly indicates that types containing molybdenum should be avoided. These would include 302, 315, 316, 317, 329, 416, 420F, and 430F. Although types 304 and 347 were recommended for Mathieson use in shipping containers, equipment, and piping, most fabrication in the last few years, has been with 304, owing to the unavailability of 347.

Olin Industries (Ref. 16) have also established that molybdenum strongly catalyzes the decomposition of hydrazine. Cylinders of various metal were exposed in the vapor phase to refluxing hydrazine and decomposition was measured by pressure rise due to evolved NH_3 and N_2. Data are summarized in Table VII. It is clearly shown that 316 stainless steel and especially Hastelloy A are decomposition catalysts.

TABLE VII

VAPOR PHASE DECOMPOSITION OF HYDRAZINE

(Pressure Rise, mm Hg in 14.5 hours)

Temp °C	Blank	304 ss	347 ss % Cb	316 ss 4% Mo	Nickel	Hastelloy A*
50	1	1.5	1	18	5	117
75	1	31	19	194	79	198 (2 hrs)
115	10	62	63	209	146	-

*60% Ni, 20% Mo

c. Inhibitors. A number of inhibiting materials have been proposed (Refs. 13, 14, 17) to reduce decomposition of hydrazine which is catalyzed by various metals. One of the most significant materials reported effective was cadmium, added as the acetate (.1-.5%) or employed as surface plating. The marked improvement in stability claimed was verified in our own laboratory tests.

Liquid Hydrazine. The conditions under which liquid hydrazine decomposes at controlled rates, or gaseous hydrazine explodes have been discussed in the foregoing section. It is desirable now to consider the evidence pertaining to the possibility of explosion in the liquid state.

Because of suspicions that hydrazine might be explosive, its sensitivity to various types of initiating impulses was tested by the U.S. Bureau of Mines (Ref. 8). The liquid showed no indication of sensitivity to impact or friction, nor to electrostatic discharges. It could not be detonated by a No. 10 Army detonator (considerably stronger than a No. 8 blasting cap), under mild confinement, at temperatures up to 105°C. At room temperature, a similar cap with a 20 gram booster charge of tetryl failed to detonate it. In these detonability tests, the containers were ruptured only at the end in which the blasting caps were inserted; and the condition of the ruptured tube gave no evidence of any more energy released from the hydrazine samples than from a blank tube filled with water.

In the ballistic mortar tests (Ref. 8) in which 10 gram charges of hydrazine were fired with Army detonators, hydrazine "showed 135 percent of the strength of 10 gram charges of TNT tested under the same conditions." Although this might be taken as an indication that the hydrazine detonated under the conditions of confinement in the mortar, it would seem more probable that the hydrazine acted as a fuel component in a mixed explosive than as an explosive per se.

This was further substantiated by three replicate tests carried out for Mathieson by Trojan Powder Co. A special detonator was fired in these tests in contact with liquid hydrazine in a stainless steel tube held against a lead plate. Part of the hydrazine was vaporized or dispersed as spray, and about a third remained in the test container. Comparison of the lead plates with similar plates fired as blanks showed that the hydrazine did not detonate.

Additional data on the lack of sensitivity of liquid hydrazine have also been reported by the NACA (Ref. 18). Tests were run in stainless bombs, using No. 6 electric caps plus 6 ml of tetranitromethane to detonate the 95.6% hydrazine. Tubes were ruptured only in the zone of the detonating charge, indicating the stability of hydrazine to shock.

Vapor Phase Explosion Pressures. Because of the ease with which explosions of hydrazine vapor can be initiated, it is important to know something of the pressures that may result from such explosions under conditions that may exist in manufacture and handling. Although data from direct experimental measurements are not available, the *maximum* attainable pressure can be estimated with sufficient accuracy for present needs.

When hydrazine vapor decomposes to its elements, the heat of reaction is sufficient to produce a temperature rise of about 1300°C. At the resulting temperature, the dissociation of any ammonia that would have resulted from slow decomposition at relatively low temperature is so nearly complete at any reasonable pressure that the only reaction that need be considered is

$$N_2H_4 \rightarrow N_2 + 2H_2$$

Using tabulated values (Ref. 19) of $E_T^o - E_0^o = \int_0^T C_v \, dT$

for the gases resulting from explosions, the heat contents of the reaction products at the original temperature can be easily estimated; and this, added to the heat of reaction, gives the total heat content of the reaction products, from which the final temperature can be estimated.

Table VIII shows the results of several such calculations for saturated hydrazine vapor in the range from 67° to 170°C.

TABLE VIII

CALCULATED TEMPERATURES & PRESSURES FROM EXPLOSION OF SATURATED HYDRAZINE AT CONSTANT VOLUME

Initial Temp. °C	Initial Press. atm.	Temp. Rise °C	Final Temp. °K	Ratio P/P	Final Pressure	
					Atm.	p.s.i.g.
67	0.167	1360	1700	15.00	2.50	22
87	0.386	1349	1709	14.23	5.50	66
96.5	0.553	1344	1714	13.92	7.69	98
113.5	1.00	1334	1721	13.35	13.35	182
140	2.30	1322	1735	12.60	29.0	411
170	5.00	1308	1751	11.85	59.3	857

If air is mixed with the hydrazine vapor, the H_2 from the hydrazine decomposition is burned, yielding $N_2 + H_2O$, with either O_2 or H_2 if the air or hydrogen is in excess. Because of the large heat of the combustion reaction, the pressure rise for explosions of air saturated with hydrazine at a total pressure of one atmosphere is greater than for explosions of pure hydrazine vapor at the same temperature, the difference being greatest for mixtures approximating the stoichiometric proportions for complete combustion. Calculated values of final temperatures and pressures from explosion of mixtures of air with saturated hydrazine vapor at one atmosphere total pressure are shown in Table IX.

TABLE IX

CALCULATED TEMPERATURES & PRESSURES FROM EXPLOSION AT CONSTANT VOLUME OF AIR SATURATED WITH HYDRAZINE VAPOR

Initial Temp °C	Final Temp °K	Final Press, psig
47	712	18.5
57	2346	100
67	3100	142
87	2526	156
96.5	2271	162

If nitrogen is substituted for air in the mixture, the calculated maximum pressure is decreased sharply to a value only slightly greater than that for pure hydrazine vapor under reduced pressure. At 87°C, the calculated maximum pressure is 76 psig, and the temperature rise is 897°C. Below 87°C, at which the vapor pressure of hydrazine is equal to its calculated partial pressure at the lower explosive limit of mixtures with nitrogen at 1 atm (Table V), no explosion should occur.

Maximum calculated pressures resulting from explosions of saturated hydrazine vapor, alone and mixed with air, are plotted against saturation temperatures as solid lines in Figure 4. The broken lines represent nitrogen saturated with hydrazine at 1 atm total pressure.

It is to be noted that although the maximum pressure developed by explosion of the pure vapor decreases rapidly as the temperature is reduced below the atmospheric boiling point, it decreases but little with temperature in that range if the pressure is maintained by admitting air, down to about 67°C, where the hydrazine and air are in stoichiometric ratio. Below this temperature, the maximum pressure decreases rapidly.

The chief advantage of padding with nitrogen is therefore to prevent forming air mixtures that remain explosive at moderately low temperatures. Secondarily, it is to be noted that dilution of hydrazine vapor with nitrogen markedly decreases the maximum temperature, although causing a slight increase in the maximum pressure developed by decomposition.

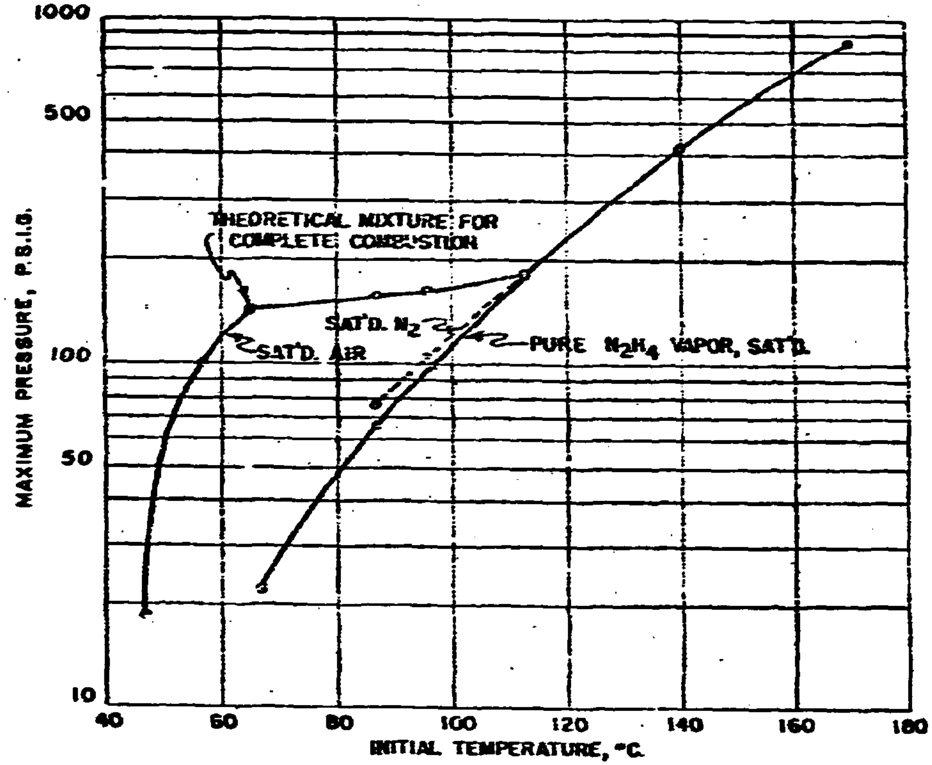


FIGURE 4. MAXIMUM PRESSURES PRODUCEC BY HYDRAZINE VAPOR EXPLOSIONS (CALCULATED)

Physiological Hazards

The qualitative knowledge that hydrazine is toxic to animals is almost as old as the compound itself. Curtius (Ref. 1) stated in 1887 that the vapor attacks the membranes of the nose and throat; and in 1890, Loew (Ref. 20) announced that plants, fungi, lower animals and mammals are killed by small quantities of hydrazine.

During the succeeding fifty years, several studies were made on the physiological effects of hydrazine in experimental animals, but without obtaining quantitative data that would be useful in evaluating hazards of industrial exposure. Similarly, experience in commercial production of hydrazine hydrate in Germany resulted in qualitative observations on reactions of human subjects, especially to hydrazine vapor in the eyes, but still without any quantitative data on the concentrations involved. These reports contain two valuable implications, however:

1. The vapor causes serious discomfort to the eyes in concentrations well below those required to cause general symptoms or damage to other organs; and

2. The effect of the vapor on the eyes is painful, but causes no permanent injury.

Subsequent reports on random observations of questionable objectivity have ascribed to hydrazine numerous effects, some of which may have been of psychological origin. In the absence of definite evidence to the contrary, these reports had to be given due consideration in the formulation of safety practices for our original pilot plant operations, with the result that our standards were stricter than necessary in some respects.

The need for reliable quantitative data has been partly met by a study made at the University of Southern California. The report (Ref. 21) on this work constitutes the best and most comprehensive treatment of the toxicity of hydrazine to date. In this study, experimental animals (rats, mice, rabbits, pigeons, and cats) were observed after measured doses of hydrazine administered in various ways, and autopsies were performed on the animals that were killed.

From data on test animals, it was concluded that single doses of 100 mg/kg of body weight or daily repeated doses of 10 mg/kg (corresponding to 7 grams and 0.7 grams, respectively, for 154 pounds of body weight) would be "extremely dangerous" for a man. The "acute toxic dose" for man was estimated at 0.5 to 1.0 grams, or about the same as the daily repeated dose that would be extremely dangerous.

Inhalation tests of 1 hour duration, chiefly on albino mice, indicated that single or occasional exposures to 1000 ppm (by volume) in air are survivable without apparent harm; 1600 ppm is dangerous, sometimes lethal; and 2000 ppm or more is almost always lethal. It was remarked, however, that "the acutely dangerous concentration in air is much higher than that of chemicals such as nitrogen dioxide, carbon monoxide, and hydrogen sulfide;" and it was suggested that "acutely dangerous concentrations would be as intolerable as strong concentrations of ammonia." It was noted also that "hydrazine vapor in air can hardly be classified as dangerously toxic in the ordinary sense."

It is Mathieson's observation that physiological hazards may be of major concern in the handling of hydrazine only when relatively concentrated solutions are involved. Dilution reduces both the vapor pressure and the corrosive effect to such an extent that solutions containing less than about 25% free base are no more hazardous than solutions of many other chemicals.

The most serious hazard is apparently from accidental splashes of concentrated hydrazine in the eyes. Proper use of goggles will prevent most such contacts; and prompt washing with water should prevent injury when splashes get by the goggles. It is reported that when hydrazine in concentrations greater than 20% comes in contact with the eye for short periods, permanent damage may result.

Accidental contact of concentrated hydrazine with the skin will cause a burn unless the hydrazine is washed off. Burned skin assumes a slightly bleached appearance and swells slightly. If more than a small area of skin is involved, there may be toxic effects as well. Protective clothing has therefore been used whenever there is danger of splashes; and provision is made for prompt and thorough washing of any hydrazine that reaches the body.

The vapor is apparently less dangerous than formerly believed. Our general rule has been to provide enough ventilation to avoid any noticeable odor of hydrazine in work spaces under normal conditions. The concentration at which the odor of hydrazine becomes noticeable has not been determined, and presumably varies with the individual; but we would estimate, on the basis of our experience, that the odor threshold is somewhere below 100 ppm as compared with about 1000 ppm survivable for one hour by mice without apparent harm.

Mathieson's only plant experience involving exposure to fumes appears to be occasional headaches. These have shown up when operators have worked in close quarters for extended periods where hydrazine vapor was apt to exist (drum filling, sampling in distillation area, etc.).

After several years of pilot plant production experience, it has been observed that the most prevalent health hazard identified with hydrazine and its salts is dermatitis. Even then, only relatively few cases have occurred. In most instances, the source of irritation appears to have been acidic salts of hydrazine rather than the free base. Mono and dihydrazine sulfate and hydrazine hydrobromide were specific causes in several cases. It has not yet been possible to separate the effect of the inorganic acid from hydrazine proper. Nevertheless, the salts are assumed to be hazardous or toxic to skin and are handled in a manner to prevent inhalation, ingestion, or skin absorption.

Safe Practices

General Principles. In formulating specific rules to be followed in design and operation of plants and equipment to handle hydrazine, the following basic facts, summarizing data from preceding sections should be taken into consideration:

1. Hydrazine vapor is combustible. Air saturated with it at temperatures above 104°F (40°C) is an explosive mixture. This corresponds to 4.7% by volume of N_2H_4. For hydrazine vapor and nitrogen, the lower explosive limit is 38%, (saturation pressure at 189°F (87°C)).

2. The vapor alone is also explosive, decomposing with a theoretical temperature rise of about 1300°C, and producing a maximum calculated pressure about 12-14 times that of the original vapor.

3. Both the oxidation and decomposition reactions may be catalyzed. The catalytic reactions, although slow at normal temperatures, may raise the temperature until reaction proceeds at a dangerous speed.

4. If a mixture of vapor and an oxidizing gas in contact with excess liquid phase is exploded, reaction is propagated through the vapor, but not through the liquid phase.

5. Both the liquid and the vapor react readily - in some cases violently - with many oxidizing agents.

6. Hydrazine is toxic when ingested by inhalation or otherwise.

Regulations. Under the regulations of the ICC, hydrazine is classified as a "corrosive liquid." This classification (Ref. 22) was established and appropriate shipping containers were specified, on recommendation of the Bureau of Explosives of the Association of American Railroads. This followed a meeting of four interested companies, at which properties of hydrazine were reviewed, and the particular classification was chosen as best affording the protection for which the regulations are intended.

Although hydrazine is a liquid, and is admittedly combustible, it is not properly classified as an "inflammable liquid," which is defined as "any liquid which gives off inflammable vapors (as determined by open-cup flash point) at or below a temperature of 80°F." The flash point of hydrazine by the specified method is about 45°F above this limit.

Regardless of this variance, it would appear that hydrazine might be classified better for safety purposes both as a corrosive and a flammable liquid with a closed cup flash point of about 104°F. It is not an explosive in the generally accepted sense of the word, nor under the definitions of most applicable laws and regulations.

<u>Materials of Construction</u>. The selection of materials of construction for use with hydrazine is largely a problem of decomposition, as has been discussed, rather than corrosion. Nevertheless, one must consider the resistance of possible materials to attack by hydrazine.

In this regard, corrosion rates were determined for various metals being considered for hydrazine service. Tests were conducted in the absence of air. Data indicated that with the exception of zinc, most metals corroded at rates of less than 0.005 inches/year. Temperatures up to the boiling point and concentrations of 54-64% and 95% N_2H_4 were involved. Typical results are given in Table X.

TABLE X

CORROSION RATES OF METALS IN HYDRAZINE & HYDRAZINE HYDRATE

(inches/year)

Metal	95% N_2H_4 114°C	95% N_2H_4 90-95°C	95% N_2H_4 25°C	Hydrazine Hydrate 120°C	Hydrazine Hydrate 90-95°C	Hydrazine Hydrate 25°C
Aluminum	.001	.000	.000	.0045	.0002	.000
Copper	.0015	.000	-	-	-	-
304 ss	.0015	.0003	.000	-	.0004	.000
321 ss	.003	-	-	-	-	-
316 ss	-	.00025	-	.0005	-	-
Steel	.001	.0006	-	-	.007	-
Nickel	-	.0001	-	-	-	-
Zinc	-	.060	.0002	-	-	.0005

Work by Picatinny Arsenal (Ref. 9) generally confirms Mathieson's studies. At 65°C after 10 months contact with 95% N_2H_4, the following losses in weight (gms/cm²) were noted: Aluminum - 0.000; 304 ss - .0012; mild steel - .127; and nickel - .040. Corrosion was excessive after 4-6 months on copper, lead, zinc, and magnesium.

There are several practical considerations that govern the choice of materials of construction once having the basic knowledge relative to corrosion and decomposition:

1. It is impractical in many cases to avoid occasional or even frequent admission of air.

2. It is often necessary to work at elevated temperatures, or impossible to be sure that desired temperatures are maintained.

3. It is sometimes necessary to handle hydrazine containing water, mineral acids, or salts.

In view of the above, Mathieson has considered it prudent to avoid materials which are attacked by hydrazine, or which become active catalysts of decomposition under any of the stipulated conditions. Thus, any metal which reacts with the atmosphere to form an oxide is to be avoided. Mild steel and copper are considered undesirable for this reason. A serious hazard would exist for example, if iron oxide should scale off and accumulate. As previously discussed, various oxides react violently with hydrazine. Problems of this kind are best avoided in our operations by use of stainless steel type 304 which is also more resistant to attack by acids.

Aluminum appears to be another suitable material for construction of drums and process equipment containing anhydrous N_2H_4. However, further tests would be desirable before use of aluminum is adopted or recommended.

Glass has been found suitable as a material of construction from both a corrosion and decomposition standpoint, except that in hot aqueous hydrazine, some solution may take place. From a safety standpoint, glass is structurally less satisfactory than metals. Its use has been restricted to essential parts where transparency is desired.

For packing and gaskets, hard (or impregnated) asbestos and Teflon have been found acceptable. Polyethylene is chemically resistant, but is limited to use at temperatures below 160°F.

Fabrication and Design. To eliminate the hazard of hydrazine combustion when exposed inordinately to air, special attention must be given to assembly, fabrication, or design methods.

On the basis of pilot plant experience, it has been found preferable to back-weld threaded fittings larger than 1/2" in size; otherwise, leaks occur frequently. Carefully threaded small-size pipe, lubricated with plastic lead seal compound, and drawn up tightly, has held hydrazine fairly well.

Care must be exercised in making all welds. Existence of flux or slag in the weld may lead to attack by hydrazine, resulting in leakage. All joints should be thoroughly tested with air or NH_3 under pressure before using with hydrazine.

It has been observed on several occasions, where process equipment was repaired or revised by welding, that accelerated decomposition of hydrazine in the process solutions took place. A technique of washing such metal surfaces with dilute hydrazine prior to regular operation has been adopted as a safety measure.

It is not economically practicable to use vessels designed to hold the maximum pressures that could be generated by explosion of hydrazine vapors within them under conditions that may occur under abnormal conditions. The test pressure specified for shipping containers, for example, is 15 psig, compared with explosion pressures of 200 psig or more that could occur if the containers were exposed to fire. Neither is it generally practicable to provide sufficient explosion relief to prevent damage to a vessel that is not designed to withstand the pressure generated by the explosion.

On the other hand, it is reasonable to require that containers be designed to withstand the maximum pressures that can be generated by explosion of any vapor mixtures that can exist within them under normal operating conditions. Mathieson has concluded that if this rule is followed, and if reasonable precautions are taken to minimize the occurrence of the abnormal conditions that could cause rupture by explosion, the resulting risk should be close to the economic minimum.

The design of vessels containing hydrazine will depend upon operating pressure and temperature and composition of vapor present. Requirements which have guided our work are summarized as follows:

1. For vessels to be used at atmospheric pressure and at temperatures below 40°C, pressure requirements were only nominal, or sufficient to withstand air pressures used in testing for leaks.

If the vessel was to be padded with nitrogen, the temperature limit for low pressure construction was extended to about 85°C.

2. For vessels to be heated to the boiling point of hydrazine or below, at atmospheric pressure, a design pressure of 200 psig was used unless temperature control and inert gas padding were provided. In such cases, a lower design pressure based on maximum pressure produced by explosion at the maximum operating temperature was used.

3. Vessels to contain hydrazine under the pressure of its own vapor at temperatures above the boiling point were designed for higher pressures as indicated by Figure 4.

Since these explosion pressures increase rapidly with temperature, it is imperative to provide effective safeguards against temperature rises above the maximum on which the design is based. Temperature controls on vessels are designed to "fail safe," and are supplemented with alarms and auxiliary cooling that operate when the temperature rises beyond a pre-determined limit. Direct injection of water into process vessels has been a practical emergency measure.

Padding with inert gas is employed wherever practicable. For unheated vessels, it is a desirable precaution; for heated vessels it is practically indispensable. A holder, riding on the line is advisable, not only to conserve gas, but to decrease the risk of exhaustion of the gas supply. In any case, however, an alarm should give warning of low gas supply, and a reserve supply should be kept connected to the system so that it can be cut in quickly when needed.

Heated vessels are designed to minimize the metal surface exposed to both liquid and vapor. Heating jackets are provided on the bottom only, in order to avoid possible exposure of hydrazine to overheated walls. Similarly, internal heating surfaces are completely immersed in the liquid at all times. Low temperature heating media are specified; and temperature differences are as low as consistent with reasonable heat transfer surface. Continuous process equipment with minimum working volume is preferable to large batch equipment. Operation under vacuum is avoided if possible.

Operations. In our operations involving hydrazine, the operating procedures have been developed in detail in advance, and followed strictly until formally changed. Such procedures have been specifically designed for each operation. A list of general principles that have been applied in our investigations and operations is given below.

1. Before filling any new piece of equipment with hydrazine, make sure that it is clean and free from scale. If it is to be used for hot concentrated hydrazine, it should first be filled with dilute hydrazine and heated, to make sure that there is no oxidizing material present. Pickling with inhibited acid to remove rust or mill scale is a desirable practice.

2. Watch new equipment carefully for leaks. Be especially alert for the first few days; and continue frequent inspections for several weeks, to be sure that no slow leaks develop.

3. Flush with nitrogen before admitting hydrazine at any temperature above 40°C, or before heating above 40°C. Shipping and storage containers should be flushed with nitrogen regardless of temperature.

4. Check all control instruments and safety devices at regular intervals to be sure that they are in good operating condition.

5. After filling each shipping container with hydrazine for the first time, store it for at least 24 hours in a location where any leak that may develop can do no damage.

6. When equipment must be opened for any reason, make certain that it is cooled below 40°C and flushed with nitrogen before opening.

7. If repairs or changes are to be made, equipment must first be flushed with water.

8. Goggles should be worn at all times in areas where hydrazine is being handled.

9. Protective clothing such as gloves, aprons, face shields, etc., is required whenever hydrazine is being handled in such manner that a splash may result. It is generally unnecessary when equipment and methods are properly designed; but should be immediately available for emergency use.

10. Gas masks are unnecessary except for emergencies, when ammonia-type masks may be used; but they should be readily available.

11. Emergency showers must be readily accessible for prompt treatment of splashes.

good housekeeping and alertness are the prime factors in detecting leaks or spillage before ignition occurs.

13. Once spillage is detected, flushing with water is a certain means of preventing or extinguishing fire. Automatic sprinklers are satisfactory for extinguishing fires, but should be supplemented with manually controlled water supply which can be used for prevention.

Acknowledgment

The author wishes to acknowledge original contributions to the text which were made by Mr. Matthew Weber, Jr.

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DETONABILITY OF SOLUTIONS OF HYDRAZINE, HYDRAZINE NITRATE AND WATER

by

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Presented by R. D. Dwiggins

INTRODUCTION

The Naval Ordnance Laboratory was assigned the task of investigating mixtures of hydrazine, hydrazine nitrate, and water for use as a monopropellant for guns. One requirement for a suitable propellant is that it will not be readily detonated. It became necessary, then, to establish the detonability of the various compositions being considered.

APPARATUS AND METHODS

The detonability test used was derived from modified gap tests as used by Dr. Noonan's group of our Explosives Research Department. A sketch of the apparatus is shown in Figure 1. A wooden stand having two shelves supported on three legs provides support for the test assembly. A brass pipe having a .001-inch copper foil soldered over one end serves as a container for the solution to be tested and holds about 46 cc. This container is made from 3-inch lengths of pipe having a 1.18-inch inside diameter and 1.50-inch outside diameter. A 50-gram tetryl pellet, 1 inch high and 1-5/8 inches in diameter, is used to initiate the test solution. The tetryl pellet is initiated by an Engineer's Special blasting cap which is supported by two wooden cylinders on a track. Figure 2 is a photograph of the apparatus. A 3/8 x 4 x 4-inch steel plate is used to indicate the nature of the explosion.

In operation, the tetryl pellet is placed in the center of the bottom shelf. The brass tube is inserted through a snug hole in the top shelf and rests on the tetryl pellet. A thin film of saran about .002 inch thick is placed between the bottom of the brass tube and the tetryl. This film extends outward one to two inches, providing an umbrella to deflect any solution which might be spilled. On two occasions prior to the use of this shield fires were started, apparently by contact of the solutions with tetryl. The solution to be tested is poured into the tube until level with the top and the steel plate is then centered on top of the filled tube.

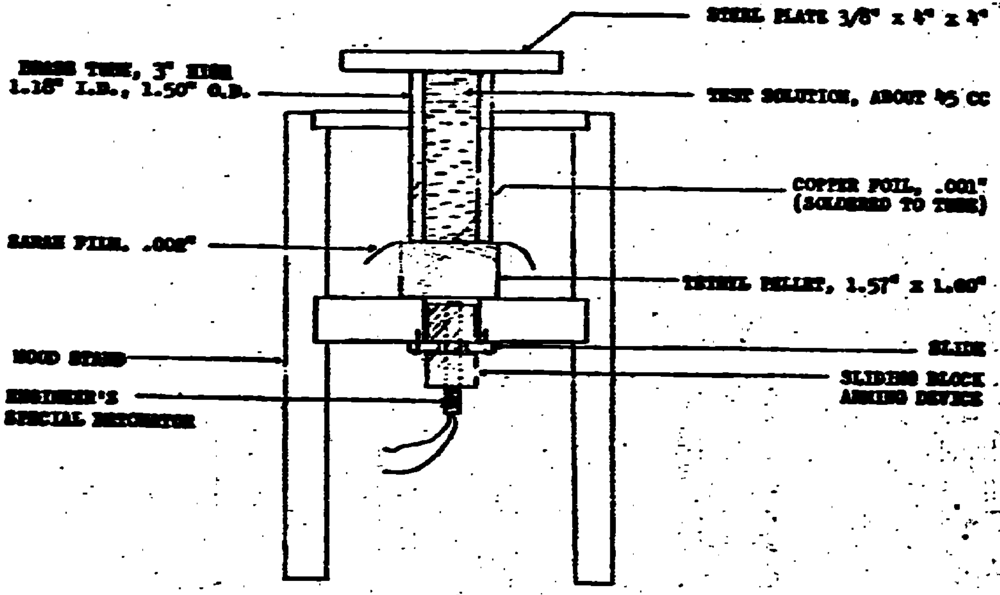
The Engineer's Special detonator is positioned on the track near the front edge, being inserted into the wooden cylinders far enough so that it just clears the tetryl pellet when slid into position. The operator then retreats from the barricade and, by means of a string, pulls the detonator into position under the center of the tetryl pellet. After firing, the metal plate is recovered and the extent of damage noted. If detonation occurs, a hole is punched through the steel plate. Ordinary explosions dent the plate but do not punch through it. Figure 3 shows, on the left, a plate after a detonation and, on the right, when no detonation occurs. In most of the work, if a detonation was obtained on the first trial, no further trials were made. At least three trials were made if detonation did not occur.

Some comparative tests with other materials were made. These results are given in Table 1. Sixty-five different compositions of hydrazine, hydrazine nitrate, and water were tested. These results are presented graphically in Figure 4. It can be seen that solutions containing more than about 25% hydrazine nitrate and up to as much as 42% water can be detonated.

TABLE 1

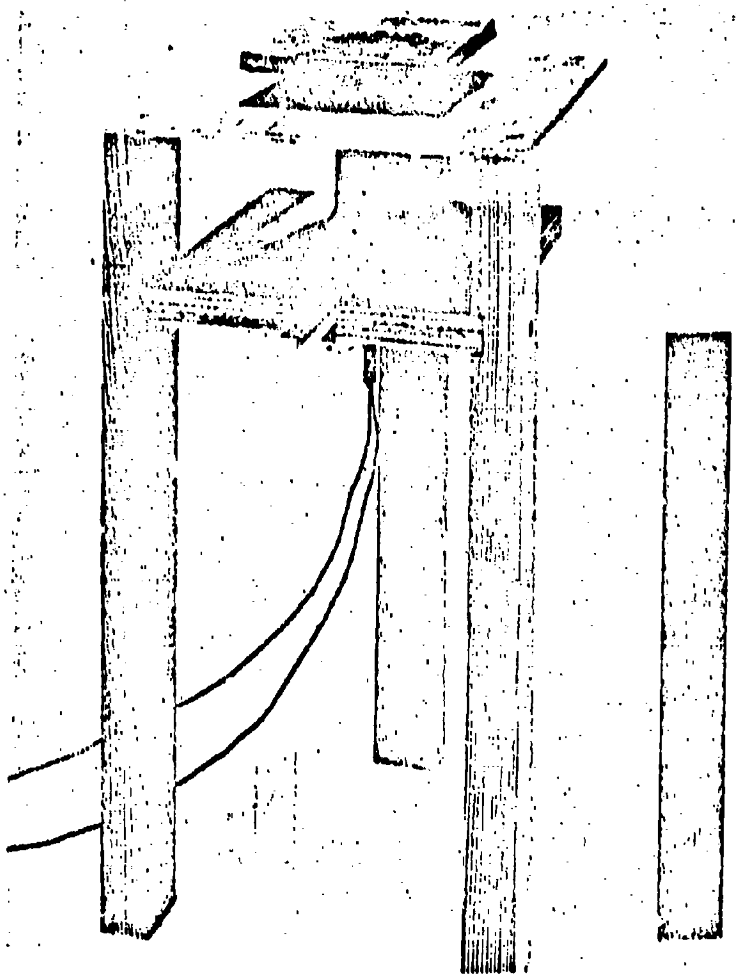
DETONATION TESTS

Material	Result D = Detonation N = No detonation
Army Black Powder, Grade A5	N
Pistol Powder, SR4990	N
Ammonium Nitrate	N
Hydrazine Nitrate, 99%	D
Ballistite	D



DETONABILITY APPARATUS

FIGURE 1



DETONABILITY APPARATUS

FIGURE 2
[illegible]

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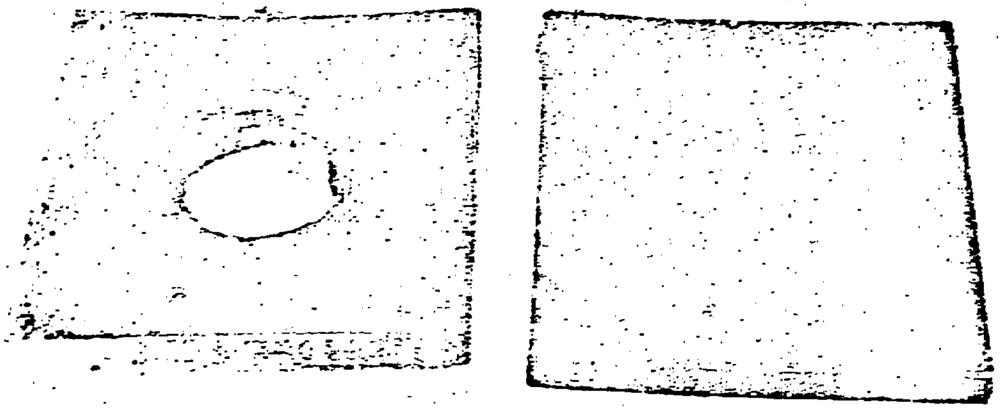
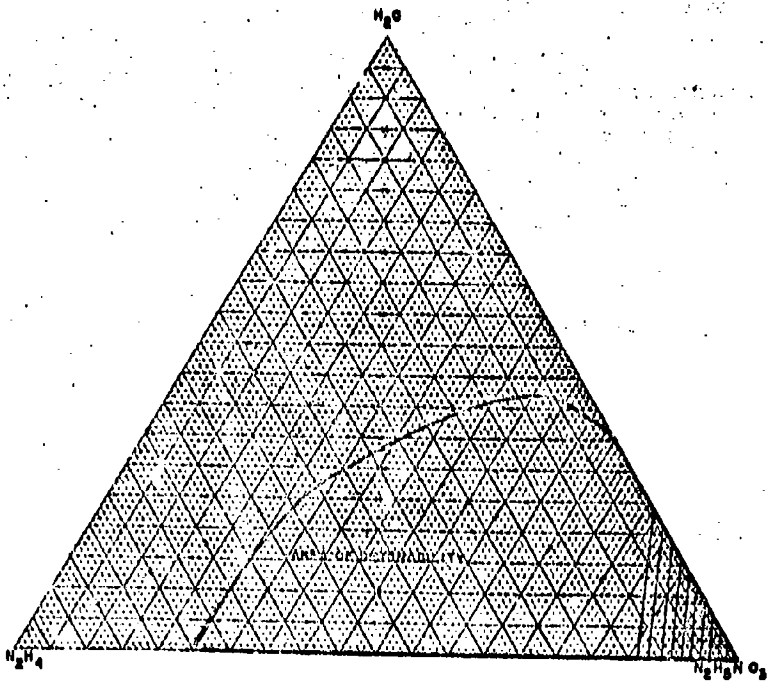


RESULTS OF DETONABILITY TESTS

FIGURE 8



DETONABLE COMPOSITIONS
SHADED AREA REPRESENTS APPROXIMATE AREA OF INSOLUBILITY FOR HYDRAZINE NITRATE AT ROOM TEMPERATURE

FIGURE 4

DISCUSSION ON PAPERS BY
MR. J. E. TROYAN AND MR. R. D. DWIGGINS

DR. W. E. LAWSON (E. I. du Pont de Nemours & Co., Inc.): I wondered whether a 10-gram primer would be suitable. This is a rather common primer.

MR. DWIGGINS: We have never made any tests with any other charge than the 50-gram tetryl pellet.

MR. RYKER: In this same connection, we are undertaking a further evaluation of this same system using a No. 8 blasting cap as our initiating source.

Some of the preliminary experiments that we have made thus far indicate that the envelope of detonability for a No. 8 blasting cap is much closer to the hydrazine nitrate vertex than these data might suggest.

In other words, I wanted to point out to the group that this is really a severe test the NOL people have applied to the solutions. I think it is valuable information but from the standpoint of handling, storage, and use, a great deal of energy is being put in those solutions. We are going to extend this work by finding out how sensitive these solutions are to a small amount of energy, for example, a No. 8 cap.

DR. EUGENE MILLER (Redstone Arsenal): Perhaps a more reasonable and practical detonability test would be the use of bullets. From the Army Ordnance viewpoint, this is the primary worry.

MR. DWIGGINS: I might say that we intend to extend this test to determine the sensitivity of detonation of these mixtures by placing plastic sheets between the booster charge and the tube and placing enough sheets so we do not get detonation. I think we can evaluate these mixtures according to the gap that we put in. When we do that I think we will have considerably more useful information.

MR. PAUL M. ORDIN (NACA, LFPL, Cleveland): We ran a number of tests using both the No. 6 and No. 8 dynamite cap with commercial anhydrous hydrazine. When the cap was immersed in the liquid, we did not get a detonation; however, with the dynamite cap placed above the liquid we always got detonation.

DR. A. M. BALL (Hercules Powder Co.): Detonation of the entire --

MR. ORDIN: No, only the liquid phase.

DR. BALL: I would like to point out the question of detonability is largely a function of confinement. For example, I might mention that we can reliably detonate dinitrotoluene with a No. 6 cap under suitable confinement. In running tests of this kind I certainly recommend that you keep track of how much confinement you have.

DR. LEWIS: I feel we must guard against confusion of the term "detonation." The occurrence of detonation is not assessed by the loudness or sharpness of an explosive report. A material will support a detonation wave if such a wave, which travels with a high and constant velocity characteristic of the material, is able to propagate through a long column of the material. In the case of anhydrous hydrazine initiation with as much as 50 gm. of tetryl at one end of a meter column of the liquid fails to initiate a detonation wave that travels throughout the column. Under the influence of the initiator the hydrazine decomposes with evolution of heat in the region of the initiator. The amount of hydrazine so affected is proportional to the size and strength of the initiator.

MR. CAMPBELL: I would like to say that at the Naval Ordnance Test Station we found that ballistite when contacted with hydrazine developed a very good fire with hydrazine within 20 seconds.

DR. NOONAN: I would like to point out that in applying such a sensitivity test, under conditions of variable humidity, it is rather essential to use plastic cards of some sort rather than paper. Paper will pick up as much as 10 or even 25 per cent moisture, and will make a different type of barrier.

The other thing to remember is to measure temperature because some things, particularly nitromethane, are temperature sensitive. This is something you also want to know if you are going to use these liquids for regenerative cooling.

In the case of nitromethane, the 50 per cent point is about twenty cards (which are ten thousandths of an inch thick), at 20 degrees Centigrade, and it goes up to about fifty cards at about 80 degrees Centigrade. So you can see it is rather important to measure temperature.

THE CHAIRMAN: Any further discussion?

DR. GANTZ: I would like to ask Dr. Haller about the cell you used for vapor detection of hydrazine. That is set up somewhere in the laboratory?

DR. HALLER: Oh, yes. It is preferable, of course, if you want to measure the concentration in the air, to have a fan or something circulating the air near it. If you have circulating air and have a particularly sensitive instrument you can take the stopper out of the bottle in the opposite corner and it will detect it over in the other side of the room.

I would like to point out in connection with Mr. Troyan's paper that one very rapidly becomes accustomed to the odor of hydrazine. We have noticed this very frequently, and the odor of hydrazine ought not to be relied on as a protection. Also, hydrazine is quite a good solvent for solidified paint. Unless there is adequate dissipation of heat, hydrazine oozes out through a pipe joint or something like that. Since there is a painted surface on the pipe under the insulation this sort of thing can raise the temperatures to the point where you can get ignition.

MR. JOHN ROBELL (Guggenheim Bros.): Mr. Troyan, you mentioned a number, of what seem to be, suitable materials of construction for hydrazine. Have you considered substituting aluminum for stainless steel in your plants?

MR. TROYAN: We have considered it, but we feel that our several years experience with stainless steel was one definite thing. We wanted to try out aluminum on a smaller scale initially before we thought about putting it in to any large extent.

MR. V. R. BONNETTE: At the Naval Proving Ground we did some work on liquid propellants, i.e., hydrazine-hydrazine nitrate-water for 40 mm. gun application. The decomposition of this propellant was apparently pressure sensitive. Using a standard 40 mm. primer containing 60 grains of black powder, we were unable to initiate ignition when the case was 50 per cent full, whereas ignition could be initiated if the volume of the case was reduced with paraffin and beeswax so that the case was 90 per cent full.

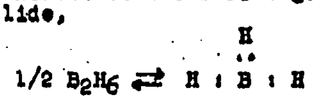
THE REACTIONS OF HYDRAZINE AND SYMMETRICAL DIMETHYL HYDRAZINE WITH DIBORANE AND WITH TRIMETHYLBORON

by

H. I. Schlesinger and Martin J. Steindler
The University of Chicago
Presented by Martin J. Steindler

Our project at the University of Chicago has as its objectives the study of the chemical properties of various types of hydrides, particularly the hydrides of boron and related compounds. The study of the behavior of hydrazine toward diborane is a part of our program but, as is true of much of our work, it was not undertaken with any specific application in mind.

To indicate why we undertook this study, attention is called to the fact that diborane, B_2H_6, behaves in many of its reactions as if it consists of two borine groups, BH_3. As is shown in the first slide,



$$1/2\ B_2H_6 \rightleftarrows H : \overset{\overset{H}{\cdot\cdot}}{B} : H$$

these groups lack an electron pair and consequently behave as Lewis acids. As a result of this property diborane reacts with ammonia derivatives to form acid-base adducts such as trimethylamineborine, $(CH_3)_3N{:}BH_3$.

$$1/2\ B_2H_6 + (CH_3)_3N \longrightarrow (CH_3)_3N{:}BH_3$$

$$1/2\ B_2H_6 + (CH_3)_2HN \longrightarrow (CH_3)_2HN{:}BH_3$$

$$1/2\ B_2H_6 + (CH_3)H_2N \longrightarrow (CH_3)H_2N{:}BH_3$$

This compound is so stable that it may be heated to 400°C without much decomposition. If one or more of the methyl groups is replaced by hydrogen atoms, the adducts lose hydrogen fairly readily. This loss frequently occurs in two steps. The first of these leads to the formation of aminoborines as shown in the slide.

$$\underset{\text{"amine borine"}}{(CH_3)_2HN{:}BH_3} \longrightarrow \underset{\text{"aminoborine"}}{\left[(CH_3)_2NBH_2\right]_x} \longrightarrow \underset{\text{"borazole"}}{\left[(CH_3)NBH\right]_y}$$

$$(CH_3)H_2N{:}BH_3 \longrightarrow \left[(CH_3)HNBH_2\right]_x \longrightarrow \left[(CH_3)NBH\right]_y$$

Attention is called to the fact that the original adducts are named amine borines, whereas the products resulting from the initial loss of hydrogen are known as aminoborines. At higher temperatures a second mole of hydrogen or a mole of methane may be lost. The aminoborines may be obtained as monomers or as dimers but the products resulting from further pyrolysis almost always trimerize to form derivatives of borazole.

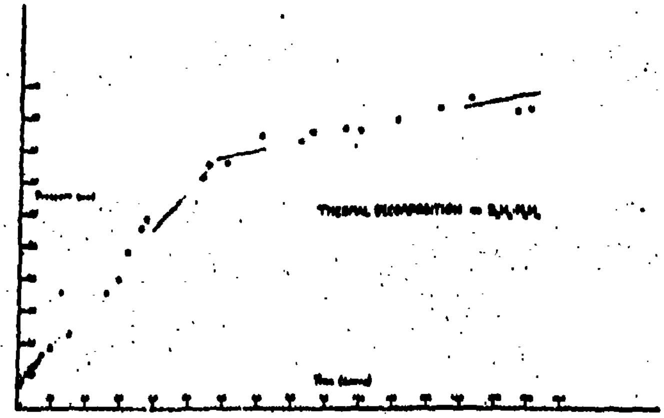
Borazole

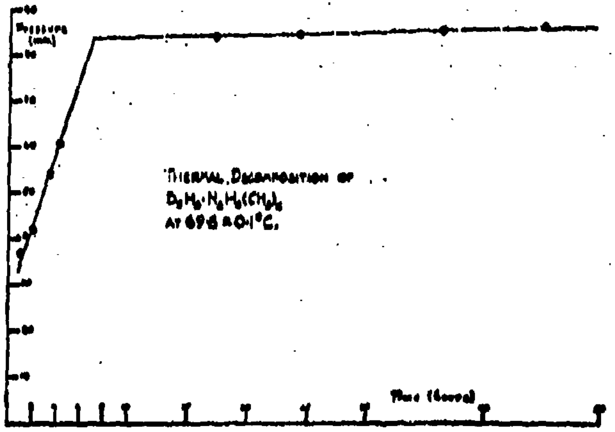
The work to be reported today was undertaken to ascertain what would be the character of the products of reaction of diborane with substances containing more than one nitrogen atom per molecule, and what would be the nature of the pyrolysis products. Compounds under consideration for this study include polyamines as well as hydrazine and its derivatives. This paper will deal only with the latter compounds.

We have thus far studied the behavior of hydrazine and symmetrical dimethylhydrazine toward diborane. Both hydrazines form 1:1 adducts which are white, crystalline solids of slight or no volatility. When hydrolyzed, they yield hydrogen and boric acid and, what is more important, regenerate the original hydrazine from which they were obtained. In other words the nitrogen-nitrogen bond is not broken in the formation of the adducts. For this reason and by analogy to the corresponding amino derivatives it seems appropriate to assign to the hydrazine adducts the formulae shown in the next slide.

$H_3B{:}NH_2NH_2{:}BH_3$	$H_3B{:}NH(CH_3)NH(CH_3){:}BH_3$
"hydrazine bis borine"	"sym-dimethylhydrazine bis borine"

Both compounds lose hydrogen when heated. The following slides show that a marked decrease in the rate of hydrogen evolution occurs when one mole of hydrogen per gram atomic weight of nitrogen has been lost.


Pressure (mm)
THERMAL DECOMPOSITION OF
Time (hours)


Pressure (mm)
THERMAL DECOMPOSITION OF
$D_2H_6 \cdot N_2H_2(CH_3)_2$
AT 69.6 ± 0.1°C.
Time (hours)

This behavior is entirely analogous to that of the amine borines.

The pyrolysis product of the simple hydrazine adduct is a non-volatile solid whose homogeneity has not yet been established. It has, for this reason, not been further studied except to show that when it is heated to 400°C an additional mole of hydrogen per mole of adduct is lost and that the solid so obtained still yields hydrazine when treated with water.

Pyrolysis of the dimethylhydrazine adduct, on the other hand, produces a liquid which has been purified by fractionation and has a vapor density corresponding to a molecular weight of 82. This molecular weight is consistent with the assumption that the liquid is dimethylhydrazino-(bis)-borine.

$$N_2H_4 \cdot B_2H_6 \xrightarrow{130^\circ C} \underset{\text{solid}}{\left[H_2BNHNHBH_2\right]_x} + 2\ H_2$$

$$N_2H_2(CH_3)_2 \cdot B_2H_6 \xrightarrow{69^\circ C} \underset{\text{liquid}}{H_2BN(CH_3)N(CH_3)BH_2} + 2\ H_2$$

Further evidence for this assumption is found in the stoichiometry of the reaction and in the fact that the nitrogen-nitrogen bond in the analogous compound obtained from the unsubstituted hydrazine is not broken even at 400°C. The first compound shown is indicated as a polymer in view of its lack of volatility; the latter probably undergoes polymerization when heated at about 60°C for prolonged periods since a solid is slowly formed without the generation of either hydrogen, nitrogen or methane.

The formation of the original adducts was carried out at -80°C in diethyl ether solution with strictly anhydrous materials and in the absence of air and moisture. Both compounds are white solids, stable at room temperature and not very reactive toward air. The hydrazine adduct is obtained as a fluffy powder, the dimethylhydrazine adduct as well defined crystals. Both are soluble in diethyl ether and were purified by crystallization from this solvent. The simple hydrazine adduct is also soluble in hydrazine but not in benzene.

The unsubstituted hydrazine adduct, though not spontaneously inflammable in air, burns vigorously when ignited. It reacts moderately slowly with water and much more rapidly with dilute acids. The next slide shows that trimethylamine displaces hydrazine from its adduct and indicates its reaction with methyl alcohol and water.

$$N_2H_4 \cdot B_2H_6 + 2\ (CH_3)_3N \longrightarrow N_2H_4 + 2\ (CH_3)_3N{:}BH_3$$

$$N_2H_4 \cdot B_2H_6 + 6\ CH_3OH \longrightarrow N_2H_4 + 6\ H_2 + 2 \cdot (CH_3O)_3B$$

$$N_2H_4 \cdot B_2H_6 + 6\ H_2O \longrightarrow N_2H_4 + 6\ H_2 + 2\ B(OH)_3$$

The latter reaction was used in the analysis. Those results are shown in the following slide.

ANALYSIS OF $N_2H_4 \cdot B_2H_6$

Sample weight 0.0780 g

Calculated for $N_2H_4 \cdot B_2H_6$

B 36.15%, N_2H_4 53.59%, H 10.12%

Found

B 36.28%, N_2H_4 53.59%, H 10.12%

The properties of the dimethylhydrazine adduct are, so far as determined, much like those of the unsubstituted hydrazine adduct. The chief exception, as has already been pointed out, is the formation of a volatile liquid pyrolysis product rather than a non-volatile solid. We have not yet completed the quantitative analysis of the adduct because we have not yet found a satisfactory quantitative method for the determination of dimethylhydrazine in its hydrolysate. We have, however, demonstrated that treatment of the solid with HCl in methanol produces the dihydrochloride of symmetrical dimethylhydrazine. Further, the atomic ratio of hydrogen to boron in the compound is 3:1 as demanded by the proposed formula. The following properties have been established for the liquid pyrolysis product of the dimethylhydrazine adduct.

Properties of $N_2(CH_3)_2(BH_2)_2$

m.p. -0.4°C b.p. (extrap.) 138.8°C

vapor tensions $\log_{10}P_{mm} = 7.8005 - 2027/T$

molecular weight at 38.4°C = 82

In addition to the study of the reaction of hydrazine and diborane, we have begun an investigation of the reaction of hydrazine and trimethyl boron. We have found that two moles of trimethyl boron react with one of hydrazine at -80°C. This adduct appears to undergo reversible dissociation above

$-30^{\circ}C$. Pyrolysis at temperatures above $200^{\circ}C$ in the presence of excess trimethylboron produces methane, but we have not yet ascertained whether this reaction can be carried out under conditions such that the hydrazine is not simultaneously decomposed. We plan to study other reactions of the types which have been mentioned and to extend our search for polymeric boron-nitrogen-hydrogen containing compounds.

MORNING SESSION (Continued)
3 February 1953

CHAIRMAN, MR. A. J. NERAD
GENERAL ELECTRIC COMPANY

THE CHAIRMAN: We are now turning to the fifth part of the program, that of applications. Before we get going, I would like to ask how many here are unacquainted with some of the terms that are used, such as specific impulse or C*? How many would like an explanation? Raise your hands. (Several hands were raised.)

We have the expert here. Let's take a few minutes off and would you, Ed, just go through this?

DR. E. H. SEYMOUR (Office of Naval Research): I think I can explain it briefly.

Rockets, as you know, are rated by thrust or the amount of push developed. If you assume the optimum expansion ratio, which is expansion to ambient pressure, you can eliminate pressure effects and figure thrust on the basis of momentum change by multiplying total propellant flow by the exhaust velocity of the gases leaving the motor. This would be a true velocity then.

The impulse is what we obtain if we multiply a force by the time in which it acts and, therefore, on a rocket total impulse means the time over which the thrust is exerted. If we divide total impulse by the weight of the propellants consumed during that period we come out with impulse per pound of propellant. This is the so-called specific impulse which appears in the units of pounds/second/pound or is sometimes referred to as seconds.

Well, you can do this by dividing the total impulse by the total weight consumed, or divide the thrust by the rate of flow of the propellant. If you compute the specific impulse theoretically on the basis of the perfect gas laws and the conservation of energy and momentum, you come up with an expression of which the significant part is the square root of a term containing an expansion factor and the ratio of the combustion chamber temperature to the average molecular weight of the exhaust product. That is the significant part of the expression. It tells you what you want in a system like this is as high a combustion chamber temperature as your propellant will provide and your materials will stand and as low an average molecular weight of your exhaust product as you can get in the exhaust gases.

THE USE OF HYDRAZINE DERIVATIVES AS FLASH AND SMOKE DEPRESSANTS IN PROPELLANTS

by

Daniel B. Murphy and Jean P. Picard
Picatinny Arsenal, Dover, N. J.
Presented by Daniel B. Murphy

ABSTRACT

Despite careful camouflage, the position of a gun is immediately revealed by the smoke and flash produced when the gun is fired. As a result, the problem of elimination of smoke and flash from the burning of a propellant has attracted the interest of explosives chemists for many years. It has long been realized, from theoretical calculations, that this problem could be solved by incorporating into the propellant, substances capable of producing a large amount of gas at low temperature when burned. Compounds having in the molecule a large amount of nitrogen which would be released as such upon decomposition, would be expected to perform this function. Such additives by lowering the burning temperature of the propellant should also prolong the life of the gun.

This paper will discuss the basic requirements of such compounds and the work done by Picatinny Arsenal and associated contractors on the preparation and evaluation of hydrazine derivatives as high-nitrogen propellant additives. Although several of these compounds have been found to possess the desired characteristics, their use on a practical scale depends ultimately upon the availability of hydrazine.

* * *

Despite careful camouflage the position of a gun is immediately revealed by the smoke and flash produced when it is fired. For this reason, it has been the desire of explosives chemists for a good many years to find a means of eliminating or reducing these secondary effects. The first step in this direction was the replacement of black powder with so-called "smokeless" or nitrocellulose propellant. It was soon realized that this had merely resulted in the substitution of white for black smoke and that there had been no decrease in the amount of flash. Attempts to reduce the flash by adding certain salts, such as potassium chloride, potassium sulfate and potassium hydrogen tartrate were at least partially successful, but these had the serious disadvantage of producing large quantities of smoke.

By empirical methods, incorporation of nitroguanidine in a propellant had also been found to materially reduce smoke and flash, but its use is accompanied by deleterious changes in the physical and chemical properties of the propellant during storage, since a large proportion of this additive must be used to give the desired results. Nevertheless, this compound was employed in standard British compositions during the last war.

In the United States, until 1931, compounds such as dibutylphthalate and methylhexalin were used as flash reducing agents, but these had the tendency to increase the smoke of the burning propellant.

In a memorandum dated October 23, 193[illegible] to the Commanding Officer of Picatinny Arsenal, Dr. George C. Hale, Chief of the Chemical Department, first suggested the use of compounds such as melamine, guanidine carbonate and guanidine nitrate, on the theory that these substances because of their high nitrogen content and relatively low percentage of carbon, would serve to reduce flash without increasing the quantity of smoke.

The flash from a gun can be considered as resulting from the rapid oxidation of hot combustible muzzle gases upon reaching the atmosphere. Smoke, on the other hand, is caused by the presence in the muzzle gases of solid particles, which may be, for example, inorganic salts, inert material or products of partial combustion. It follows that, in order to disperse the smoke, dissipate the heat, and reduce the likelihood of ignition of the combustible muzzle gases, the substance to be added to the propellant should, upon burning, yield a large volume of gaseous products at low temperature.

The relative force (F) of a propellant is a measure of its ballistic potential and is defined by the equation $F = nRT$ where n is the number of moles of gas produced per gram of propellant burned, R is the usual gas constant, equal to 1.987 calories, and T is the adiabatic flame temperature. It can be seen from this equation that addition of a substance which lowers the flame temperature will be accompanied by a decrease in the propellant's ballistic potential, unless the value of n is correspondingly increased. Obviously, then, for optimum effect, a flash reducing agent should produce, on burning, the largest number of moles of low molecular weight gas possible per gram of propellant consumed. An advantage of a low flame temperature will be an increase in the life of the gun barrel.

From the above considerations, a compound containing in the molecule large numbers of nitrogen atoms which would be released as such upon decomposition, should be expected to have the desired characteristics of a flash reducing agent. These compounds should also serve to reduce smoke formation since they contain a relatively small percentage of carbon, and at the same time, the large volume of gas which they produce will greatly dilute, and aid in dissipating any smoke formed by the other ingredients of the propellant.

As early as 1938, several nitramines and nitrosamines had been investigated at Picatinny Arsenal as possible flash-reducing agents, but all were found unsatisfactory because of poor stability or low nitrogen content. The first experimental high-nitrogen compound to undergo firing tests at Picatinny Arsenal was dicyandiamide. The method used as a preliminary test consisted of replacing a part of the standard charge of .50 Caliber IMR Propellant with the test material. The round was assembled, shaken to mix the propellant and test material uniformly and fired. Addition of 15% dicyandiamide to the propellant resulted in reducing the intensity of the flash to about 2/3 that of a standard charge. Increasing the proportion of additive to 20% reduced the flash to a trace.

Although the desired effect upon the flash was achieved, this additive had a serious drawback in that the relative force (F) was reduced in proportion to the amount of dicyandiamide added. In other words, the dicyandiamide was acting essentially as an inert material. At any rate, the common characteristic of high nitrogen content in nitroguanidine (53.8%) and dicyandiamide (66.7%) lent support to the belief that addition of compounds with this characteristic to propellants would result in a reduction of flash. This suggested that the investigation be extended to other similar substances.

About 1943, Captain L. F. Audrieth, as officer in charge of the Research Division, was instrumental in directing attention to the possible usefulness of hydrazine derivatives for this purpose. Under a contract with Picatinny Arsenal, certain selected compounds were prepared at the Polytechnic Institute of Brooklyn under the direction of Professor G. B. L. Smith. In addition to those prepared by Professor Smith two other compounds, cyanuric hydrazide and guanidine perchlorate were prepared at Picatinny Arsenal. The explosive and stability characteristics of these compounds were determined in addition to their physical properties.

Table I shows that within a given homologous series, progressive substitution of hydrazine groups for amine and imine radicals in guanidine results in an increase in brisance and sensitivity to impact. The stability of these carbonic acid derivatives does not appear to be affected by the presence of hydrazine radicals, but it does increase qualitatively with increased melting point (Table II).

F. R. Benson in a technical report dated 1944, suggested that the observed increase in impact sensitivity with increasing introduction of hydrazine groups may be due to the presence of a nitrogen to nitrogen bond in each such group. A similar situation involving the nitramine rather than the hydrazine radical is found in the case of guanidine nitrate and nitroguanidine. Here again, formation of an N-N covalent bond increases the sensitivity to impact.

In order for any one of these compounds to be considered as a possible flash reducing agent, it must not only have a high nitrogen content, but must also satisfy the requirements for propellant ingredients. These latter requirements are that the compound must be stable at 100°C, not render nitrocellulose unstable when mixed with it, be non-hygroscopic and not appreciably water-soluble and have an acceptable impact sensitivity.

A large number of these carbonic acid derivatives were eliminated from consideration because of their solubility in water, low nitrogen content or both. For example, di- and triaminoguanidine nitrates are both too soluble in water. Their picrates, on the other hand, although sufficiently insoluble, were considered to contain too little nitrogen. It should be pointed out, however, that many of these compounds, although not suitable as flash reducing agents have shown interesting potentialities as high explosives. For example, triamino guanidine nitrate is close to RDX in power. It might also be worthwhile to reexamine certain of these compounds in the light of present experience since their water solubility may no longer be a criterion for their acceptability.

Of the remaining compounds, two, cyanuric hydrazide and 5-aminotetrazole were considered of greatest interest because of their high nitrogen content, (73.6% and 82.3% respectively), stability and relative insensitivity to impact. When these substances were tested as flash reducing agents it was found necessary to use them in about the same proportions as dicyandiamide, that is, approximately 20% of the weight of the propellant, in order to reduce the flash to a trace. Unlike dicyandiamide, however, cyanuric hydrazide and 5-aminotetrazole did not act as

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TABLE I

RELATION BETWEEN NUMBER OF HYDRAZINE GROUPS AND EXPLOSIVE PROPERTIES

	Number of hydrazine groups	Impact 2 Kg, cm	Millimolar Brisance g. sand crushed per millimole
Guanidine nitrate	None	100+	None
Diamino Guanidine nitrate	2	40	10.5
Triamino Guanidine nitrate	3	28	14.5
Amino Guanidine picrate	1	100+	4.8
Diamino Guanidine picrate	2	30	30.5
Triamino Guanidine picrate	3	80	35.6
Guanidine perchlorate	None	40	20.6
Triamino Guanidine perchlorate	3	7	26.2

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TABLE II

RELATION BETWEEN STABILITY AND M.P.

	Loss in weight after 90 hours at 80°C, and 90 hours at 100°C*	Vacuum Stability Tests 100°C cc gas	Vacuum Stability Tests 100°C hours	Vacuum Stability Tests 120°C cc gas	Vacuum Stability Tests 120°C hours	Melting Point °C
Guanidine nitrate	-	-	-	0.23	40	212
Diaminoguanidine nitrate	Nil	0.77	40	1.92	40	142-144
Triaminoguanidine nitrate	0.31	-	-	1.06	40	216-217
Aminoguanidine picrate	Nil	0.20	40	0.37	40	183-184
Diaminoguanidine picrate	0.19	0.02	40	0.43	40	188-190
Triaminoguanidine picrate	0.70	0.43	40	1.45	40	170-172
Guanidine perchlorate	-	0.36	40	1.16	40	240
Triaminoguanidine perchlorate	3.53	0.66**	40	11+**	23	128

* determined at the Polytechnic Institute of Brooklyn

** 1.00 gm sample used

TABLE III

PHYSICAL CHARACTERISTICS OF HYDRAZINE DERIVATIVES

	% N	Impact 2 Kg. cm	Solubility g/100g H_2O 25.46°C	100°C Heat Test, % Loss 1st 48 hrs	2d 48 hrs	Expl in 100 hrs	100°C Vac Stab cc gas/ 40 hours	120°C Vac Stab cc gas/ 40 hours
Guanidine nitrate	45.9	100 +	-	-	-	-	-	-
Diamino guan. nitrate	55.2	40	v.s.	0.15	0.02	None	0.77	1.92
Triamino guan. nitrate	58.7	28	4.37	0.36	0.15	None	-	1.06
Amino guan. picrate	32.4	100 +	0.36	0.15	0.05	None	0.20	0.37
Diamino guan. picrate	35.4	80	0.29	0.02	0.00	None	0.02	0.48
Triamino guan. picrate	37.8	80	0.54	0.38	0.01	None	0.43	1.45
Guanidine perchlorate	26.3	40	v.s.	0.07	0.00	None	0.36	1.16
Triamino guan. perchlorate	41.0	7	v.s.	0.20	0.20	None	0.68	11+(23 hrs)
Nitroguanidine	53.8	47	-	-	-	-	-	-
Nitroamino guanidine	58.7	34	1.16	0.23	0.10	None	0.85	11+
Formaldehyde nitroguanyl hydrazone	53.9	34	0.26	0.93	0.44	None	-	11+(1 hr)
Acetaldehyde nitroguanyl hydrazone	48.6	33	0.64	0.33	0.19	None	5.69	11+(24 hrs)
Azodicarbamidine dinitrate	57.8	18	3.36	0.18	0.11	-	4.57	10.77
Guanyl azide nitrate	56.8	20	v.s.	4.19	18.51	None	-	-
Cyanuric hydrazide	73.6	100+	-	0.26	0.13	None	-	0.98
Diguanazole oxalate	48.6	95	-	0.38	0.04	None	0.40	0.55
5-Amino tetrazole	82.3	80	2.16	0.27	0.02	None	-	0.09

inert materials, and propellants made with these materials had a relative force of 93.1 - 99.4% that of the Standard IMR Propellant. 5-aminotetrazole possesses the further advantage of increasing the ballistic potential of a propellant containing it. This arises from its large positive heat of formation (40 k. cal/mole) which results in more energy being released upon combustion than from nitroguanidine (picrite), which has a negative heat of formation of 19 k. cal/mole.

5-aminotetrazole is somewhat hygroscopic and it was soon realized that despite their obvious advantages, 5-aminotetrazole propellants were too sensitive to humidity changes for satisfactory performance. An investigation was then carried out to determine whether or not these propellants could be improved by either the application of coating agents or by the reaction of aminotetrazole with formaldehyde to give a non-hygroscopic condensate which could be used in its place. Unfortunately, neither approach was successful.

Interest in tetrazole derivatives had continued at Picatinny Arsenal in the hope of preparing a compound having the desirable characteristics inherent in the tetrazole ring without the disadvantage resulting from the latter's hygroscopicity. Two such derivatives have been prepared which appear promising in this regard. The first of these, guanylaminotetrazole, appears satisfactory in all respects. Its preparation is difficult, however, and the yields are poor. The other, nitroguanylaminotetrazole, can be prepared only in extremely small yield at this time and so has not been considered further.

Cyanuric hydrazide, previously mentioned as being comparable to 5-aminotetrazole as a flash reducing agent, does not have the disadvantage of hygroscopicity. It is not, however, available in commercial quantities at the present time. It may be easily prepared by the reaction between cyanuric chloride and hydrazine hydrate, and, should hydrazine become more readily available in the future, it is quite possible that this compound will find application as a propellant ingredient.

Melamine, which is a cyclic trimer of cyanamide has been considered as a propellant additive. Preliminary trials indicated that it met the requirements of a flash reducing agent, but the incorporation of melamine in propellants was found to decrease their rate of burning when compared with nitroguanidine propellants. This results, in many cases, in incomplete combustion and the formation of large amounts of smoke.

Up to this point, the work carried out under the sponsorship of Picatinny Arsenal, in addition to yielding several new compounds of interest had confirmed the original concept of the function of a flash-reducing agent and the value of high-nitrogen content compounds for this purpose. Of these, the derivatives of hydrazine which include the tetrazoles are of the greatest interest.

In 1949, the first of several contracts having for their purpose the study of compounds of high nitrogen content as potential flash-reducing agents, was entered into between Picatinny Arsenal and Professor Audrieth of the University of Illinois. Under these contracts, a large number of hydrazine derivatives have been prepared, several of which, for example, carbohydrazide-N-carboxyamide, carbohydrazide-N,N'-dicarboxyamide and ureido tetrazole, offer considerable promise. Other compounds prepared at the University of Illinois, such as hydrazine derivatives of thiocarbonic acid are not being further evaluated. A ready source of hydrazine should improve the availability of high-nitrogen flash and smoke reducing agents. For this reason, in July 1952, at the request of Picatinny Arsenal, and under the sponsorship of the Office of Ordnance Research, ar investigation of possible new routes for the synthesis of hydrazine has been initiated at the University of Illinois under the supervision of Professor Audrieth, but it is yet too early to report at this time.

PRELIMINARY STUDIES OF HYDRAZINE - HYDRAZINE NITRATE MIXTURES FOR PROPELLANT USE

by

Saul Wolf
U. S. Naval Underwater Ordnance Station

Abstract

The possible application to torpedo propellant use of hydrazine-hydrazine nitrate-water systems is discussed. Theoretical performance data are given together with the results of the preliminary evaluation of shock sensitivity, thermal stability, density, viscosity, and freezing point of each system. The proposed program for the experimental evaluation of the performance of the most promising of these systems is outlined.

* * *

The primary objective of the work at USNUOS on propellants is the attainment of greater torpedo speed, range, or payload by providing with the least weight and in the smallest volume an energy source which will provide the maximum amount of available energy for extraction by the power plant. The more nearly this objective is realized, the greater becomes the probability of obtaining a truly high speed, long range torpedo.

High propellant efficiency, while always desirable, can be sacrificed to some extent for the increased reliability and lowered cost of a more simple valving and tankage system. This sacrifice can quite readily be made, for example, in small ASW type torpedoes or for mine use. It was with such possible applications in mind that the Newport monopropellant study was begun.

The selection of a propellant system is based not only upon its thermodynamic performance but also upon the wake it can be expected to produce. To properly safeguard the submarine's greatest offensive advantage - stealth - the torpedoes it launches should be essentially wakeless. The presence of wake from aircraft or surface craft launched torpedoes is much less critical. For certain special applications, such as exercise firing, wake is not merely permissible, but is a major requirement.

The ideal monopropellant for torpedo heat engine use should decompose smoothly and rapidly into products of high temperature and low molecular weight. Cooling of these products to the 1800°F maximum permissible working medium temperature for torpedo turbine use would be accomplished by dilution with pumped sea water. For internal combustion engine use (with practically no flame temperature limitation) dilution would probably be unnecessary.

Thermodynamic analyses were carried out for various monopropellants. The results of these analyses together with the results of similar analyses of other types of propellant systems are shown in Figure 1. Also shown in Figure 1 is the mole of non-soluble gases per hp-hr calculated for each system. This value is an indication of the relative wake to be expected from each system in similar torpedoes of equal horsepower. The results of those thermodynamic analyses indicate that, even for larger torpedo turbine power plants, the use of monopropellants should be considered. The small available energy difference between H_2O_2 - Diesel Fuel - carried diluent and certain of the monopropellants would be more than counterbalanced by the increased reliability resulting from the reduced tankage and valving requirements of a monopropellant.

These results also indicated that a thermodynamic analysis of hydrazine-hydrazine nitrate mixtures for monopropellant reciprocating engine application was warranted. Figure 2 is indicative of the results of this analysis.

It is rather difficult to compare the theoretical performance of a hydrazine-hydrazine nitrate solution in a given reciprocating engine to the experimental performance of a more familiar propellant system. Should, however, both systems have identical reaction efficiencies, a 10-90 mixture containing 20% water would give a propellants consumption rate per horsepower hour approximately equal to that of the present reciprocating engine propellant system (85% H_2O_2-Diesel Fuel). The theoretical analyses indicated clearly that hydrazine-hydrazine nitrate solutions merited further study for torpedo power plant application. Since the literature survey made in connection with the USNUOS monopropellant program revealed no data on hydrazine-hydrazine nitrate solutions of more than 50% hydrazine nitrate, a preliminary experimental evaluation of the more concentrated solutions was initiated.

Preliminary evaluation tests were made of various hydrazine-hydrazine nitrate mixtures. anhydrous solutions containing 50 to 95% by weight $N_2H_5NO_3$ and water solutions of the 10% N_2H_4 - 90% $N_2H_5NO_3$ mixture.

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Theoretical Performance
of
Stoichiometric Hydrazine-Hydrazine Nitrate-Water Solutions
in an
Internal Combustion Engine

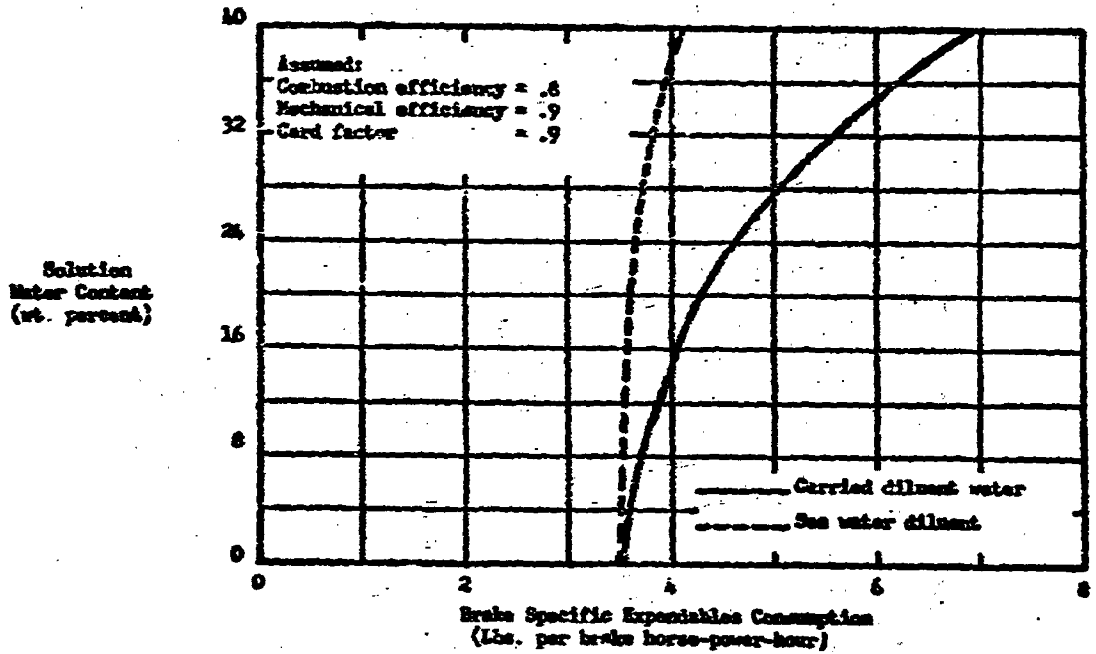

FIGURE 2

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These tests, made for USNUOS by the Buffalo Electrochemical Company, are outlined as follows:

a. Impact sensitivity at room temperature and at temperatures up to 212°F.

b. Thermal sensitivity tests at ambient pressure up to mixture boiling point and bomb tests up to explosion of the mixtures.

c. Detonation propagation tests.

d. Determination of freezing point and room temperature densities and viscosities.

Mixtures of hydrazine and hydrazine nitrate were prepared by reacting ammonium nitrate with anhydrous (95%) hydrazine. Solutions prepared were 5-95[*], 10-90, 20-80, 30-70, 40-60, 50-50 weight percent hydrazine-hydrazine nitrate mixtures plus the 10-90 mixture with 47.7, 37, 30, and 20% water by weight.

The mixtures were tested for impact sensitivity in a modified Bureau of Mines liquid explosive impact tester, using a 100 kg-cm impact for all tests. A heated anvil was used for tests above room temperature. The criterion for a non-impact sensitive mixture was established as no detonation in ten tests.

Ambient pressure thermal stability tests were made in a 50 cc glass beaker with provision made for variable heating rate. Temperature of the sample was recorded continuously. The thermal stability bomb tests were made in a constant volume bomb containing five or more drops of test solution and provided with a heat source. Temperature of the vapor over the liquid was recorded continuously. No attempt was made to measure the pressure attained.

Detonation propagation tests were made in stainless steel tubes (3/8" diameter, 3 feet long) filled with the test solution, and fitted with No. 4 electric blasting caps or MD-24 cannon primers. The tests were first made with cannon primers. If no propagation occurred, the larger No. 4 caps were tried. To provide a basis for comparison, tests with each detonator were made using water as the test solution.

The viscosity of all the mixtures was determined at room temperature (70°F) with a 100 Ostwald viscometer. Hydrometers accurate to 1% were used for the determination of density at 75°F. Freezing point tests were made in a bath-cooled test tube containing 20 cc samples and fitted with thermometer and stirrer. Points

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[*] 5-95 denotes 5% hydrazine, 95% hydrazine nitrate by weight

of first crystallization and of complete solidification were obtained with an accuracy of 1%. There appeared to be no tendency to supercool.

The results of the 100 kg-cm impact tests are summarized in Figure 3. These tests show that the sensitivity of the mixtures increased with hydrazine nitrate content and also with storage time during the first week or two. Removal of NH_3 gas from a fresh 50-50 mixture by evacuation did not change the impact sensitivity limit. The increased sensitivity on storage may be due either to chemical reaction or to precipitation of small quantities of hydrazine nitrate crystals. The crystals are believed to be rather impact sensitive.

All of the mixtures tested behaved similarly in the open beaker thermal stability tests, the results of which are shown in Figure 4. Vigorous decomposition of the mixtures without water occurred between 440 and 490°F. The 10-90 mixture in water decomposed vigorously between 475 and 570°F. The slightly lower reaction temperatures of the 10 and 20% hydrazine content samples may be due to experimental error. A substantial density increase was noted in a 30-70 mixture after heating to 300°F and then cooling to room temperature. This solution became almost crystalline on cooling. This indicates that in all these tests the more volatile hydrazine and water had boiled off, leaving the nitrate behind to react. These boiling tests indicate that the mixtures tested can be heated safely to at least 400°F in open containers with no reaction other than evaporation.

The closed bomb thermal stability tests gave temperature - time curves which indicated reaction at temperatures lower than those in the open beaker tests. A typical temperature-time curve is shown in Figure 5. The results of these tests are summarized in Figure 6.

Mixtures containing less than 63% hydrazine nitrate showed no sudden temperature rise, but had regions of constant temperature. Those mixtures containing more than 30% water gave no definite reaction. The tests indicate that 250°F is the upper safe temperature limit for hydrazine-hydrazine nitrate mixtures in confined containers having an air space. It is possible that hydrazine-hydrazine nitrate-water mixtures containing more than 30% water can be kept confined at much higher temperatures, since the water vapor formed would act as an inert diluent of the combustible vapor in the closed system.

The detonation propagation tests were made immediately after preparation of the test solutions and at one week intervals thereafter. A summary of the results is shown in Figure 7. Where

EXPERIMENTAL RESULTS-IMPACT SENSITIVITY OF HYDRAZINE-HYDRAZINE NITRATE MIXTURES

EFFECT OF STORAGE (IMPACT = 100 kg-cm)

% N_2H_4	% $N_2H_5NO_3$	IMPACT SENSITIVITY TEMP LIMIT-FRESH SOLN	TEMP LIMIT AFTER 1 WEEK'S STORAGE
5	95	140°F	R. T.
10	90	176°F	R. T.
20	80	176°F	R. T.
30	70	185°F	R. T.
40	60	185°F	86°F
50	50	194°F	140°F
10	90 + 48% H_2O	Solutions 3 weeks old non-impact sensitive up to 212°F	
10	90 + 37% H_2O		
10	90 + 30% H_2O		
10	90 + 20% H_2O		

FIGURE 3

EXPERIMENTAL RESULTS - OPEN BEAKER THERMAL STABILITY OF

HYDRAZINE-HYDRAZINE NITRATE MIXTURES

% N_2H_4	% $N_2H_5NO_3$	% H_2O	Temp. at which Vigorous Decomposition Starts	Final Reaction Temp.	Heating Rate °F/Min	Final Reaction
50	50	—	460°F	610°F	14	Evaporated to Dryness
40	60	—	490°F	600°F	14	Smooth Combustion
30	70	—	470°F	590°F	14	Explosion
20	80	—	475°F	615°F	20	"
10	90	—	470°F	560°F	14	Smooth Combustion
10	90	—	450°F	540°F	12	" "
10	90	—	440°F	540°F	16	" "
5	95	—	460°F	540°F	30	" "
5	95	—	475°F	560°F	17	" "
5.2	46.8	48.0	540°F	630°F	9	Evaporated to Dryness
5.2	46.8	48.0	475°F	625°F	8	" "
6.3	56.7	37	530°F	620°F	14	Explosion
6.3	56.7	37	560°F	620°F	7	"
7.0	63.0	30	560°F	610°F	11	"
7.0	63.0	30	570°F	620°F	14	"
8.0	72.0	20	550°F	610°F	11	"
8.0	72.0	20	550°F	620°F	18	"

FIGURE 4

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Vapor Temperature - Time Plot
5 wt % Hydrazine -95 wt % Hydrazine Nitrate
Solution Heated in a Constant Volume Bomb

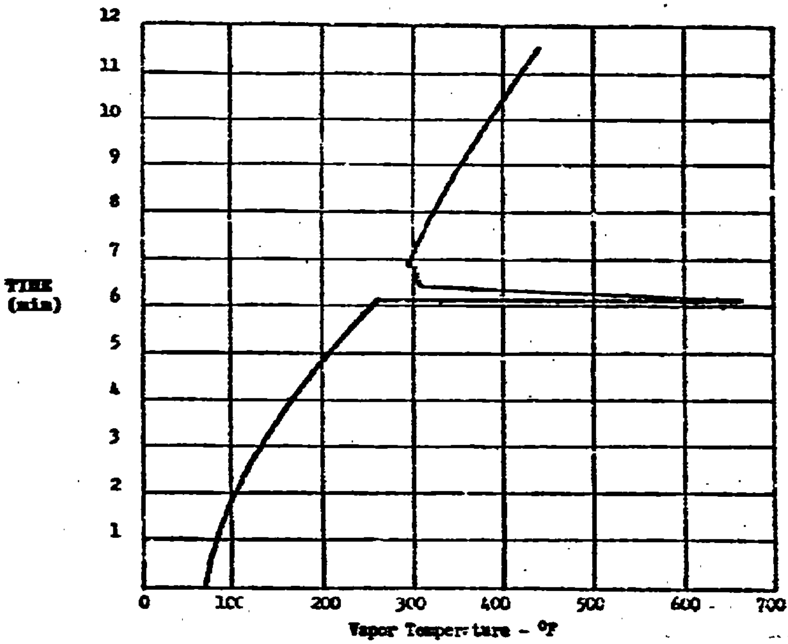

FIGURE 5

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EXPERIMENTAL RESULTS - CLOSED BOMB THERMAL STABILITY TESTS OF HYDRAZINE-HYDRAZINE NITRATE MIXTURES

MIXTURES, WT %			TEMPERATURE - AT WHICH TIME-TEMP. CURVE CHANGE	EFFECT
N_2H_4	$N_2H_5NO_3$	H_2O		
5	95	—	205°F	Sudden temperature rise
10	90	—	210°F	Sudden temperature rise
20	80	—	240°F	Sudden temperature rise
30	70	—	250°F	Sudden temperature rise
40	60	—	245 & 310°F	Temperature remains constant
50	50	—	230 & 335°F	Temperature remains constant
5.2	46.8	48	—	Time-temperature plot nearly a straight line
6.3	56.7	37	—	" " " " " "
7.0	63.0	30	250-290°F	Sudden sharp temperature rise
8.0	72.0	20	" "	" " " "

FIGURE 6

EXPERIMENTAL RESULTS - CLOSED BOMB THERMAL STABILITY TESTS OF HYDRAZINE-HYDRAZINE NITRATE MIXTURES

MIXTURES, WT % N_2H_4	$N_2H_5NO_3$	H_2O	TEMPERATURE - AT WHICH TIME-TEMP. CURVE CHANGES	EFFECT
5	95	—	265°F	Sudden temperature rise
10	90	—	270°F	Sudden temperature rise
20	80	—	270°F	Sudden temperature rise
30	70	—	250°F	Sudden temperature rise
40	60	—	245 & 310°F	Temperature remains constant
50	50	—	230 & 335°F	Temperature remains constant
5.2	46.8	48	—	Time-temperature plot nearly a straight line
6.3	56.7	37	—	" " " " " "
7.0	63.0	30	250-290°F	Sudden sharp temperature rise
8.0	72.0	20	" "	" " " "

FIGURE 6

RESULTS OF DETONATION PROPAGATION TESTS WITH HYDRAZINE-HYDRAZINE NITRATE MIXTURES

SOLUTION USED		MD-24 CANNON PRIMER DETONATED			NO. 4 ELECTRIC BLASTING CAP			
% N_2H_4	% $N_2H_5NO_3$	FRESH SOLN	1 WK OLD	2 WKS OLD	FRESH SOLN	1 WK OLD	2 WKS OLD	3 WKS OLD
		—	—	—	—	—	—	
5	95	X	X	—	0	X	—	—
10	90	0	X	—	0	X	—	—
20	80	—	0	—	0	X	—	—
30	70	—	0	X	X	X	—	—
40	60	—	—	0	0	0	X	—
50	50	—	—	—	0	0	0	0
10	90 + 48% H_2O	—	—	—	0	0	0	0
10	90 + 37% H_2O	—	—	—	0	0	0	0
10	90 + 30% H_2O	—	—	—	0	0	0	0
10	90 + 20% H_2O	—	—	—	0	0	0	0

Code — 0 - No propagation
X - Propagated detonation
— - Not tested

FIGURE 7

reaction was initiated by the detonator, the brisance or shattering effect was such as to indicate that explosion rather than detonation had occurred. The results indicate that mixtures containing no water are unsafe to handle and that those containing water are relatively safe.

The results of the physical properties determinations are shown in Figures 8, 9, and 10. As expected, the viscosity of the hydrazine-hydrazine nitrate mixtures increased as the nitrate content increased and the viscosity of the 10-90 mixture decreased with increased water content. Density behaved similarly.

The point of first crystallization on cooling occurred at a higher temperature as the water content of the mixtures increased. The mixture containing 20% water showed a sharp freezing point while the mixtures of higher water content formed slushy mixtures a few seconds after the appearance of the first crystal. The 40-60 mixture showed no crystal formation down to -41°C. where cooling was discontinued.

To recapitulate, the results of this preliminary experimental evaluation indicated the following:

a. Hydrazine - hydrazine nitrate mixtures containing 50 to 95% of the nitrate are stable in air up to 400°F and in a confined volume with air space are stable to 250°F. The range of heat stability is increased by the addition of water.

b. The hydrazine-hydrazine nitrate mixtures above 50% nitrate were sensitive to impact at or near room temperature and were exploded after one to two week storage at room temperature.

c. The 10-90 mixtures with 20 to 48 wt percent water were not sensitive to 100 kg-cm shock at temperatures up to 212°F and were not exploded by a No. 4 electric blasting cap after three weeks' storage at room temperature.

d. The points of first crystallization from the mixtures containing water were well below the freezing point of water. Mixtures containing more than 20% water did not freeze solid at the point of first crystallization.

It appears at this stage that the mixtures containing water still warrant consideration for monopropellant use in torpedo propulsion. Further evaluation is, of course, necessary. Reaction stand and dynamometer studies as well as long term storage and handling tests will be made as the work load at Newport permits.

ROOM TEMPERATURE (70°F) VISCOSITIES OF VARIOUS HYDRAZINE-HYDRAZINE NITRATE MIXTURES

MIXTURES, WT %			NUMBER OF TESTS	AVERAGE VISCOSITY CENTISTOKES
N_2H_4	$N_2H_5NO_3$	H_2O		
5	95	0	5	8.54
10	90	0	5	7.33
20	80	0	5	5.41
30	70	0	5	3.92
40	60	0	5	3.42
50	50	0	5	2.53
5.2	46.8	48	5	2.008
6.3	56.7	37	5	2.226
7.0	63.0	30	5	2.569
8.0	72.0	20	5	3.222
0	0	100	5	1.010
Literature value for water			5	1.007

FIGURE 8

DENSITY OF N_2H_4 - $N_2H_5NO_3$ MIXTURES AT 73°F

MIXTURES, WEIGHT %			DENSITY AT 73°F
N_2H_4	$N_2H_5NO_3$	H_2O	Gms/cc
5	95	0	1.38
10	90	0	1.35
20	80	0	1.29
30	70	0	1.24
40	60	0	1.22
50	50	0	1.18
100	--	0	1.013
0	0	100	0.997
5.2	46.8	48	1.255
6.3	56.7	37	1.245*
7.0	63.0	30	1.280
8.0	72.0	20	1.290

* Experimental error - according to curve should be 1.271

FIGURE 9

POINT OF FIRST CRYSTAL FORMATION IN HYDRAZINE-HYDRAZINE NITRATE-WATER MIXTURES

% N_2H_4	% $N_2H_5NO_3$	% H_2O	TEMPERATURE - °F
40	60	--	-41.8 (no crystals)
5.2	46.8	48	-21.0
6.3	56.7	37	-45.4
7.0	63.0	30	-51.6
8.0	72.0	20	-61.5

FIGURE 10

It is hoped that this program will result in a torpedo monopropellant of practical utility, a monopropellant comparable to H_2O_2 - diesel fuel - carried diluent in energy and having acceptable storage and handling characteristics.

EXPERIENCE IN USING HYDRAZINE AS A LIQUID ROCKET FUEL AND AS AN IGNITER FLUID

by

R. B. Foster and J. Smerda
Bell Aircraft Corporation

Presented by
R. B. Foster

PART I

Use of Hydrazine as a Liquid Rocket Fuel

In February 1948 the Bell Aircraft Corporation undertook the development of a liquid propellant rocket engine using hydrogen peroxide as the oxidizer and hydrazine as the fuel. This power plant was designed as a ground launched air-to-air test vehicle for Project METEOR, sponsored by the Bureau of Ordnance of the Navy Department.

The reasons for selecting these propellants were as follows:

a. Good Performance -- A relatively good impulse, particularly density impulse, which was important for this type of missile.

b. Comparatively well suited to use aboard ship. The relatively high freezing points of both propellants was not as serious a drawback as in other applications. Freezing point depressants for both propellants appeared to be possible.

c. No other agency was working on this propellant combination and it appeared to be worthy of development.

d. Propellants were hypergolic and permitted rapid ignition and rapid rates of chamber pressure rise. This was particularly important because of the short firing time.

The concentration of the hydrogen peroxide used was 90%. That of the hydrazine was nominally 95%. However, a combustion catalyst was added to the fuel to aid in the decomposition of the peroxide. This catalyst consisted of:

1.18 grams of potassium ferricyanide per 1000 cc of fuel.
0.47 grams of cuprous cyanide per 1000 cc of fuel.
0.30 grams of sodium cyanide per 1000 cc of fuel.

These catalysts were first dissolved in a small quantity of water and the solution was then added to the hydrazine. This resulted in an actual concentration of about 93% hydrazine. The ignition delay time of this fuel with hydrogen peroxide appeared to be about four milliseconds or less under room temperature conditions.

The performance obtainable with this propellant combination is shown in Figure 1. The theoretical specific impulse was calculated on the basis of shifting equilibrium and indicated a maximum specific impulse of 243 seconds at an oxidizer to fuel ratio of 2.04 for a chamber pressure of 300 psig. The actual design operating point of the power plant was at a mixture ratio of 1.67 where a specific impulse of 226 to 228 seconds was obtained at rated chamber pressure of 300 psig. This represented 94% of the theoretical specific impulse obtainable at this mixture ratio. The average propellant density was 76.2 lb/cu ft. This resulted in a density impulse of 17,400 lb sec/cu ft.

Later in the development program the chamber pressure was raised to 450 psig in order to reduce the volume of the power plant. At this chamber pressure an actual specific impulse of 239 seconds was obtained in a ceramic chamber having a characteristic length of 40 inches.

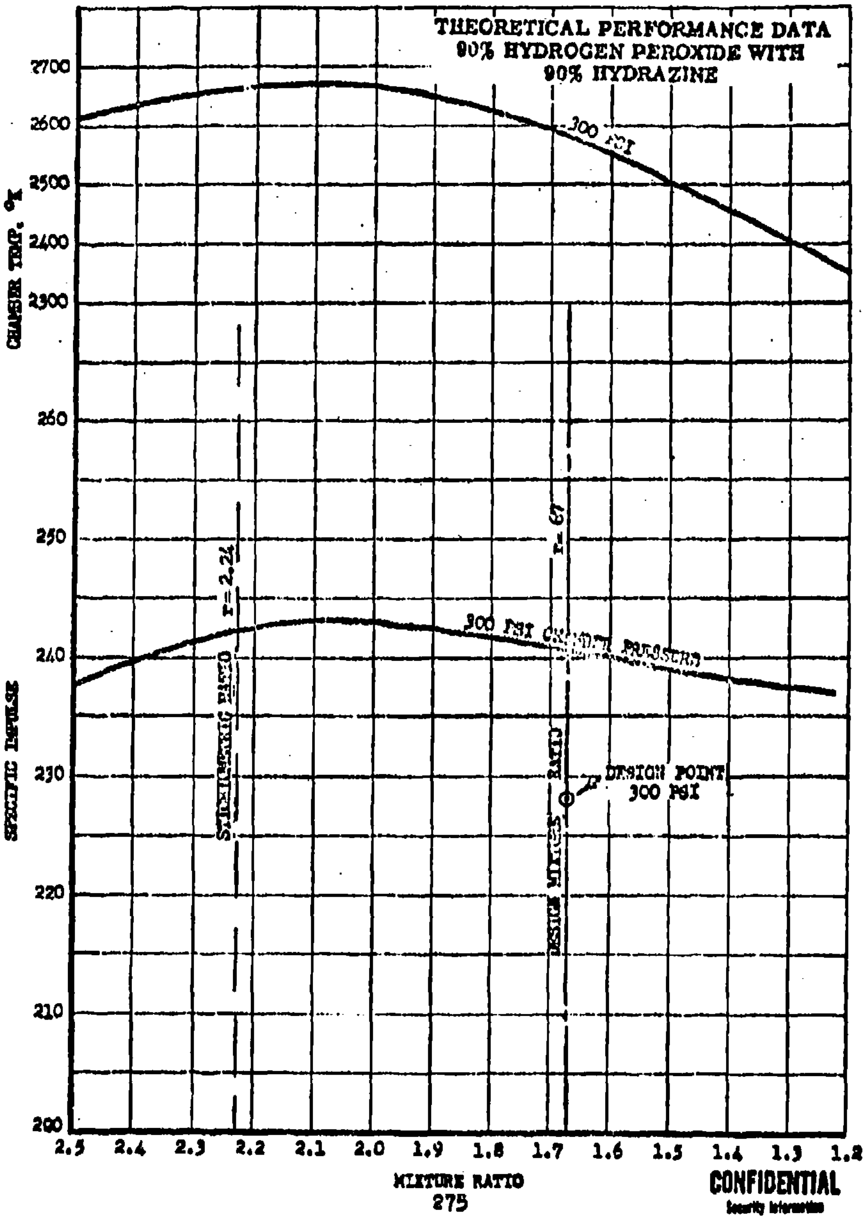
The performanse data for the power plant is presented in the following table:

TABLE I

Thrust	350 lb
Duration	15 sec
Mixture Ratio (O/F)	1.67
Weight of Oxidizer	14.6 lb
Weight of Fuel	8.35 lb
Total Propellant Weight	22.95 lb
Actual Specific Impulse	228 sec
Density Impulse	17,400 lb sec/cu ft
Overall Specific Impulse	109 sec at sea level; 118 sec in flight
Thrust to Engine Weight Ratio	7.28

The size and configuration of the missile itself is shown in Figure 2. The missile was accelerated to supersonic speed by a

FIGURE I


THEORETICAL PERFORMANCE DATA
90% HYDROGEN PEROXIDE WITH
90% HYDRAZINE
CHAMBER TEMP. °K
2700
2600
2500
2400
2300
300 PSI
SPECIFIC IMPULSE
260
250
240
230
220
210
200
300 PSI CHAMBER PRESSURE
STOICHIOMETRIC RATIO r = 2.24
DESIGN MIXTURE RATIO r = 67
DESIGN POINT
300 PSI
2.5
2.4
2.3
2.2
2.1
2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
MIXTURE RATIO

[redacted]

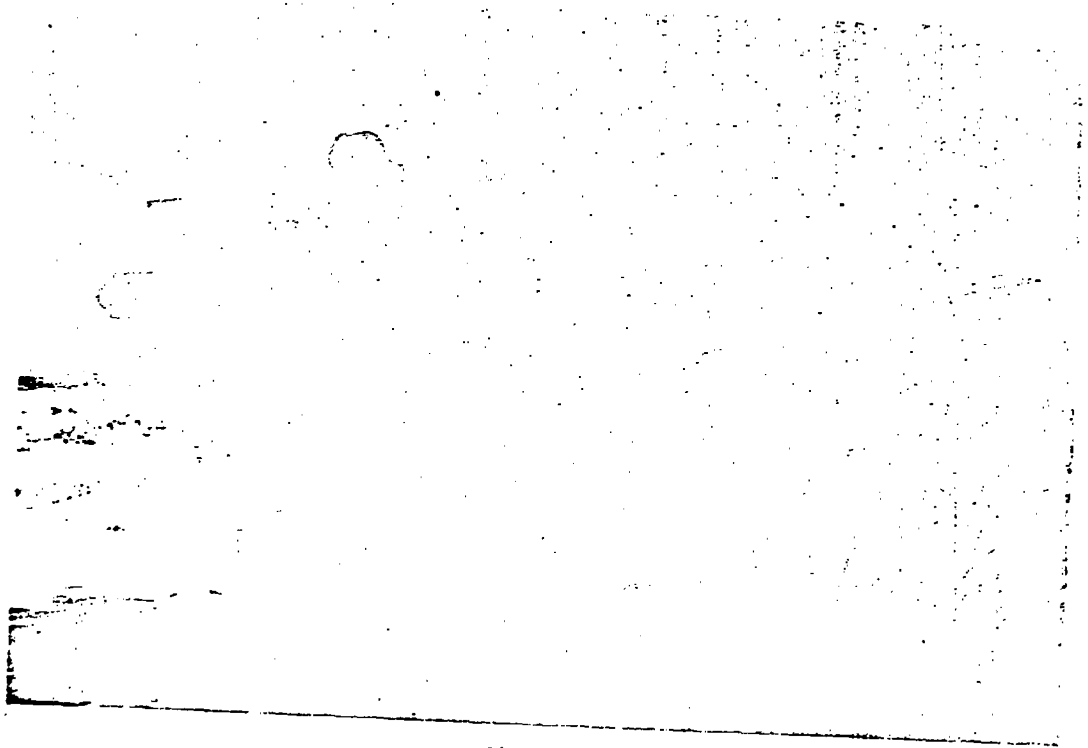


Figure 2

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solid propellant booster rocket. When the boost rocket was exhausted and detached, the liquid propellant rocket in the missile was fired and sustained the high velocity attained for a period of 15 seconds. The missile was six inches in diameter and about 7 feet long.

Since space was at a premium, the power plant had to be made as compact as possible. This was one of the factors favoring hydrazine as a fuel. Figure 3 shows the power plant components of the missile assembled as in the missile. The tanks were located close to the center of gravity of the missile in order to minimize c.g. travel during expulsion of the propellants. The individual components of the power plant can be better identified in Figure 4 which shows them disassembled but in their proper relative positions.

The short large tank was the nitrogen pressure accumulator. Gas was fed from this reservoir through the start valve and pressure regulator to a tee from which separate nitrogen lines were run through stainless steel check valves to each propellant tank. The large long tank had a partition in it which separated the fuel tank from the oxidizer tank. The fuel tank was the smaller portion forward while the oxidizer tank was the larger section immediately behind it. The pressurization system down to the check valves was made of aluminum primarily.

The propellant tanks and feed lines were made of 347 stainless steel. Any 300 series stainless would have been satisfactory for the hydrazine tank but, because of the hydrogen peroxide present, 347 stainless steel was used for both tanks. Some of the smaller detail parts of the hydrazine tank were made from 304 stainless steel, however.

Attachments to the tanks were made using snap rings. Neoprene rubber "O" rings were used for seals in the hydrazine system while polyethylene "O" rings were used in the peroxide system. Frangible discs were used to control the flow of propellants from the tank to the thrust chamber. These were made of aluminum in both propellant systems. The only conventional valves used were in the nitrogen pressurization system.

Expulsion bladders were used to insure complete expulsion of the propellants without passage of gas bubbles. The bladder used in the hydrazine tank was made of neoprene rubber while the one used in the hydrogen peroxide tank was made of polyethylene.

The thrust chamber consisted of a stainless steel injector attached to a steel shell containing a Niafrax ceramic chamber and nozzle insert.

[redacted]

Figure 3

[redacted]
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[redacted]

Figure 4

[redacted]
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The complete power plant weighed approximately 48 pounds empty.

One of the characteristics of this propellant combination is the relatively low luminosity of the combustion gases. When the power plant is running the exhaust jet is just visible. The flame has a transparent green color with a few reddish streaks in it (Figure 5).

In starting the rocket engine, it was found necessary to lead with the oxidizer or at least to have a simultaneous entrance of the propellants. This was accomplished by having a thicker frangible disc on the hydrazine tank outlet. Shutdown could be safely accomplished by running out of either propellant. In one instance, where hydrogen peroxide was inadvertently shut off, the motor continued to run using hydrazine as a monopropellant. The ceramic chamber was red hot, of course, when the peroxide flow was stopped.

The loading of the missile was accomplished by using tanks containing the amount of propellant required to properly fill the missile tanks. Transfer could thus be accomplished readily with a minimum of spillage or hazard (Figure 6). Although the technicians wore protective clothing primarily because of the hydrogen peroxide being used, the clothing was useful in minimizing the hazards of skin contact with hydrazine.

No difficulties were experienced due to decomposition of hydrazine. However, precautions were taken to ensure that test equipment and power plant components were always clean and free of dirt and grease or other contaminants. In fact, for purposes of standardization, the same procedures were used for cleaning the hydrazine system as were used for the hydrogen peroxide system. Quantities of hydrazine have been stored at Inyokern for periods of six months with negligible decrease in the concentration of hydrazine. No personnel injuries or illness occurred during approximately four years of operations which could be attributed to the use of hydrazine.

PART II

Use of Hydrazine as an Igniter Fluid

Some liquid rocket propellant combinations are non-hypergolic. That is, they do not burn upon mixing and must be ignited by means of an electric spark, glow plug, or other means.

Probably the simplest method of obtaining ignition is to start the combustion using hypergolic propellants and then switch

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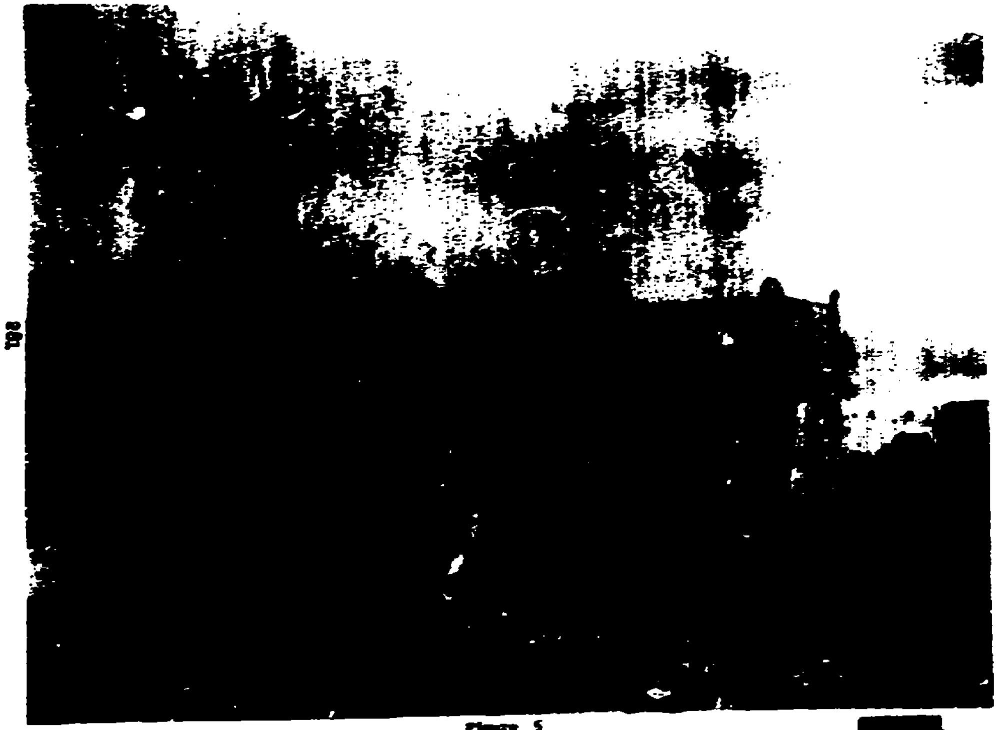

Figure 5

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[redacted]

Figure 6

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to the non-hypergolic propellants. This method has been used at Bell Aircraft Corporation for a number of years as a means of obtaining ignition in acid-gasoline or jet fuel thrust chambers. Combustion is initiated by means of a slug of hydrazine placed in the fuel line ahead of the jet fuel. This has proved to be a simple and reliable means of igniting acid-jet fuel rocket engines where repeated starting is not required.

The hydrazine used for this purpose is not anhydrous hydrazine but is a composition close to the eutectic composition; namely, 68-69% hydrazine. The remainder is water. It can be seen in Figure 7 that the freezing point of this liquid is well below -40°F, which is the freezing point of white fuming nitric acid. Satisfactory starts have been made consistently at all temperatures from -40°F to plus 160°F.

The reasons for selecting hydrazine as an igniter fluid are:

1. It is very hypergolic with white fuming nitric acid, and

2. It burns without leaving any soot, coke, or other residue.

Its major disadvantage is its high cost. However, approximately 8 oz of hydrazine is used per start and this is considered economical because of the reliability of operation and freedom from clogging which is obtained.

During four years of operation approximately 5000 rocket motor firings have been made using hydrazine as an igniter fluid. Since records of these firings are incomplete, it is not possible to determine the exact number of starting malfunctions which were due to the use of the starting fluid. The number is not large; probably not over twenty.

Four are known to have been caused by accidental dilution of hydrazine with water. These resulted in no ignition at all. This has been avoided by purchasing hydrazine in the desired concentration and acceptance testing the fluid to a specification.

A few were caused by using too small a quantity of hydrazine. These resulted in no ignition or in a small pressure rise and failure to sustain combustion.

Probably the greatest number were caused by the presence of jet fuel ahead of the slug of hydrazine. This usually resulted in an explosion. It occurs only on re-running a test thrust chamber as a result of incomplete purging of fuel from the previous run. It would not occur in operation of a missile.

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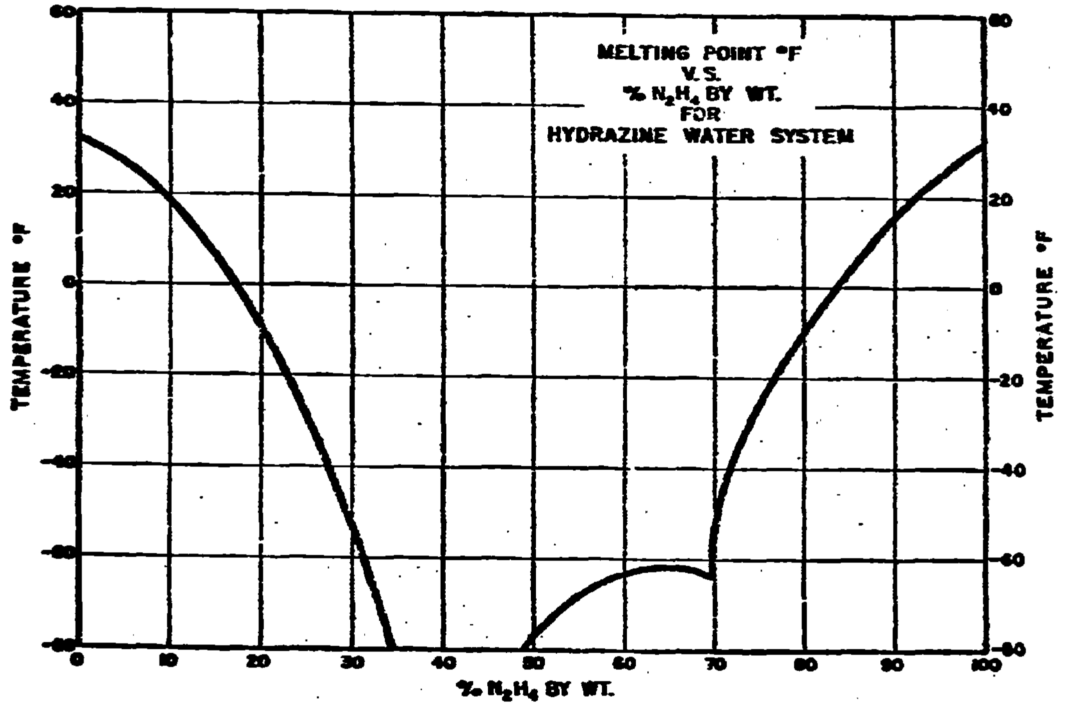

Figure 7

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Dilution of hydrazine with jet fuel is avoided by inserting the hydrazine in a portion of the fuel line between two valves. The dilution which occurs after opening of the valves is insufficient to affect ignition.

These are the only causes of failure experienced with the use of hydrazine. All of these causes can be corrected or avoided by proper design of the fuel system components.

Recently the position of hydrazine for this purpose has been threatened by the development of mixed alkyl trithiophosphite. This compound has been evaluated as an igniter fluid in comparison with hydrazine and has been found to have a shorter ignition delay time. The amounts of deposits which form in the chamber are not serious and the cost of the material is expected to be considerably lower. If freezing point depressants for WFNA become feasible or if RFNA is used, some such fluid as this must be used since the freezing point of the hydrazine is too high.

Therefore, the continued use of hydrazine for this purpose does not appear too promising in the light of future requirements and recent developments in hypergolic fuels.

GENERAL EXPERIENCE WITH HYDRAZINE AT AEROJET

by

E. M. Wilson, S. B. Kilner, R. Gordon, and C. L. Randolph
Aerojet-General Corporation

Presented by
E. M. Wilson

Rocket Motor Studies

During a study at Aerojet of the use of hydrazine in rocket motors, gas generators employing hydrazine both as a monopropellant and in very fuel-rich bipropellant systems with nitric acid were briefly investigated. Because other contractors were examining the monopropellant system with some care, the main effort was concentrated on determining the feasibility of operating a gas generator with hydrazine while simultaneously injecting small quantities of white fuming nitric acid. It should be pointed out that this work was done several years ago and was only exploratory in nature. Primary decomposition of hydrazine to ammonia and nitrogen is easily accomplished, but yields noxious gases at 2509°F. The further decomposition completely to nitrogen and hydrogen absorbs heat (reducing the chamber temperature to 1070°F) and requires a rather large catalyst bed to obtain a high gas yield. By initially injecting a 1:1 mixture of hydrazine and nitric acid, a temperature of 4670°F is obtained, and by then injecting further hydrazine, complete decomposition results, in a much smaller volume than is possible when only the pure fuel is used. Calculations show that approximately 6% of nitric acid is sufficient to produce final gas temperatures of 1425° to 1525°F, a convenient temperature range both for gas turbine operation and effective decomposition.

The gas generator chamber used in these tests was of 1.75 in. inside diameter, and had provisions for the measurement of temperature along the wall at one inch intervals. The injector consisted of eight groups of like-on-like impinging hydrazine streams, the WFNA being introduced as an impinging stream with 2 hydrazine jets in a centrally located ninth group; a molybdenum baffle was present three inches from the injector face to help mix the hot gases. An L* of 393 inches was used, and 66% of the chamber volume was filled with a catalyst consisting of equimolar quantities of iron, nickel, and cobalt salts on aluminum oxide pellets. Temperature profiles for three different mixture ratios in this gas generator are shown in Figure 1. It was concluded that with further development work a gas generator that would be smaller and more efficient than one using hydrazine alone could be built, it having been shown that the system is feasible.

Time does not permit going into the details of the extensive testing of hydrazine and WFNA in a 400-lb thrust rocket motor. Results available in Aerojet Report No. 488 show that smooth combustion and performance values in excess of 95% of theoretical can be obtained. Several short duration tests at a thrust level of approximately 4000 lb also were made without difficulty.

Analysis of Hydrazine

In order to meet the need for a rapid method for the routine analysis of hydrazine samples, attention was given to methods other than the classical potassium iodate titration of a hydrochloric acid solution of hydrazine. Although capable of a high degree of accuracy, this latter procedure is not rapid, and determination of the exact end point is often difficult. Since this titration results in the quantitative liberation of nitrogen, a series of tests was made to determine whether sufficient accuracy could be achieved by the collection of the nitrogen in a simple gas measuring apparatus. Because potassium permanganate is usually available in any laboratory, this oxidizer was chosen for the tests, the liberation of nitrogen being quantitative in basic solution. The equipment is shown in Figure 2. The 500-ml eudiometer was constructed by drilling a hole in the bottom of an ordinary graduate cylinder. A sample of approximately 0.5 g was weighed by difference from a hypodermic syringe, introduced into the 250-ml Kjeldahl flask, and 10-ml of 4N sodium hydroxide was added immediately before connecting the flask to the rubber tubing beneath the burette. A saturated solution of potassium permanganate was then added from the burette until an excess was visually present (approximately 40 ml); the volume of gas was then read and corrected to standard conditions. A correction for the volume of titrant added was also made. Hydrazine solutions in water of various concentrations were analyzed in this manner, as well as some containing small quantities of ammonia, the common impurity in hydrazine. Results shown in Table I indicate that even with the simple equipment used, the method yields results sufficiently accurate for many needs. Because no standardized solutions are needed, the method should prove convenient for field analysis of hydrazine for rocket units. With a more accurate gas-measuring device, such a method also appears worthy of the more exacting demands of the research laboratory.

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FIGURE 1

TEMPERATURE PROFILE OF

HYDRAZINE – NITRIC ACID GAS GENERATOR

CHAMBER L* = 395 IN.
CATALYST L* = 255 IN.
MIXTURE RATIO, M.R. = WT FUEL/WT OXIDIZER

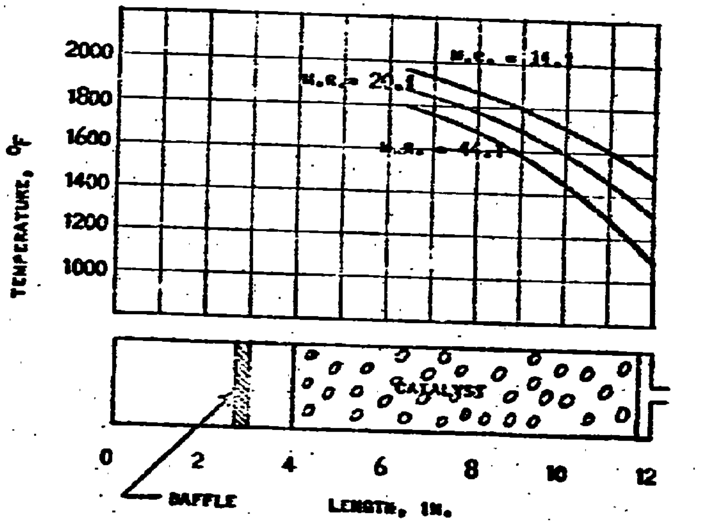

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FIGURE 1

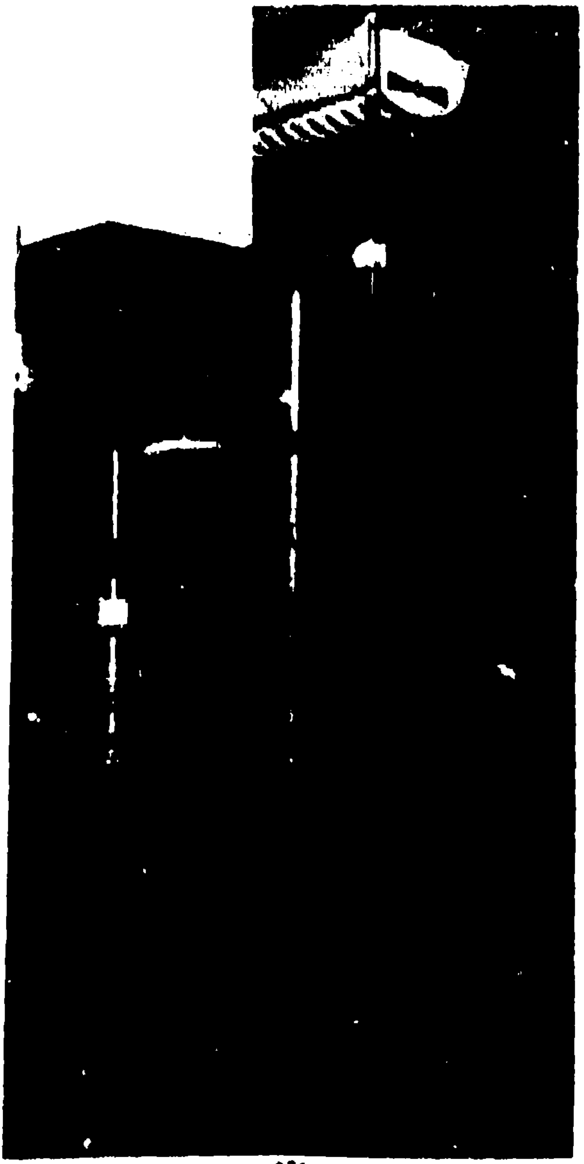

TABLE I

AZOMETRIC ANALYSIS OF HYDRAZINE

Sample	Wt % N_2H_4 by KIO_3 Titration (av)	Wt % N_2H_4 by Gas Volume
Comm. N_2H_4	95.0	95.3 95.0
		Av 95.1
Comm. $N_2H_4 + H_2O$	35.3	35.3 35.0
		Av 35.1
Comm. $N_2H_4 + NH_4OH$ to give 1.7% NH_3	87.2	87.4
Comm. $N_2H_4 + NH_4OH$ to give 7.0% NH_3	74.6	75.4 74.1
		Av 74.7
Comm. N_2H_4 (Redistilled from KOH)	98.0	98.6 98.2 99.0 98.5 99.4 99.0
		Av 98.8

DISCUSSION ON PAPERS BY
DANIEL B. MURPHY, SAUL WOLF, R. B. FOSTER, AND E. M. WILSON

THE CHAIRMAN: We can now open for discussion of the papers just given; discussion and questions.

MR. WILSON: I will raise one. Does anyone see anything wrong with this method of analysis we have been using? We would like to know if you do. It is far quicker than the other methods I have seen so far.

(No comment)

MR. CAMPBELL: I would like to ask Mr. Foster what was the chamber pressure of the METEOR.

MR. FOSTER: 300 pounds.

A LOW-FREEZING HYDRAZINE FUEL FOR ROCKETS

by

E. D. Campbell, H. P. Jenkins, Jr., and Wm. Cohen
U. S. Naval Ordnance Test Station

Presented by
E. D. Campbell

This paper concerns the fuel that was developed in the Liquid Propellants Branch of the Naval Ordnance Test Station for the LAR rocket.

The LAR is an experimental aircraft rocket 5 inches in diameter and 110 inches long. It has the very short burning time of 0.5 second and produces a thrust of 17,500 pounds. The burnt velocity is about 2400 ft/sec. Because of overall size limitations, the combustion chamber of the LAR cannot be larger than 5.0 inches in diameter, nor have a characteristic chamber length (L* = ratio of chamber volume to nozzle throat area) much greater than 8 inches. Yet, 40 pounds of liquid propellants must burn in it in 1/2 second. Such a high burning rate has never before been approached in a conventional liquid propellant rocket motor of this size. This was made possible only by utilizing a fuel and oxidant combination which was capable of reacting with a very high velocity. Thus it was that hydrazine was chosen as the fuel, and RFNA containing 20 percent NO_2 for the oxidant.

The use of hydrazine as the LAR's fuel has been of paramount importance in its development program. Its high performance and speed of combustion have made it virtually the only fuel capable of meeting the stringent requirements for use in the LAR.

But hydrazine of course has its limitations. Design specifications for the LAR require that it shall be operative at temperatures as low as -65°F (-54°C), necessitating that the fuel freeze at or below this temperature. Also, our engineers have estimated that the viscosities of the propellants should not be greater than 35 centistokes at all temperatures to attain Reynolds numbers of at least 4000, which, it is believed, would permit a satisfactory degree of turbulence to promote efficient mixing. Thus, a problem of considerable magnitude presented itself.

Approximately 120 freezing point depressants were considered and rejected as unsuitable, usually because of insufficient solubility or because the quantities of additives required to lower the freezing point adequately also decreased the performance to a degree unacceptable for the LAR. Ammonium thiocyanate, as first suggested by North American Aviation, Inc. (Ref. 1) was finally selected for use in the LAR development program.

Preliminary work indicated that a mixture containing 30 parts by weight of ammonium thiocyanate in 70 parts commercial anhydrous hydrazine had a freezing point close to the desired value of -54°C. Therefore, until a fuel of optimum properties could be devised and its characteristics determined, hydrazine containing 30 percent ammonium thiocyanate was utilized in our rocket firings.

A partial freezing-point-composition diagram of the system hydrazine-ammonium thiocyanate has been plotted as shown in Figure 1. Mathieson hydrazine assaying 96.0 percent N_2H_4 was used. The ammonium thiocyanate was Baker and Adamson reagent grade dried to constant weight and assayed as 98.4 percent NH_4SCN. Inspection of the curve reveals that by increasing the amount of thiocyanate from 30 to 32 percent the desired FP of -54° may be obtained.

The viscosity of the 30 percent thiocyanate fuel was measured with a Fenske-modified Ostwald viscosity pipet placed in a thermostated clear Dewar flask. A plot of viscosity vs temperature is seen in Figure 2. It will be noted that the viscosity at the freezing point (-46.25°C) is about 32 centistokes - that is, within the acceptance limit. At the time of this writing, viscosity data on hydrazine containing 32 percent thiocyanate, - the composition which meets the freezing point requirement - had not yet been obtained. However, it is expected that the viscosity at -54° will be unacceptably high. Therefore, work will be directed toward finding a suitable additive to lower the viscosity. Ammonia, perhaps, can be utilized for this purpose.

An impinging jet apparatus has been used to measure the ignition delays of these fuels. Using the LAR oxidant, RFNA containing 20 percent NO_2, hydrazine gave a delay of 5.1 ± 0.7 msec, whereas hydrazine containing 30 percent ammonium thiocyanate had a delay of 22 ± 1 msec. These measurements were made at ambient temperature. When the 30 percent thiocyanate fuel was fired at -40°C a value of 62 ± 5 msec was obtained.

In order to evaluate the performance of the 30 percent thiocyanate fuel at low temperatures a small motor of 1500 pounds thrust was utilized until tests could be made with the LAR. The 30 percent thiocyanate fuel with RFNA as oxidant was fired in this motor at -43°C with moderate success.

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FIGURE 1

FREEZING POINT VS. WT. PER CENT AMMONIUM THIOCYANATE ADDED TO COMMERCIAL ANHYDROUS HYDRAZINE

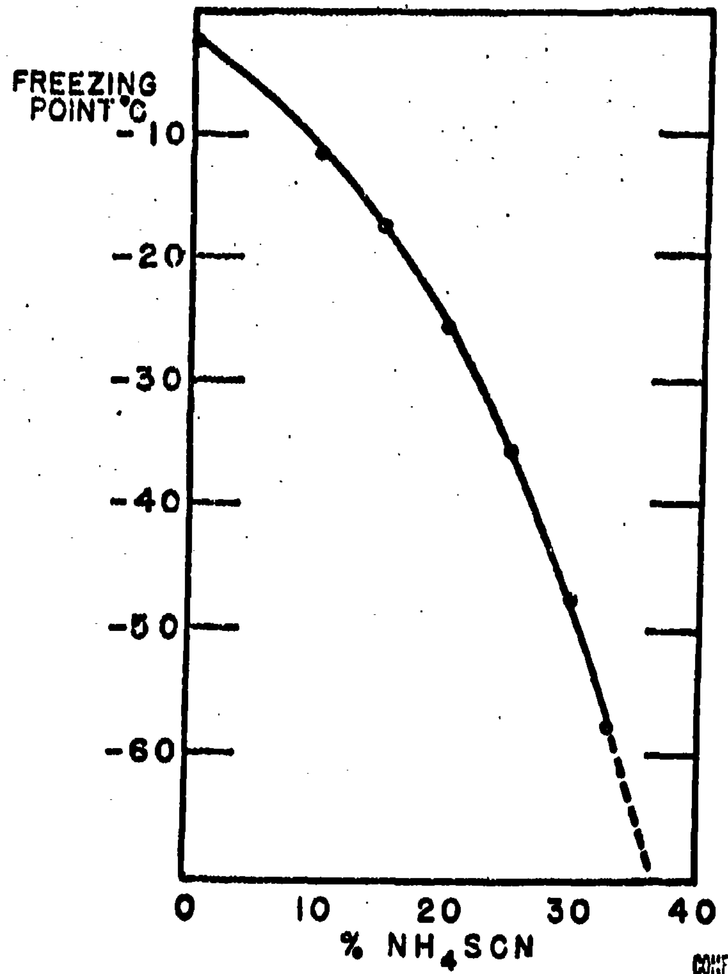

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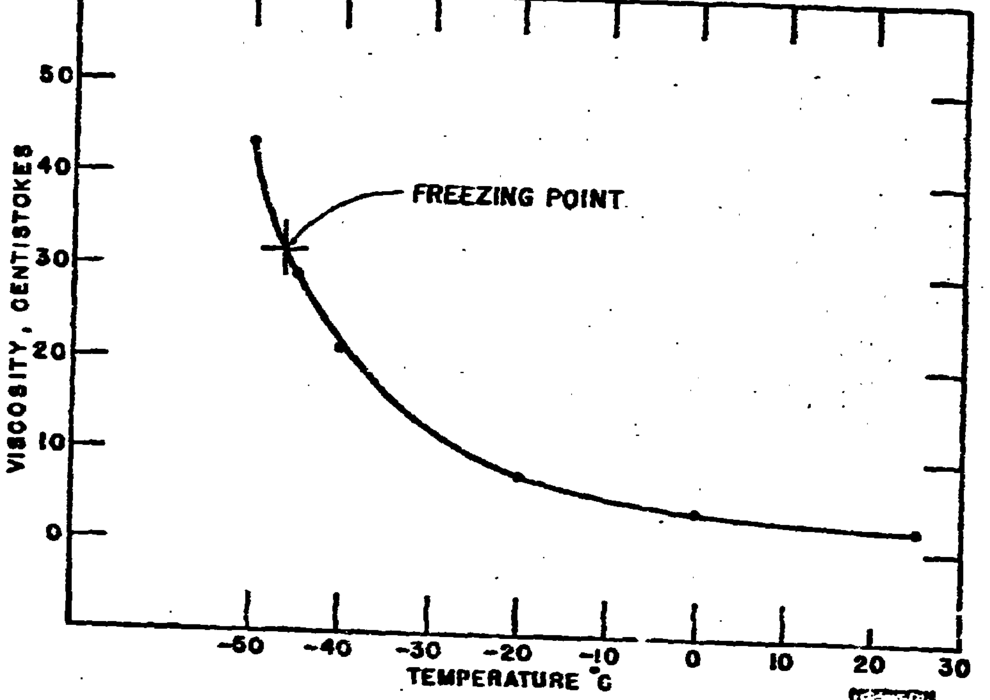
FIGURE 2
70% HYDRAZINE
30% AMMONIUM THIOCYANATE

KINEMATIC VISCOSITY VS. TEMPERATURE



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Firings of the LAR at low temperatures will be made in the near future.

A limited investigation concerning the corrosion and compatibility of the 30 percent thiocyanate fuel with common materials of construction and handling have been made.

Figure 3 presents data obtained in the evaluation of metals. Aluminum alloys were far superior to any of the other metals tested. AISI 347 stainless steel was attacked, and colored the fuel solution within one week's time. Unplated mild steel was rapidly attacked and a precipitate appeared in the fuel within 24 hours. Chromium plated mild steel, however, appeared to be satisfactory for about one month before the plating film broke down.

Figure 4 lists the results of tests with non-metallic materials. As expected, teflon and polyethylene seemed resistant to attack by the fuel. We were surprised, however, when Kel-F darkened after one month's exposure and had lost some elasticity after two months. Saran and neoprene both suffered attack within 40 hours, and tygon became opaque and hardened in less than one day, apparently due, at least in part, to leaching of the plasticizer.

An unusual feature of using ammonium thiocyanate in hydrazine is the solvolytic reaction which occurs. Figure 5 illustrates the hydrazinolysis of ammonium thiocyanate: hydrazine and ammonium thiocyanate are in equilibrium with hydrazonium thiocyanate and ammonia. Obviously if the solution is in an open system, ammonia will be lost, and the composition will change. This is undesirable because the ammonia appears to depress the viscosity. In order to study the effect of allowing ammonia to escape, a surveillance test was made. Samples of freshly prepared 30 percent ammonium thiocyanate solution in hydrazine were placed in a freezing point cell and in a viscosity pipet and allowed to stand at ambient room temperature, protected, but vented.

Figure 6 indicates the change that occurred in the viscosity of the fuel upon standing at ambient temperature. The temperature of these viscosity measurements was -40°C. In a period of 35 days the viscosity increased from about 20 to 55 centistokes, which of course is beyond the limit of acceptance.

Figure 7 shows the change that occurred in the freezing point of the solution after standing 36 days at room temperature. It dropped from -46 to about -50, where it appeared to level off. Again this change is attributed to loss of ammonia.

FIGURE 3

COMPATIBILITY OF METALS WITH HYDRAZINE CONTAINING 30% NH_4SCN (AT AMBIENT TEMPERATURE)

	Satisfactory for One Year or Longer	Satisfactory for One Month	Satisfactory for One Week	Satisfactory for a Few Hours
Aluminum Alloys (3S, 14S, 24S)	x			
1020 Mild Steel, Chromium Plated		x		
Monel			x	
Inconel			x	
347 Stainless Steel			x	
1020 Mild Steel				x
1020 Mild Steel, Cadmium Plated				x

FIGURE 4

COMPATIBILITY OF NON-METALS WITH HYDRAZINE CONTAINING 30% NH_4SCN
(AT AMBIENT TEMPERATURE)

Plastic Materials	Satisfactory for Two Months or Longer	Satisfactory for One Month	Possibly Satisfactory For One Day	Unsatisfactory
Teflon	x			
Polyethylene	x			
Kel-F		x		
Saran			x	
Neoprene			x	
Tygon				x

[redacted]

FIGURE 5

HYDRAZINOLYSIS OF AMONIUM THIOCYANATE

$$N_2H_4 + NH_4SCN \rightleftharpoons N_2H_5SCN + NH_3$$

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FIGURE 6

VISCOSITY (AT—40°C) SURVEILLANCE HYDRAZINE + 30% NH_4SCN

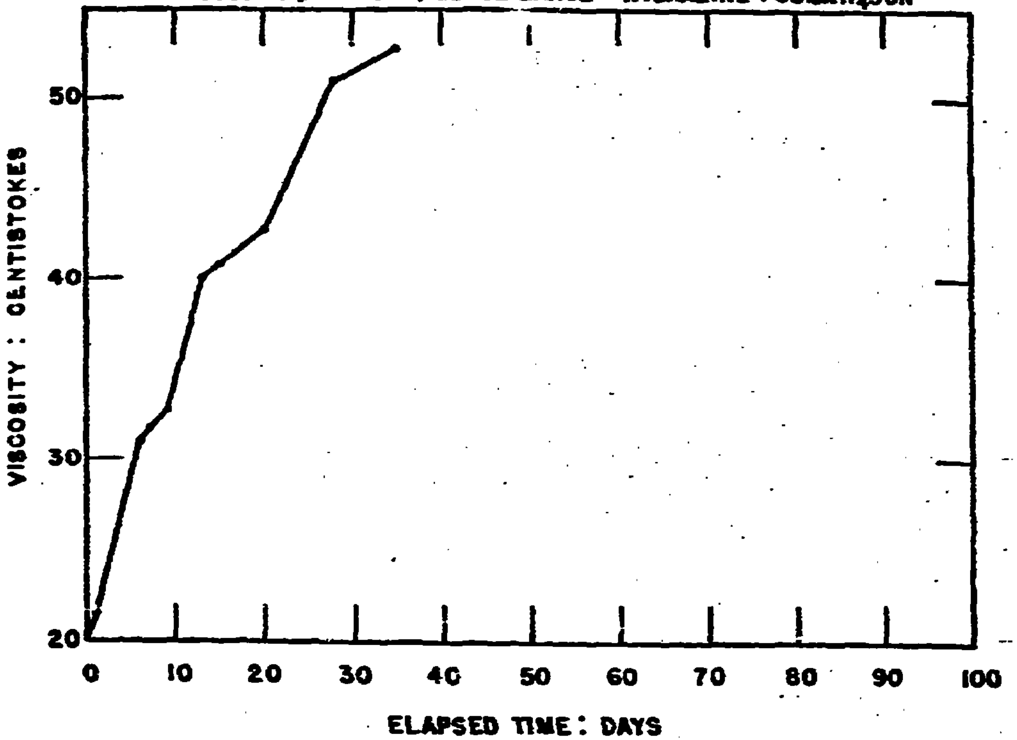

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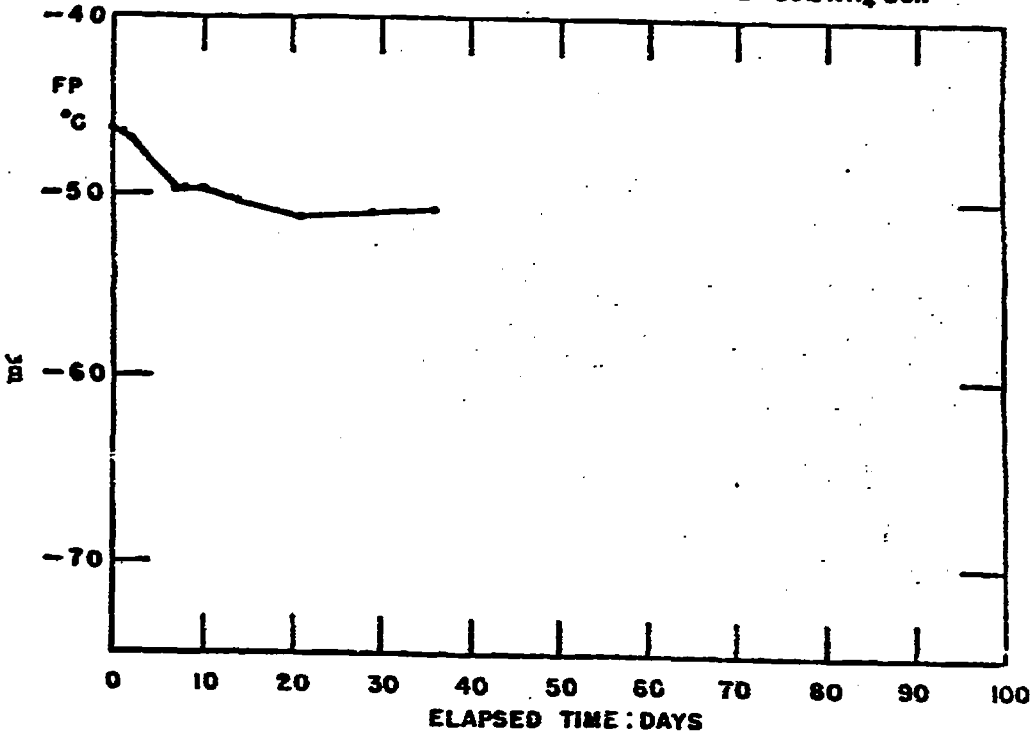
FIGURE 7

[redacted] FREEZING — POINT SURVEILANCE HYDRAZINE + 30% NH_4 SCN



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In addition to these solutions which were stored under vented conditions a sample of the original solution was stored in a pressure tight bottle. At the end of 37 days the freezing point and viscosity were virtually unchanged, indicating that careful handling and storage are necessary to preserve the composition and therefore the desired freezing point and viscosity of the solution. Attempts to analyze these solutions have not been completely satisfactory but have revealed one important fact: those solutions which were stored under vented conditions lost from 40 to 96 percent of the available ammonia.

To investigate the possibility of depressing the freezing point even lower without increasing the weight of ammonium thiocyanate, the use of mixed additives was considered.

Figure 8 is a plot of freezing point vs the composition of additive. Water and ammonium thiocyanate are utilized in various proportions, the total amounts of both materials always equaling 30 percent. The scatter of points is quite pronounced, probably due to ammonia being lost in inconsistently variable amounts. However a trend is indicated: the composition resulting from about 21 percent water and 9 percent of the thiocyanate freezes at about -59°C. This is about 5° and 13° lower than obtained with 30 percent water and 30 percent ammonium thiocyanate, respectively.

Plots of theoretical calculations comparing specific impulse and density impulse versus propellant mixture ratio are presented in Figure 9. The oxidizer is RFNA containing 20 percent NO_2. It is seen that use of the 30 percent thiocyanate fuel instead of hydrazine decreases the theoretical value of both of these parameters by about 5 percent when compared at the mixture ratios giving maximum impulses.

A specific impulse of not less than 205 lb sec/lb must be obtained in practice if the LAR is to meet design specifications. These plots show that at least in theory this value can be attained. A large number of static firings with the 30 percent thiocyanate fuel gave an average specific impulse of 202 sec/lb, although in a number of firings values as high as 230 lb sec/lb have been attained. It should be pointed out that these values are obtained by integrating the oscillogram trace of combustion chamber pressure vs time. This includes the anomalous end-effects of both starting and ending of burning. Thus, the instantaneous specific impulse during the stable combustion period is actually somewhat higher than that obtained from consideration of the firing as a whole.

FIGURE 8

[illegible] FREEZING POINT OF COMMERCIAL HYDRAZINE CONTAINING 30% ADDITIVE VS. COMPOSITION OF ADDITIVE

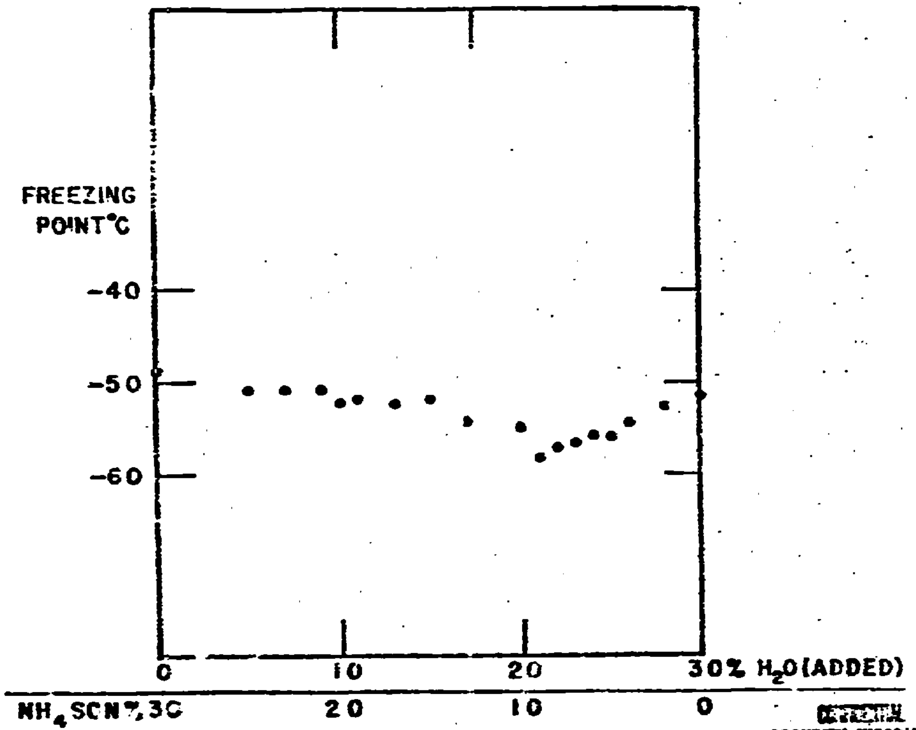

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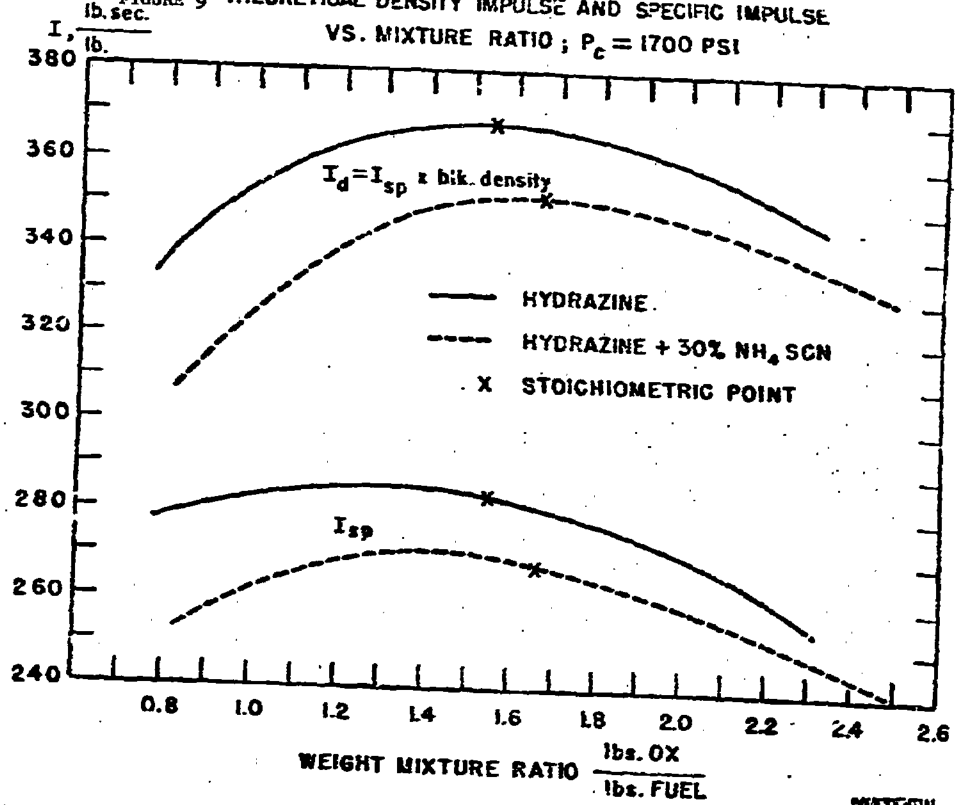
FIGURE 9 THEORETICAL DENSITY IMPULSE AND SPECIFIC IMPULSE VS. MIXTURE RATIO ; $P_c = 1700$ PSI



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A limited number of ground launched flight tests of the LAR have been made with the 30 percent thiocyanate fuel and the results were encouraging. Burnt velocities of 2330 ft/sec were attained with accelerations up to 190 g's. More flight tests are scheduled very soon to test improvements in design and obtain additional ballistic data.

These data are necessarily crude and preliminary since time for a more comprehensive and careful study has not been available due to tight scheduling in our development program.

The preceding has covered the highlights of our fuel problems and our attempts to solve them. This discussion has necessarily been of the nature of a progress report, since work is continuing. There is still much to be investigated and accomplished.

Reference

1. NAAI Report No. AL-612, Sept. 17, 1948 (Confidential)

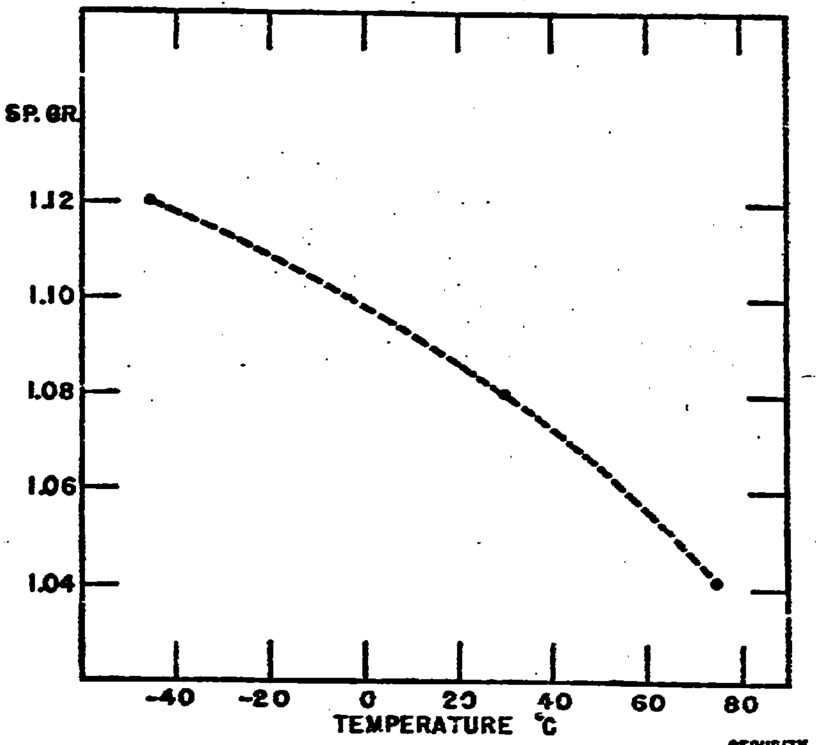
* * *

SECRECY ORDER NOTICE, U. S. PATENT OFFICE

This paper contains information relating to a pending patent which is subject to secrecy orders issued by the U. S. Commissioner of Patents (35 USC (1952) 181-188), disclosure of which is authorized under Permit A for the purpose of this symposium and its proceedings only.

* * *

TYPICAL SPECIFIC GRAVITIES OF HYDRAZINE
CONTAINING 30 % NH_4SCN



SOME THEORETICAL AND EXPERIMENTAL STUDIES OF HYDRAZINE AND HYDRAZINE SYSTEMS AS ROCKET FUELS

by

Paul M. Ordin
National Advisory Committee for Aeronautics

Introduction

The interest in hydrazine and hydrazine systems as rocket fuels and as starting fuels for many non-hypergolic propellant combinations is primarily due to the high specific impulse available, high reaction rates, and low ignition delays. The disadvantages of the hydrazine system which affect its position as potential rocket fuels are its thermal and shock stability, freezing point, toxicity, and cost.

The work of the NACA on hydrazine or hydrazine as a fuel blend is concerned with its use with fluorine and oxygen bifluoride for long-range applications, with chlorine trifluoride as a high-performance, storagable propellant combination, and as starting fuels for non-hypergolic propellant systems. Concerning the use of hydrazine systems for long-range applications, the theoretical performance of hydrazine, hydrazine/ammonia mixtures, and ammonia with liquid fluorine and liquid oxygen bifluoride at various chamber pressures and altitudes are presented. The report also includes some experimental results obtained in 100-pound thrust rocket engines using the hydrazine-chlorine trifluoride, hydrazine/ammonia fluorine, and ammonia-fluorine propellant combinations. Also included are the results of ignition delay studies using hydrazine fuel systems with white fuming nitric acid and hydrogen peroxide and some results involving the use of the hydrazine system as transition fuels for the gasoline-white fuming nitric acid propellant combination.

Theoretical Performance

The theoretical performance calculations were based on a chosen reaction and exhaust pressure and were carried out by a rapidly convergent, successive-approximation process developed by the NACA as described in Reference 1. This method was adapted for use with an IBM Card Programmed Electronic Calculator. The calculations were carried out on the basis of equilibrium composition during expansion rather than on the assumption of constant composition during expansion. Experimental data from rocket engines indicates that recombination takes place in the exhaust nozzle with a resulting tendency to approach equilibrium composition operation with fuels like hydrazine, ammonia, or hydrogen where hydrogen is the major component.

Performance calculations for hydrazine and fluorine were made at combustion pressures of 300, 600, and 1200 psia and at exit pressures corresponding to nozzles designed for complete expansion at altitudes of 0, 10,000, 30,000, 40,000, and 77,250 feet. Curves of specific impulse at a chamber pressure of 300 psia plotted against weight percent fuel for the 5 altitudes are shown in Figure 1. The maximum specific impulse for the sea-level curve is 316 pound-seconds per pound and increases to a value of 411 pound-seconds per pound at an altitude of 77,250 feet. The values of specific impulse plotted against weight percent fuel for the three chamber pressures expanding to sea level are shown in Figure 2. Included in the figure are lines of constant chamber temperature and moles per weight. The maximum specific impulse values are in the slightly fuel-rich region and increase from 316 pound-seconds per pound at 300 psia to 368 pound-seconds per pound at 1200 psia. On missile designs for long-range applications using the hydrazine-fluorine propellant combination it is of interest to know the optimum performance at altitude as well as at high chamber pressures. The maximum theoretical specific impulse available at altitudes from sea level to 77,250 feet for rocket combustion chamber pressures of 300, 600, and 1200 psia is shown in Figure 3. The peak specific impulse values at sea-level expansion increase over 16 percent in going from a chamber pressure of 300 psia to 1200 psia; at altitudes of 77,250 feet, the maximum specific impulse increase is slightly over 4 percent through the same chamber pressure range. These results indicate the importance of design altitude as an aid in determining the optimum chamber pressures. Calculations made with several rocket propellant combinations to determine the separate effect of increasing chamber pressure and the nozzle expansion ratio are presented in Reference 2. The results indicate that an increase in specific impulse obtainable with an increase in chamber pressure is almost entirely caused by the increased expansion ratio through the nozzle.

A serious limitation in the use of hydrazine as a rocket fuel is its freezing point. The use of additives to lower the freezing point of hydrazine from 0°C has been under investigation by many laboratories. Ammonia, which is a good rocket fuel by itself, has been used as an additive to lower the freezing point of hydrazine. In addition, the use of hydrazine as an additive to ammonia results in a reduction in the vapor pressure of pure ammonia. A fuel mixture containing 60 percent hydrazine and 40 percent ammonia has a vapor pressure at 0°C of 2.7 atmospheres compared to 4.7 atmospheres for 100 percent ammonia. Theoretical performance values of

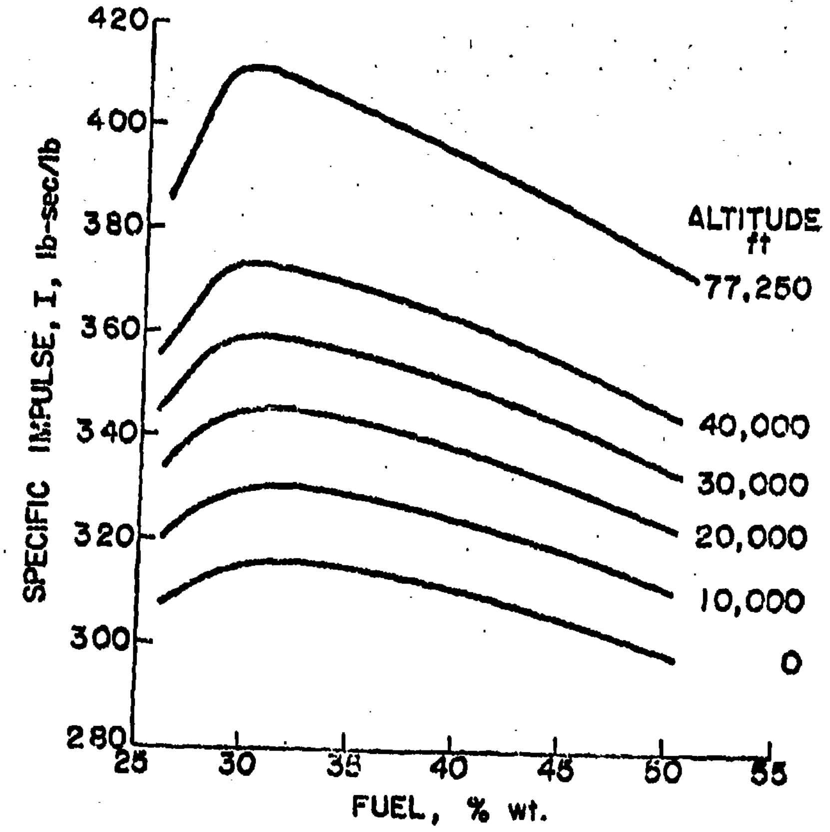


Figure 1. - Theoretical specific impulse of hydrazine with liquid fluorine; chamber pressure, 300 psia, exit pressure corresponding to altitude indicated.

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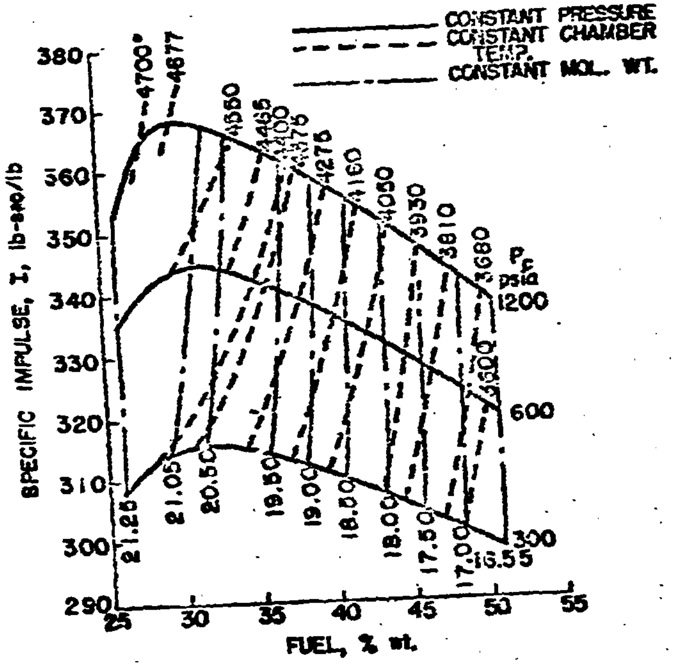

Figure 2. - Theoretical specific impulse of hydrazine with liquid fluorine.

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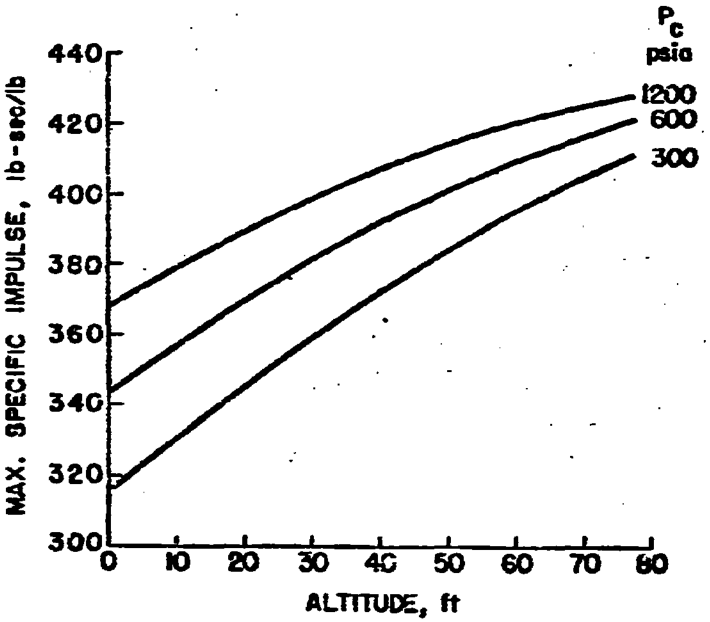

Figure 3. - Maximum theoretical specific impulse of hydrazine with liquid fluorine.

mixtures of hydrazine and ammonia with liquid fluorine at a combustion chamber pressure of 300 psia and sea level expansion are given in Figure 4. The maximum specific impulse increases linearly from about 311-pound-seconds per pound for 100 percent ammonia to 316 pound-seconds per pound for 100 percent hydrazine. Similarly, a linear relationship exists between the chamber temperatures (at the peak specific impulse) which vary from about 4300° K for ammonia to 4420° K for hydrazine and the exit temperatures which vary from about 3100° K for ammonia to 3240° K for hydrazine. These calculations indicate the slight performance differences that exist between the readily available ammonia and the rather costly hydrazine.

Further consideration has been given to the use of hydrazine and hydrazine-ammonia mixtures with oxygen bifluoride as the rocket oxidant. The advantages of oxygen bifluoride include its density (1.77 gr/cc compared to 1.56 gr/cc for fluorine) and its potential cost as an oxidizer with respect to fluorine. The high cost of fluorine is a major deterrent in its projected use for long-range missiles, and a decided cost advantage at a slight lowering in performance could be obtained by the use of mixtures of oxygen and fluorine either as oxygen bifluoride or as physical mixtures of the two. A comparison of the maximum theoretical performance of hydrazine with liquid oxygen bifluoride and with liquid fluorine at 300 psia chamber pressure and at various exhaust pressures is given in Figure 5 (complete theoretical performance data for hydrazine and oxygen bifluoride published in Ref. 3). The maximum specific impulse for the hydrazine-oxygen bifluoride combination at 300 psia chamber pressure and sea-level exhaust pressure is 298 pound-seconds per pound; at an altitude of 70,000 feet, the maximum specific impulse for the hydrazine-oxygen bifluoride increased over 29 percent to 385 pound-seconds per pound. In general, an increase in performance of approximately 6 percent is obtained with fluorine as the oxidant as compared with oxygen bifluoride.

The chamber temperatures for the hydrazine-oxygen bifluoride combination are approximately 8 percent lower than for the hydrazine-fluorine and the exit temperatures approximately 12 percent lower. The use of ammonia as an additive to hydrazine with oxygen bifluoride as the oxidant has also been investigated, and the theoretical performance values for a chamber pressure of 300 psia and sea-level exit pressure are presented in Figure 6 (complete theoretical values presented in Ref. 4). The specific impulse and chamber and exit temperatures are plotted against weight percent hydrazine in the fuel mixture and show the increases to be linear with the percentage of hydrazine in the fuel mixture. The specific impulse increases from 291 pound-seconds per pound for ammonia-oxygen bifluoride to 298 pound-seconds per pound for hydrazine plus oxygen bifluoride. The chamber temperature decreases from 3940° K for

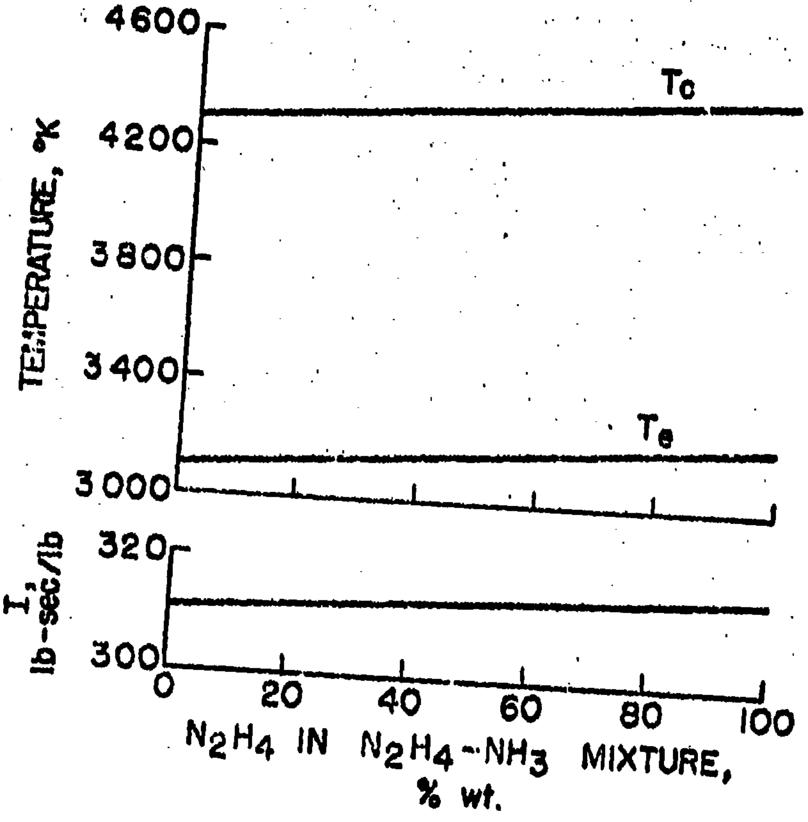

Figure 4. - Maximum specific impulse, chamber and exit temperatures of hydrazine-ammonia mixtures with liquid fluorine; chamber pressure, 300 psia.

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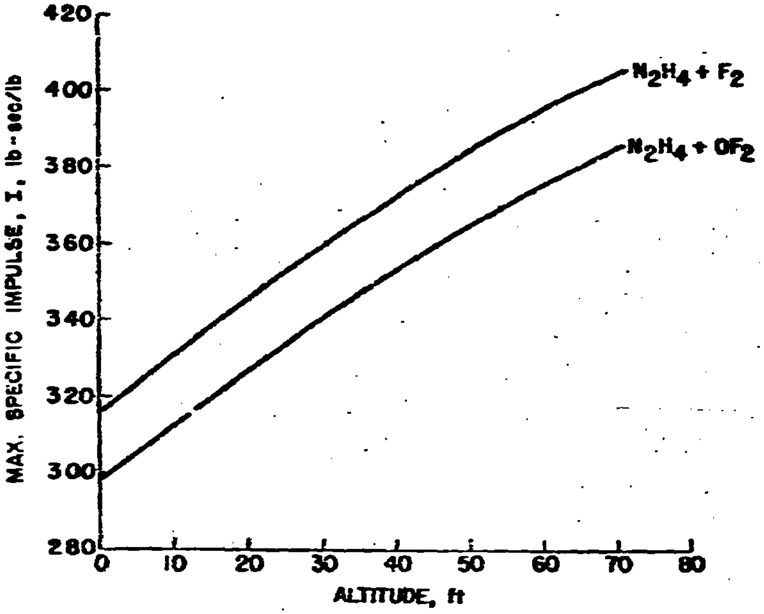

Figure 5. - Maximum theoretical specific impulse of hydrazine with liquid oxygen bifluoride and liquid fluorine; chamber pressure, 300 psia.

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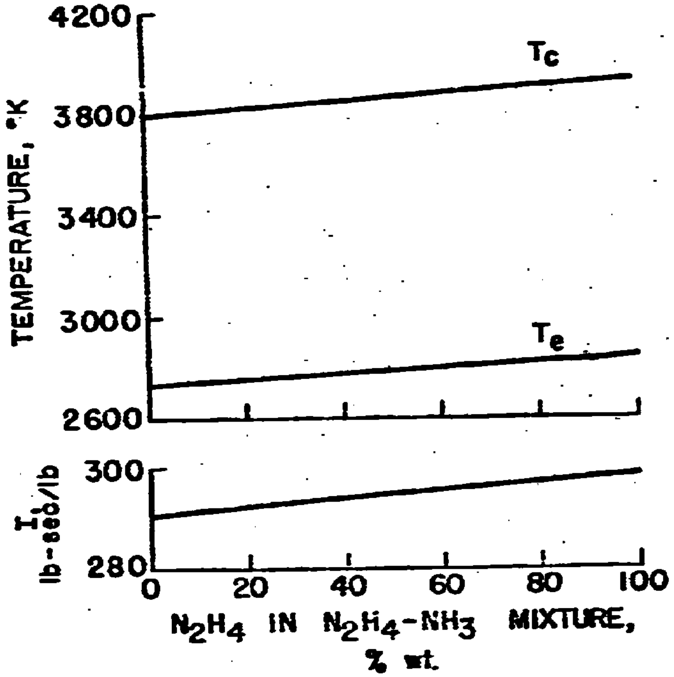

Figure 6. - Maximum specific impulse, chamber and exit temperatures of hydrazine-ammonia mixture with liquid oxygen bifluoride at a chamber pressure of 300 psia.

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hydrazine to 3792° K for ammonia and the exit temperature from 2848° K for hydrazine to 2722° K for ammonia. These calculations indicate again the slight performance differences between hydrazine and ammonia as rocket fuels.

Experimental Performance

The results of these calculations indicated the direction of our experimental work involving fluorine as the oxidizer and hydrazine, ammonia, and mixtures of the two as fuels. The initial fuel selected was a 40 percent ammonia in hydrazine mixture in an effort to compromise the performance and physical properties of the hydrazine and ammonia. The freezing point of the fuel mixture, which was analyzed to be 37 percent ammonia, 59 percent hydrazine, and 4 percent water, was -34° C. The maximum theoretical performance of the propellant combination is 314 pound-seconds per pound. The experimental investigation was carried out in 100 pound thrust rocket engine and the results published in Ref. 5. A diagrammatic sketch of the 100-pound thrust unit used is shown in Figure 7.

Helium cooled in a liquid nitrogen bath was used to force the propellants into the combustion chamber. The fuel mixture was prepared by introducing weighed amounts first of commercial hydrazine and then of ammonia into a mixing tank. Fluorine was condensed from the supply cylinder into the oxidant tank which was maintained in a liquid nitrogen bath. A photograph of the thrust stand with a rocket mounted is shown in Figure 8. The rocket engines were designed to deliver 100 pounds thrust at 300 psia chamber pressure. A dimensional sketch and photograph of an annular water cooled engine are shown in Figure 9. The experimental specific impulse is shown by Figure 10 for a propellant mixture range of 16 to 44 weight percent fuel; the theoretical (ideal) curve based on equilibrium composition expansion is also shown for comparison. Several different types of injectors were investigated and the curves are drawn through the experimental points obtained with a 50 L* engine using a 1 to 1 impinging jet injector with a turbulence coil, a 1-1 impinging jet injector, and a showerhead type injector.

The maximum performance values in the region from 17 to 35 weight percent fuel were obtained with the 1-1 impinging jet injector with the turbulence coil, and followed the theoretical curve within 80 to 90 percent. The peak experimental value with the 1-1 coil injector of 276 pound-seconds per pound was obtained at 33 weight percent fuel compared with the theoretical maximum of 313 pound-seconds per pound, at 28 percent fuel. The stoichiometric ratio was 26.8 percent. Specific impulse values obtained

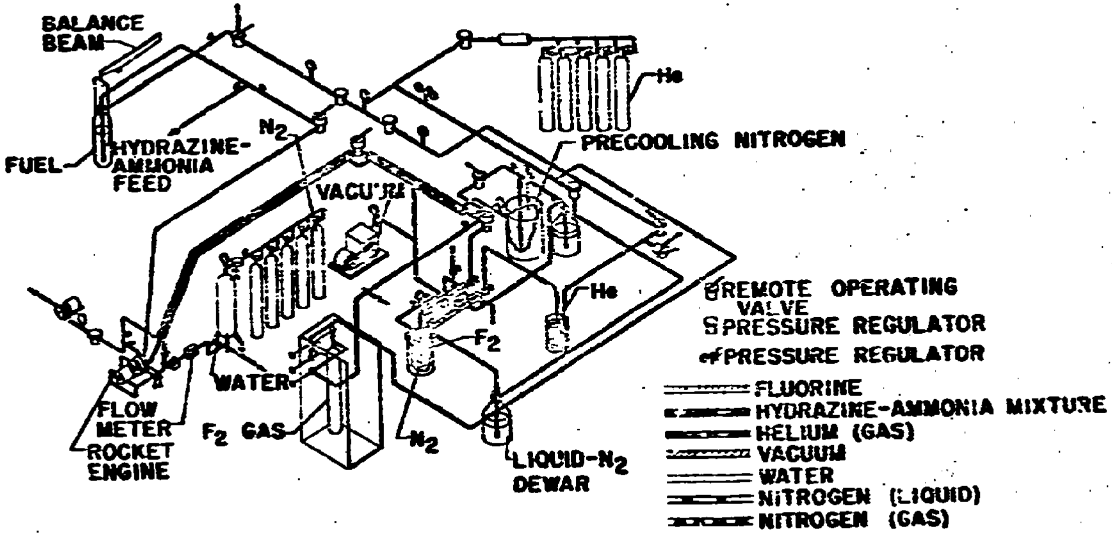

Figure 7. - Diagrammatic sketch of 100-pound-thrust rocket apparatus for investigation of liquid fluorine - hydrazine/ammonia.

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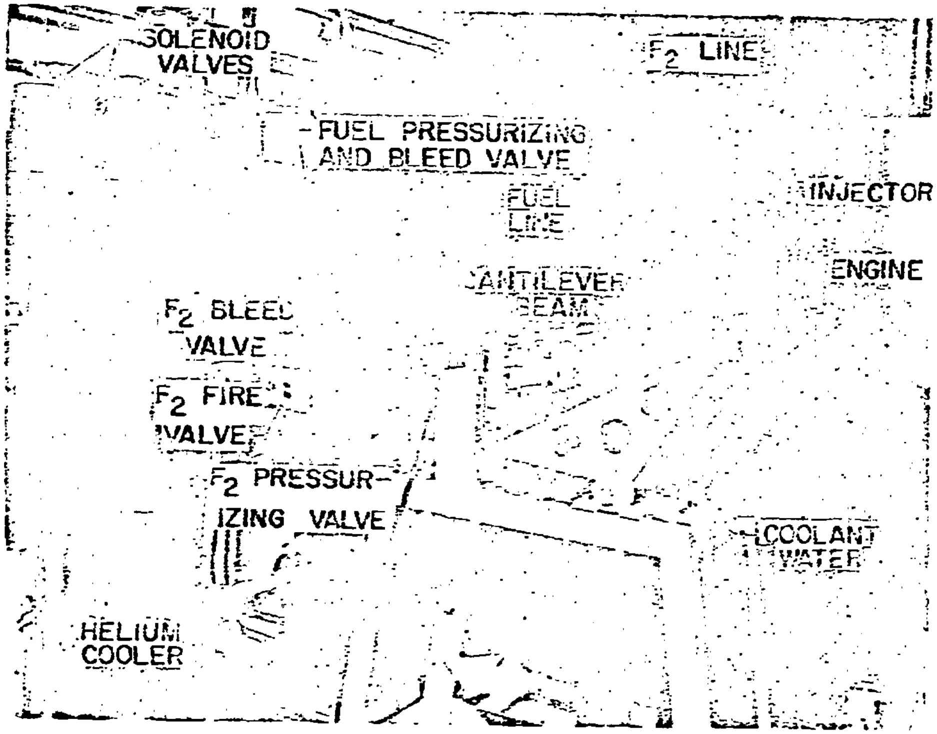
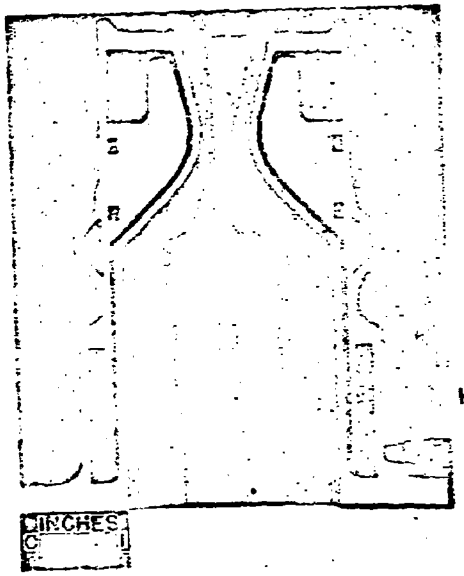
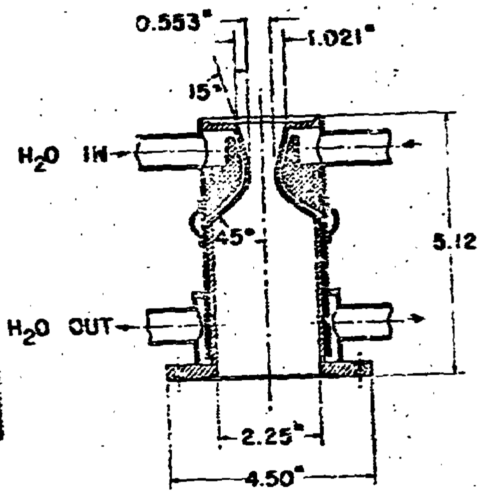


Figure 8. - Thrust stand for 100-pound-thrust fluorine - hydrazine ammonia rocket engine.



SECTION THROUGH CHAMBER AND NOZZLE



DIAGRAMMATIC SKETCH

Figure 5. - Combustion chamber and nozzle of 50L^* engine.

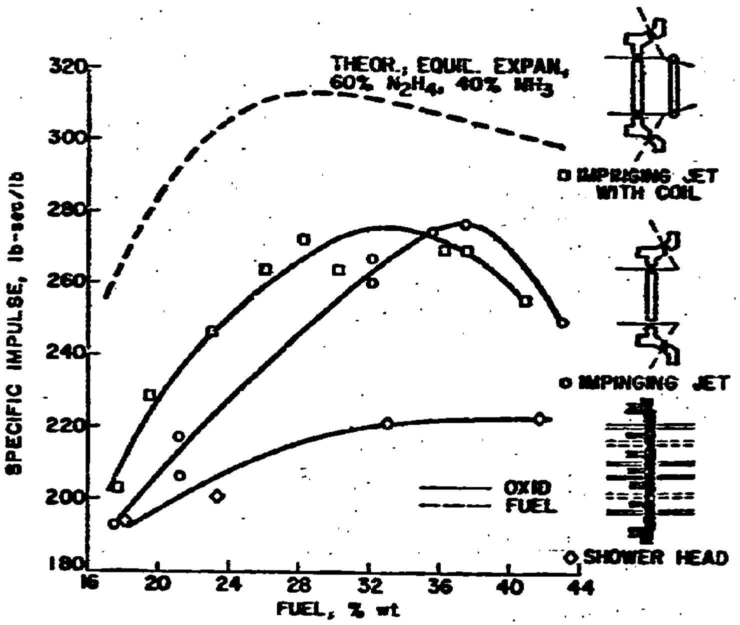


Figure 10. - Theoretical and experimental specific impulse of liquid fluorine and hydrazine-ammonia fuel in 100-pound-thrust rocket engine.

with the 50 L* engine and 1-1 impinging jet injector were lower in the region of 17 to 35 percent fuel; however, in the region greater than 35 percent fuel, the experimental performance with the use of the 1-1 impinging jet injector without the turbulence coil was slightly higher than with the coil. The maximum experimental value of 277 pound-seconds per pound at 37 percent fuel was obtained with the 1-1 impinging jet injector.

Since the fuel can be considered as a coolant, the greater performance obtained in the fuel rich region is desirable. The use of a more efficiently designed turbulence coil with the 1-1 injector would probably have given even higher performance, inasmuch as at weight percent fuels greater than 35 percent, the angle of the resultant propellant stream was sufficiently large to miss the turbulence coil. Specific impulse values obtained with the shower-head injector were considerably lower throughout the complete fuel oxidant range. The theoretical curve corrected for non-parallel flow from the exhaust nozzle and for the composition of the fuel (4 percent water) is lowered approximately 4 percent, while the experimental curve corrected for heat rejection and for deviations from the reference combustion chamber pressure of 300 psia is increased about 3 percent.

The corrected values show a maximum theoretical specific impulse of 301 pound-seconds per pound and a corrected experimental peak performance of about 284 pound-seconds per pound, 94 percent of the theoretical value. Values of characteristic velocity and heat rejection plotted against weight percent fuel are shown in Figure 11. Maximum values of C* were obtained with the impinging jet turbulence coil injector. The peak value of 6820 feet per second was obtained at 33 percent fuel which compares favorably with the theoretical maximum of 7080 feet per second at 31 weight percent fuel. In the region from 22 to 40 percent fuel, experimental values from 90 to 96 percent of the ideal theoretical values were obtained. Heat rejection values of 2.5 to 3.5 Btu per second per square inch were obtained with the 50 L* engine in which the impinging jet turbulence coil injector was used.

The results, in general, have indicated that the attainment of maximum performance with liquid fluorine and a 60-40 hydrazine/ammonia mixture requires a critical study of injector design in spite of its very high reactivity. Several runs were made with hydrazine as the fuel using a 4 oxidant on 1 fuel impinging jet injector, all resulting in extremely low performance. In addition, a considerable number of runs made with pure ammonia as the fuel indicated the same trend as with hydrazine and the hydrazine-ammonia mixture, the injector design being the critical factor in obtaining high performance. The experimental performance obtained with

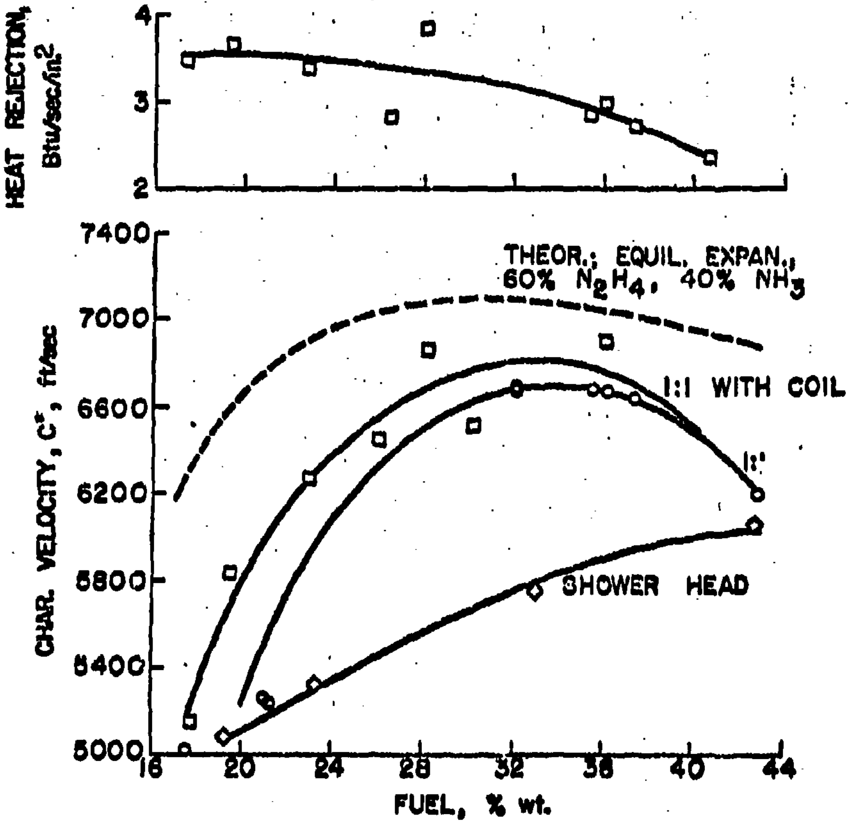


Figure 11. - Theoretical and experimental characteristic velocity and experimental heat rejection of liquid fluorine hydrazine-ammonia fuel in 100 pound-thrust engine.

ammonia plus fluorine is shown in Figure 12. Various injectors were investigated with a 100-pound thrust engine at a combustion chamber pressure of 300 psia. Maximum performance was obtained with a triplet type injector, two oxidant streams hitting one fuel stream. The maximum specific impulse obtained was 270 pound-seconds per pound, approximately 87 percent of the ideal theoretical value. Correcting the experimental values for the heat rejection increased the peak performance to 274 pound-seconds per pound, 91 percent of the theoretical value for the actual nozzle used.

Since the problems associated with the attainment of high performance appear to be similar for hydrazine, ammonia, and mixtures of the two with liquid fluorine, the NACA is continuing its studies of high energy propellants with the ammonia-fluorine propellant combination. The small sacrifice in performance in using ammonia rather than hydrazine appears to be warranted because of the high cost and physical properties of the hydrazine.

The consideration of hydrazine with chlorine trifluoride as a high performance storageable propellant combination involved its experimental evaluation in a 100-pound thrust engine at a chamber pressure of 300 psia. The experimental specific impulse plotted against weight percent fuel for the hydrazine-chlorine trifluoride combination is shown in Figure 13. (Complete experimental results published in Ref. 6.) The ideal theoretical curve, theoretical curve corrected for the fuel and nozzle used and the experimental curve corrected for heat rejection are included for comparison. The peak experimental value obtained, with a double impinging jet injector, was 234 pound-seconds per pound at 33 weight percent fuel; 88 percent of the ideal theoretical maximum of 264 pound-seconds per pound. Correcting the experimental performance for the heat rejection increased the peak value to 248 pound-seconds per pound, approximately 98 percent of the theoretical value for the fuel and nozzle used. Experimental values of characteristic velocity and heat rejection are presented in Figure 14. The maximum C value obtained was 5590 feet per second and the heat rejection varied from 0.8 to 1.5 Btu/second per square inch. The results of this investigation indicated the ease of ignition and high performance available. The peculiar shape of the curves indicating a sharp rise in performance and in heat rejection at approximately 29 percent fuel is attributed to the injection system used.

The third phase of the NACA work with hydrazine systems involved the study, to a limited extent, of their ignition delay with several oxidizers and their application as transition fuels for the white fuming nitric acid-gasoline propellant combination.

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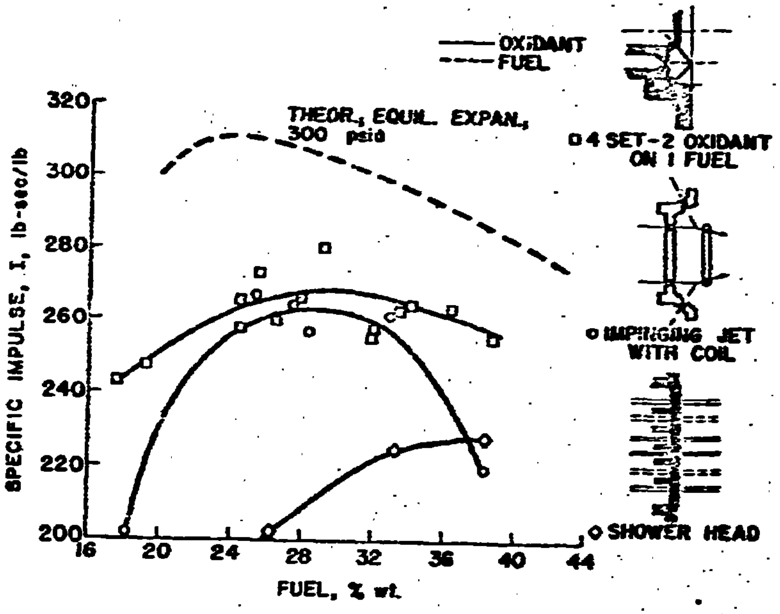

Figure 12. - Theoretical and experimental specific impulse of liquid fluorine and liquid ammonia in 100-pound-thrust rocket engine.

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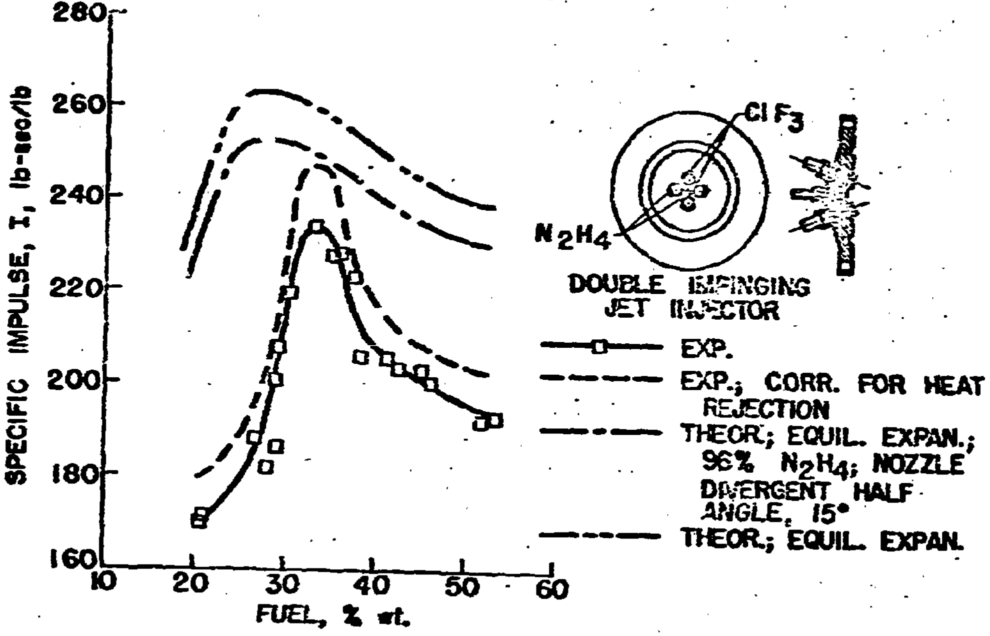

Figure 13. - Theoretical and experimental specific impulse of chlorine trifluoride-hydrazine in 100-pound-thrust engine.

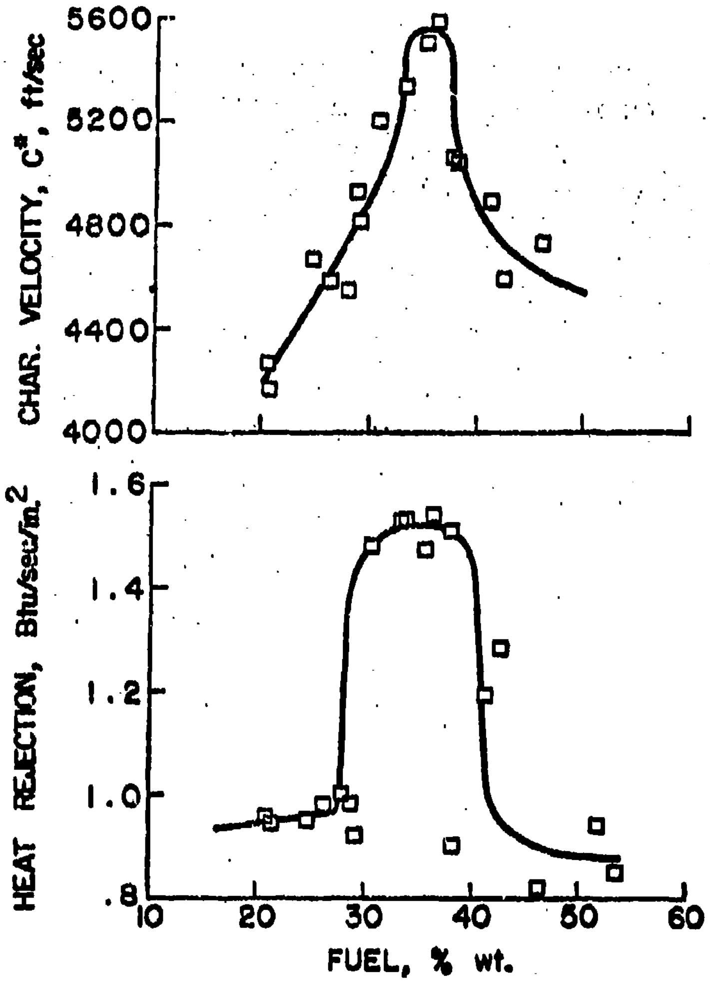

Figure 14. - Experimental characteristic velocity and heat rejection of chlorine trifluoride - hydrazine in 100-pound-thrust engine.

Results of ignition delay studies involving hydrazine fuel systems have been published in Refs. 7 and 8. Ignition delay measurements of many fuels and oxidants were made at various temperatures and pressures using a small scale rocket engine of approximately 50 pounds thrust. The small scale rocket engine apparatus used for the ignition delay studies is shown diagrammatically in Figure 15. The apparatus, described in detail in Ref. 8, consists of a transparent-sided engine of approximately 50 pounds thrust, propellant tanks, a constant temperature for regulating propellant temperatures, and a high speed camera to record the action in the combustion chamber.

A summary of ignition delay data obtained with the small scale rocket engine apparatus using hydrazine hydrate and hydrazine with white fuming nitric acid and hydrazine with hydrogen peroxide are presented in Table I.

Hydrazine hydrate and white fuming nitric acid. Fourteen runs were conducted at temperatures from 110° to -40° F at sea level pressure. A plot of ignition delay against temperature is shown in Figure 16. The dotted lines enclose all the runs; the ignition delays ranged from an average of approximately 16 milliseconds at 110° F to approximately 146 milliseconds at -40° F.

Hydrazine and white fuming nitric acid. Twelve runs were made with one resulting in an explosion. The ignition delay of all measurable runs was 5.5 ± 1.5 milliseconds. These runs were conducted at temperatures from 72°F to 36°F, initial ambient pressures from 760 to 50 millimeters of mercury. For the runs at low initial ambient pressures, the average delays were slightly longer than for those at sea-level pressure. All runs resulted in "hard starts" as indicated audibly and by the high speed pictures. The run that was terminated by an explosion had a delay of 8.4 milliseconds.

Hydrazine and hydrogen peroxide. Nine runs were made; the first seven were terminated by explosions. The explosion damage was confined to the shattering of the plastic combustion chamber. The widely variant ignition delays ranged from 9.3 to 33.5 milliseconds and could not be correlated successfully with either temperature, initial ambient pressure, or fuel/oxidant ratio. The temperature ranged from 72°F to 36°F, the initial ambient pressure from 760 to 50 mm.

The results of the ignition delay studies made in the 50-pound thrust engine indicate the suitable starting characteristics of the hydrazine-white fuming nitric acid combination at temperatures of 36°F and the hydrazine hydrate-white fuming nitric acid combination at temperatures down to -40°F.

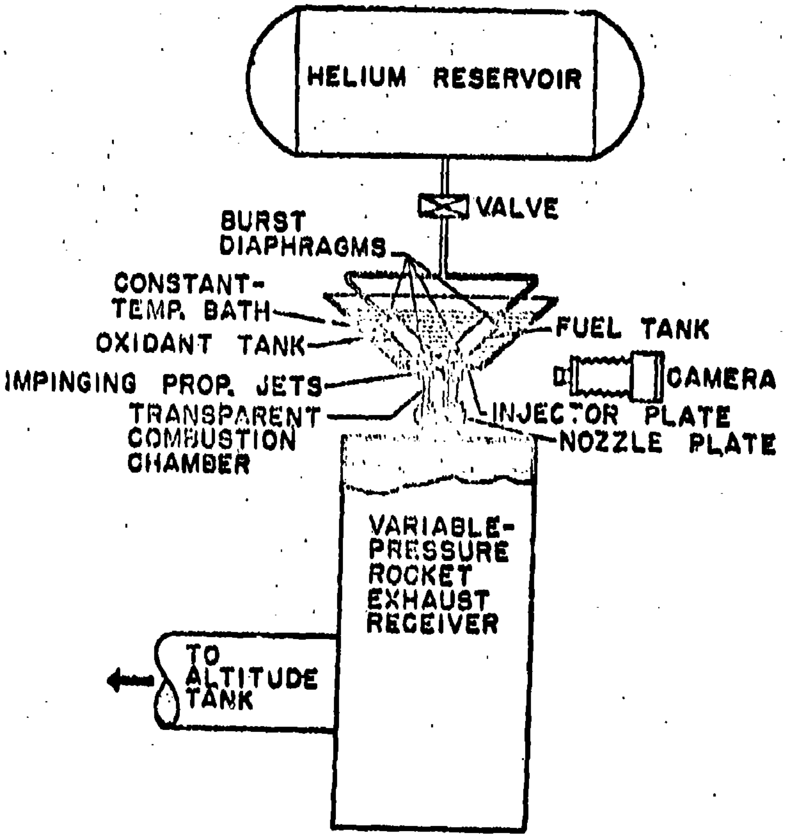

Figure 15. - Small-scale rocket engine ignition delay apparatus.

TABLE I

SUMMARY OF DATA OBTAINED IN SMALL-SCALE ROCKET-ENGINE APPARATUS

Average propellant temp. °F	Initial Ambient pressure mm Hg	Peak combustion-chamber pressure lb/sq in gage	Time to attain peak combustion chamber pressure, sec	Ignition delay millisec
		Hydrazine and White Fuming Nitric Acid		
72	760	333	1.6	5.5
72	760	347	1.8	5.8
36	760	385	1.4	5.9
36	760	a---	a---	8.4
36	760	345	1.1	5.1
72	48.5	377	1.8	6.0
72	50.0	378	1.1	6.9
72	760	371	0.9	4.5
72	760	379	1.2	5.4
71	760	402	1.5	4.0
72	760	404	1.7	5.5
		Hydrazine and Hydrogen Peroxide		
72	760	a---	a---	24.7
73	760	208	1.9	4.5
36	760	a---	a---	9.3
36	760	a---	a---	16.5
72	48.5	a---	a---	33.5
72	48.5	a---	a---	10.8
72	760	a---	a---	13.3
72	760	a---	a---	18.4
		Hydrazine Hydrate and White Fuming Nitric Acid		
110	760	b---	b---	17.0
110	760	237	2.5	15.3
80	760	174	2.7	19.1
80	760	216	2.5	16.7
50	760	170	2.7	23.6
50	760	227	2.6	26.2
20	760	192	2.6	29.6
20	760	235	2.5	50.1
-9	760	181	2.4	59.5
-10	760	224	2.3	104.7
-10	760	179	2.2	70.2
-10	760	220	2.2	54.4
-39	760	a---	a---	>631
-41	760	139	5.0	130.7

[a] Explosion

[b] Clogged combustion-chamber pressure tap

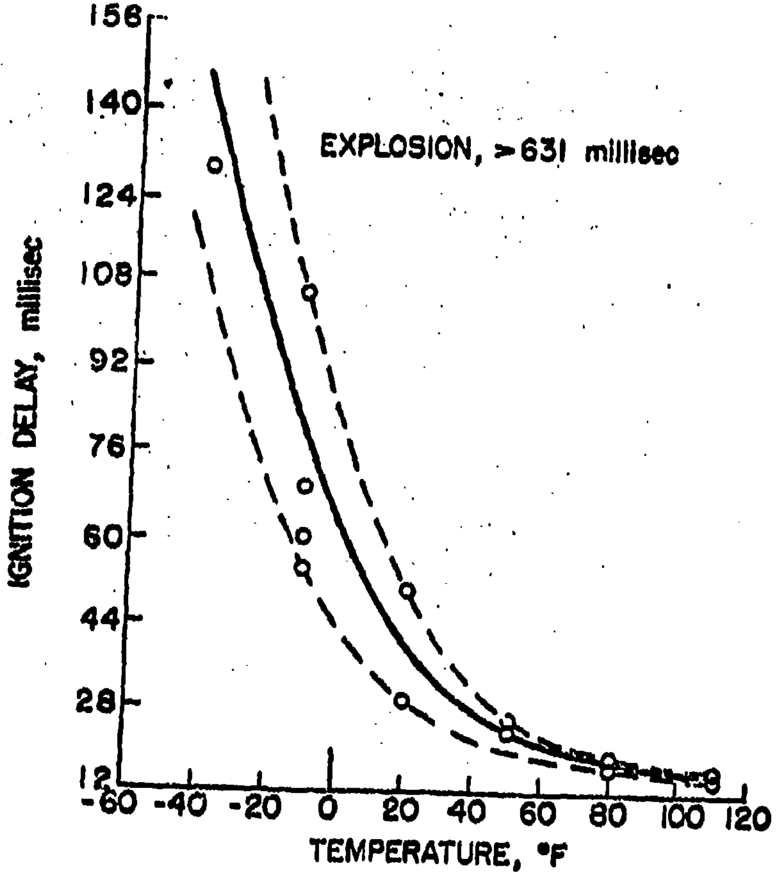

Figure 18. - Ignition delay of hydrazine-water and white fuming nitric acid (USAF specification No. 14104) at sea-level pressure.

The use of small quantities of fluids that ignite spontaneously with white fuming nitric acid was investigated as igniter fluids for the acid-gasoline reaction. The preliminary investigation which included hydrazine hydrate as one of the igniter fluids was carried out in a 200-pound thrust rocket engine and the results published in Reference 9. With respect to ignition of propellants in the unit, it was found that ignition could be obtained at -85°F with fuel blends of aromatic amines and triethylamine utilizing red fuming nitric acid as the oxidant. Satisfactory ignition was adjudged by sound and a continuously rising chamber pressure trace consistent with valve opening time. A summary of the ignition and transition results is presented in Table II.

At temperature of 40°F, transition to gasoline was obtained with hydrazine hydrate and mixtures of aromatic amines with white fuming nitric acid as the oxidant. For the same thrust cylinder design as was used in this investigation, the Aerojet Engineering Corporation has designed a propellant valve which gives transition from hydrazine hydrate to gasoline at -40°F with white fuming nitric acid (Ref. 10). The flow characteristics of their main propellant valve are such that a small amount of gasoline enters the chamber along with hydrazine hydrate during the ignition phase. With the present engine configuration, this condition was simulated by suspending 5 percent gasoline in the hydrazine hydrate which resulted in satisfactory transition at -40°F. When 10 percent gasoline was dissolved in the triethylamine-orthotoluidine blend, a similar transition at -40°F could not be obtained.

Thus, it appears that in an engine of low characteristic length, it is necessary to introduce the gasoline while a substantial portion of the igniter fluid is still entering the chamber and reacting.

Conclusion

The theoretical specific impulse for hydrazine with fluorine at 300 psia and sea-level exit pressure is 316 pound-seconds per pound which is the maximum for chemical propellants excepting the hydrogen-fluorine, lithium-fluorine, and hydrogen-ozone propellant combinations. The high performance and density of hydrazine are its main advantage, but the cost and freezing point would appear to make its use for long-range missiles problematical. It appears to be more advantageous to use ammonia or, possibly, ammonia-hydrazine blends as the fuel. The peak performance of the ammonia-fluorine combination is 311 pound-seconds per pound, slightly lower than hydrazine with fluorine, but the ammonia is cheap and widely used in industry.

TABLE IX

SUMMARY OF TRANSITION DATA

OXIDANT	IGNITER FUEL	-85°F		-40°F		40°F	
		IGNITION	TRANSITION	IGNITION	TRANSITION	IGNITION	TRANSITION
RFNA	Hydrazine Hydrate[1]	Propellants Freeze		Yes	No	Yes	Yes
RFNA	Hydrazine Hydrate[1] Plus 5 percent suspended gasoline	Propellants Freeze		Yes	Yes	Yes	Yes
RFNA	50 percent Triethylamine 50 percent Diallylaniline	Yes	No	Yes	No	Yes	Yes
RFNA	70 percent Triethylamine 30 percent Orthotoluidine	Yes	—	Yes	No	Yes	Yes
RFNA	63 percent Triethylamine 27 percent Orthotoluidine 10 percent Gasoline (MIL-F-5572)	—	—	Yes	No	—	—

[1] 64 percent Hydrazine

Hydrazine alone does not appear to have an advantage over ammonia or a mixture of the two with fluorine with respect to the problems of attaining peak experimental performance. The injector design problem has been found to be similar for the three fuels. With a limited number of injectors tried, experimental specific impulse values of about 90 percent of the theoretical have been obtained for a hydrazine-ammonia mixture and ammonia with fluorine in 100 pound thrust rocket engines. Initial results with hydrazine and fluorine have given extremely low values and further injector design studies would be required should work on this combination be continued.

Hydrazine and hydrazine hydrate do appear to be promising as igniter fluids with acid at moderate temperatures. Temperature limits restrict the use of hydrazine; however, hydrazine hydrate has ignited satisfactorily at -40°F. Hydrazine hydrate has been used successfully as a transition fuel, at -40°F, for the gasoline-white fuming nitric acid propellant combination; at much lower temperatures, however, other fuels are required.

* * *

Abstract

The theoretical performance of hydrazine and hydrazine-ammonia mixtures with fluorine and oxygen bifluoride at various chamber pressures and altitudes was determined. Experimental results of the hydrazine-chlorine trifluoride, hydrazine/ammonia mixture - fluorine and ammonia-fluorine propellant combinations obtained in 100-pound thrust rocket engines are described and discussed. Ignition delay studies involving hydrazine and hydrazine-water mixtures with white fuming nitric acid and hydrogen peroxide and some results using the hydrazine fuel system as transition fuels for the gasoline-white fuming nitric acid combination are presented.

* * *

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DISCUSSION ON PAPERS BY
ERNEST D. CAMPBELL AND PAUL M. ORDIN

THE CHAIRMAN: The speakers have cooperated beautifully this morning and we have some time for discussion if anyone has any matters to bring up.

DR. LEWIS: Mr. Ordin, in your first slide you showed the change of impulse with increasing altitude. Were these calculations made on the basis of the ambient pressure or was the pressure the same regardless of the altitude? If the latter, what pressure?

MR. ORDIN: The pressures were all at 300 pounds per square inch.

DR. LEWIS: In the chamber?

MR. ORDIN: Yes

DR. LEWIS: The pressure dropped?

MR. ORDIN: It was a matter of expansion ratio because the exit pressure dropped.

DR. MILLER: I would like to ask Mr. Campbell, in his reaction between the hydrazine and the ammonium thiocyanate, if equilibrium pressure measurements have been made.

MR. CAMPBELL: I believe that measurements are under way at this time to measure the pressure.

DR. MILLER: How high is it?

MR. CAMPBELL: Crudely speaking at 65°C, I think probably in the nature of about 3 atmospheres.

MR. WILSON: A question of Mr. Campbell. Were the freezing points taken of the thiocyanic acid in it or the equilibrium ammonium solution?

MR. CAMPBELL: In the preparation of solutions there is some ammonia loss during the preparation if it is in an open system.

MR. WILSON: What percent?

MR. CAMPBELL: There is a distinct loss, probably in the nature of about 20 percent of the available ammonia if it is in an open system.

MR. R. A. McALLISTER (Georgia Institute of Technology): I would like to ask Mr. Ordin to describe the turbulence coil, and to name its material of construction.

MR. ORDIN: The rocket engines used for the fluorine work were made of nickel, brass, and copper. We have a number of rocket engines made of these materials and they all work quite well. The engines used have been water cooled. The turbulence coils consisted of copper coils and were so designed to permit the resultant of the fuel and oxidant stream to impinge on the coil when operating the engine through a wide fuel oxidant ratio. The fuel ratios could be varied by changing the pressures on the propellant tanks. The change in fuel oxidant ratio would, however, change the angle of the resultant stream and for several of the runs the angle was sufficiently great to miss the coil. The turbulence coil was essentially a single coil placed in front of where it was felt the resultant streams would be for most of the runs. The turbulence coil was water cooled.

MR. BRADFORD DARLING (Massachusetts Institute of Technology): I would like to ask Mr. Campbell to describe the technique of the ignition delay measurement.

MR. CAMPBELL: We have a metal chamber which can be placed in a thermostated box to attain any desired temperature. Near the bottom of the chamber is a small concave cup. The propellants are injected to impinge on or near the surface of the cup. We always lead with a small amount of oxidizer first. This triggers a sweep circuit on an oscilloscope; a photo cell senses the appearance of flame and stops the timing measurement.

MR. DARLING: What is the magnitude of the lead?

MR. CAMPBELL: In the neighborhood of about 1 millisecond. It is calibrated each time.

THE CHAIRMAN: That seems to be all the questions. What was interesting to me was the fact that the first speaker mentioned the efforts of a manufacturer to bring down the cost and almost every subsequent speaker mentioned that one of the considerations was the cost of the material we are dealing with. I think you are all to be congratulated on being so cost conscious.

NOL PROGRAM FOR THE INVESTIGATION OF THE HYDRAZINE MONOPROPELLANT SYSTEM FOR GUN APPLICATION

by

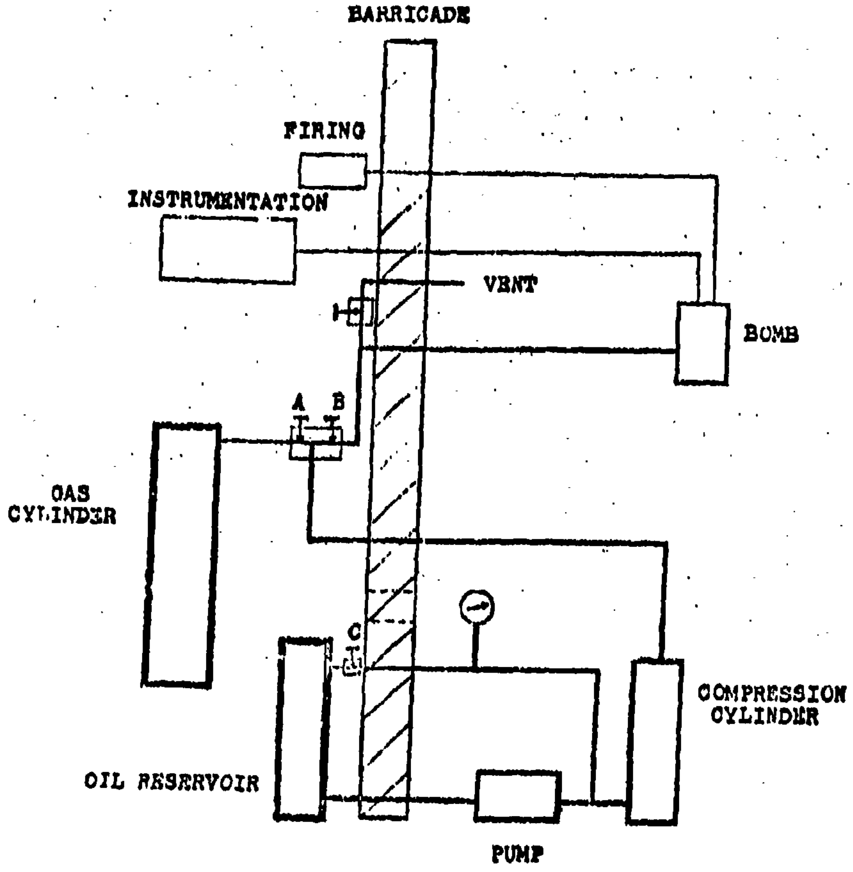
Louis LoFiego
U. S. Naval Ordnance Laboratory

The Bureau of Ordnance assigned NOL a general task for the investigation of the hydrazine-hydrazine nitrate-water monopropellant system. In the discussion that follows the tri-component mixtures used in this system will be referred to simply as hydrazine mixtures. The purpose of this discussion is to outline what has been done at the Laboratory and briefly describe the program now being conducted.

Three reports to date have been published in connection with the Laboratory studies of the hydrazine mixtures. NAVORD 2355 dated February 1952 covers the investigations of the physical and chemical properties. Densities, refractive indices, freezing points, sensitivities, impetus values, and vapor pressures of various hydrazine mixtures are reported. NAVORD 2563 dated August 1952 covers detonability, stability, and compatibility studies. Another paper presents details of the detonability studies. Stability and compatibility studies will be briefly presented later in this discussion. NAVORD 2715, now being processed, describes analytical procedures developed at NOL and presents additional compatibility data. The paper describing analytical procedures has been made available to members of this Symposium.

At present the program includes five tasks.

<u>Task 1 -- Burning Rate Studies at Pressures up to 100,000 psi:</u> Initial determinations of the linear burning rate of various hydrazine mixtures are being made in equipment that will permit studies up to 30,000 psi. A diagram of the equipment is shown in Figure 1. The system is filled with nitrogen from a standard cylinder through valves A and B. The oil reservoir is at atmospheric pressure. Valve A is closed and pumping is started. This pumps oil into the compression cylinder, thereby compressing the nitrogen. When the compression cylinder is nearly filled with oil, valve B is closed and the oil returned to the reservoir through valve C using tank pressure. The cycle is repeated until the desired pressure is reached. Figure 2 is a photograph of the burning



BURNING RATE BOMB ASSEMBLY

FIGURE I

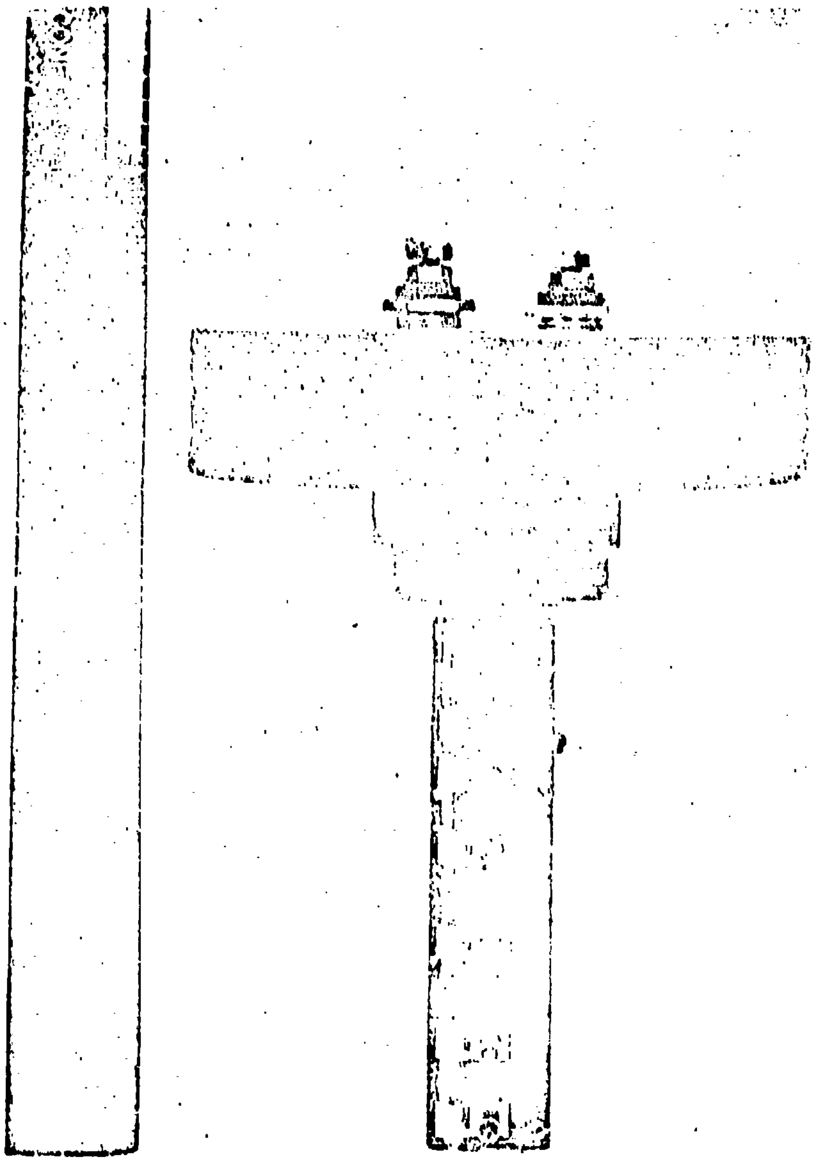


FIGURE 2. BOMB CAP WITH BURNING RATE TUBE ASSEMBLY

rate tube assembly attached to the bomb cap. The column of liquid in the vycor tube is ignited by a hot coil and the rate is determined by a series of burn-out wires.

The Bureau of Ordnance requested the Laboratory to investigate the combustion of the hydrazine mixtures in a closed system up to 80,000 psi. Dr. Noonan of the Laboratory has assembled a high-pressure system (Figure 3) that will permit burning rate studies up to 100,000 psi. Nitrogen gas is fed into the system from a group of series-connected gas cylinders. The first stage consists of a double-acting liquid pump with two low-pressure accumulators (C_1 and C_2). Oil is supplied to the pump at 1000 psi by a pump between the first stage and the oil reservoir. Movement of the piston pulls gas into one accumulator while compressing the gas into the other accumulator. The check valves prevent the gas pressure from backing into the supply tanks.

The second stage automatically takes over when the first stage reaches a pressure of approximately 15,000 psi. The pump forces oil into accumulators D_1 and D_2, where a system of check valves permits the high-pressure gas to be fed into the bomb and prevents any gas flow into the first stage. The sequence valve is pressure-operated and switches from Stage 2 to Stage 1 when the pressure between stages drops to a pre-set value. Figure 4 is a photograph of the high-pressure assembly. The assembly is operated by remote control behind the barricade shown.

Task 2 -- Ignition Studies. A closed bomb as shown in Figure 5 will be used in these studies. The bomb has a diaphragm that will shear when pressures exceed 4,000 psi. It is felt that sustained burning of the liquid mixture will occur if pressures of this order are obtained in the bomb. It is planned to vary the loading density of the bomb. A study of the P-T curves that will be recorded during ignition and combustion may provide a basis of comparison of the various ignition systems that will be investigated. Experimental pyrotechnic mixtures that have been prepared at the Laboratory in connection with solid propellant ignition studies will be investigated, along with other conventional ignition systems.

Task 3 -- Stability and Compatibility Studies. Stability and compatibility studies have been conducted at ambient temperature in the closed system shown in Figure 6. Various materials were placed in contact with representative hydrazine mixtures and changes in pressure in the system noted. Control solutions provided a reference indicator. The stability of the control solutions was considered satisfactory; however, there was an initial reaction that ceased once the oxygen in the closed system

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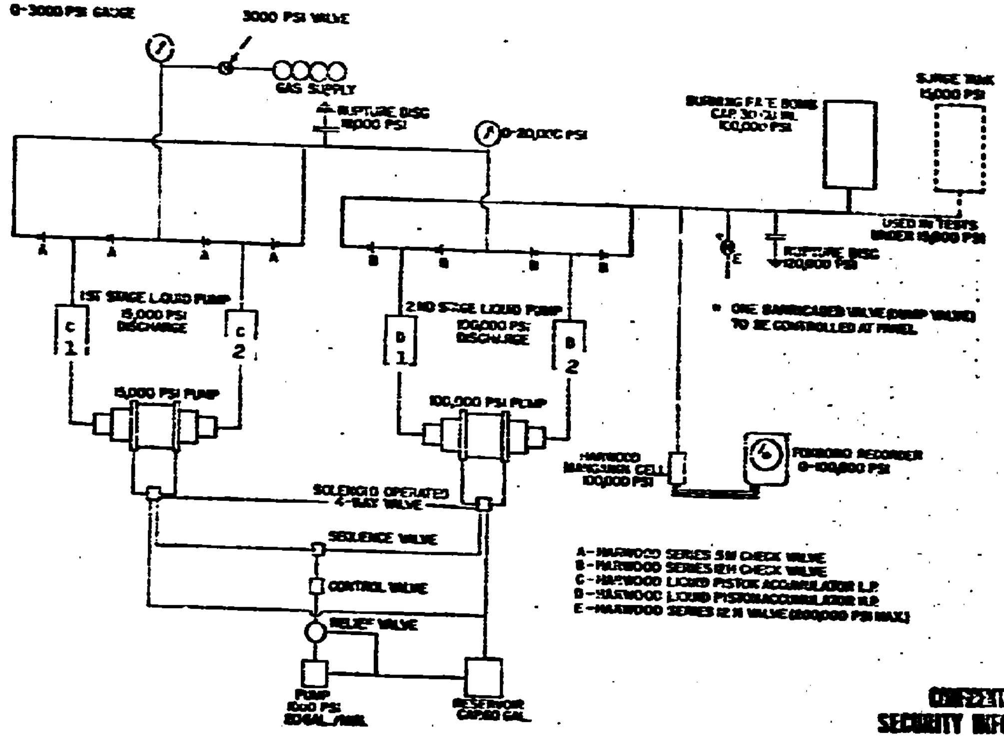
FIGURE 3



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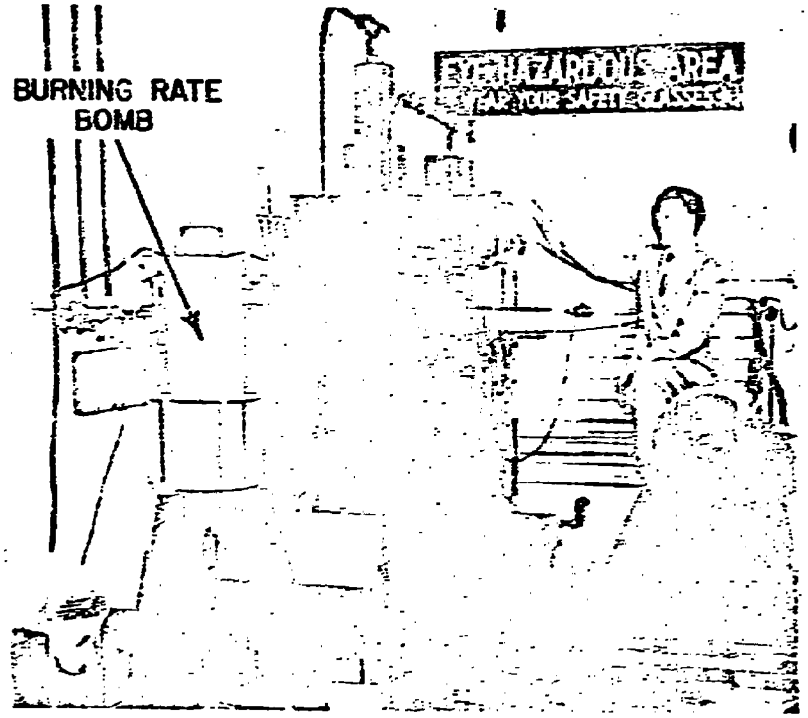
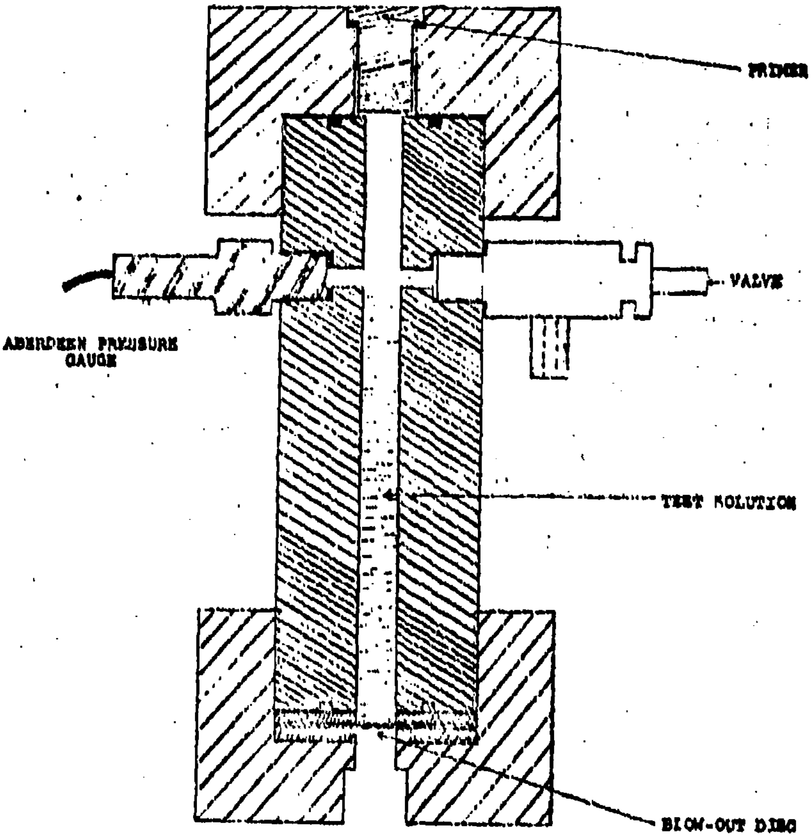


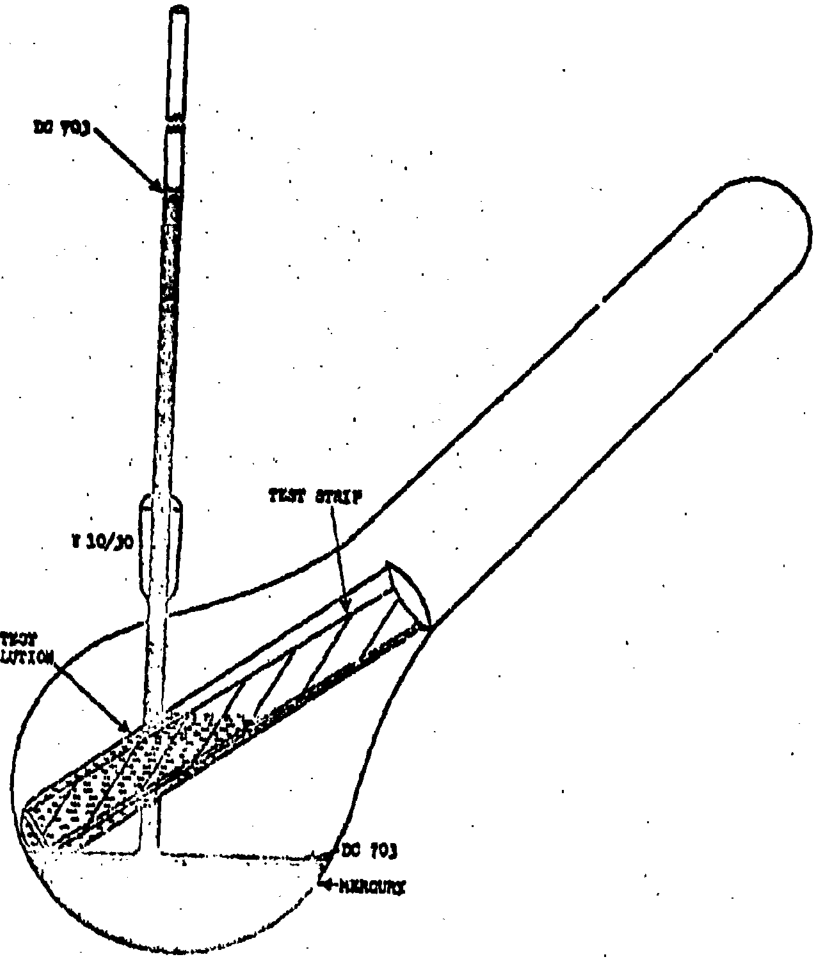
APPARATUS FOR HIGH PRESSURE BURNING RATE STUDIES

FIGURE 4



IGNITION STUDY BOMB

FIGURE 5



CLOSED SYSTEM COMPATIBILITY APPARATUS

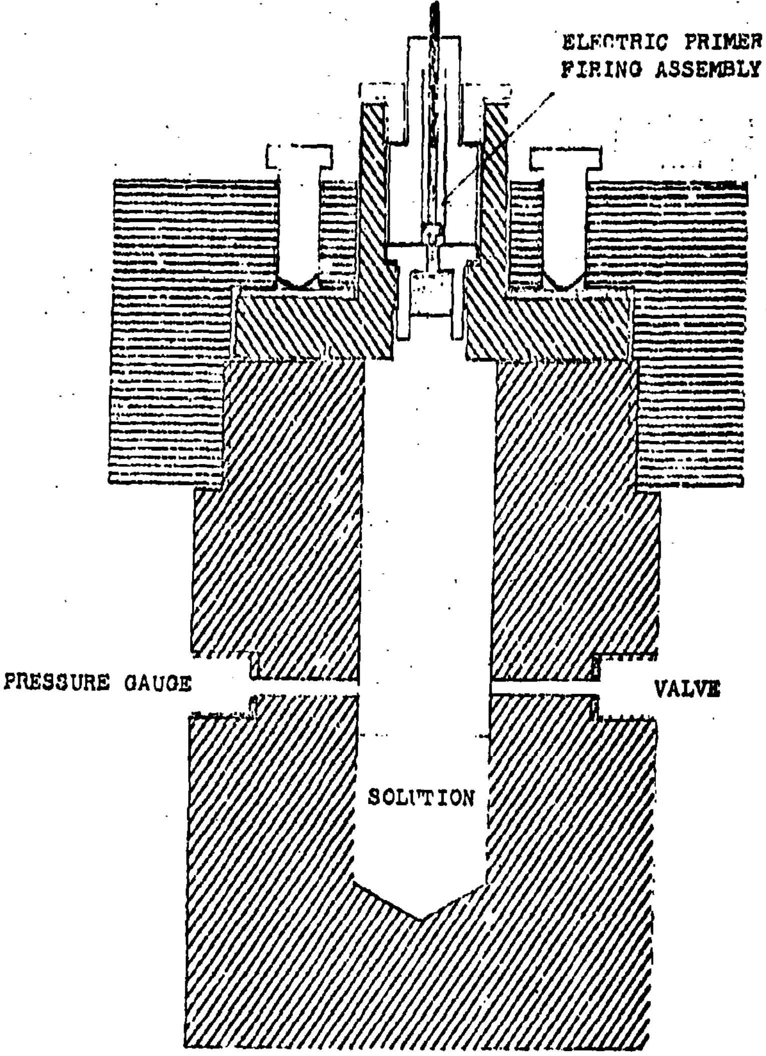
FIGURE 6

was consumed. Teflon, nylon, polystyrene, polyethylene, tantalum, and titanium were found compatible with the hydrazine mixtures. Contradictory results were obtained with 2S aluminum.

Compatibility studies at 160°F have been planned. The solution and material to be tested will be placed in a closed tube with a horizontal closed-end calibrated manometer. The tube will be placed in a bath and pressure changes in the closed system will be noted.

Task 4 -- Impetus Measurements. One of the requirements specified by the Bureau of Ordnance for the hydrazine mixtures is a minimum impetus of 350,000 ft lb/lb. A closed bomb, Figure 7, has been used to determine the impetus of various hydrazine solutions. The peak pressure developed in the bomb, multiplied by the volume, provides a PV value that is a measure of the impetus. Some of these measurements are reported in NAVORD 2255. Additional measurements will be made correcting for covolume and loss of pressure due to cooling. All compositions that have an impetus in the order of 350,000 ft lb/lb will be checked by NHT calculations.

Task 5 -- Determination of the Shock Sensitivity of Hydrazine Mixtures. The purpose of these studies is to determine how the shock sensitivity of the hydrazine mixtures compares to the solid propellants now being used in guns and rocket motors. The test procedure used for determining the detonability of the hydrazine of the hydrazine as described in Mr. Dwiggins' paper will be modified to include plastic discs between the tetryl pellet and the hydrazine solution. The number of discs required to prevent the detonation of hydrazine solution by the tetryl will be used as a basis for comparing the sensitivity of the hydrazine mixtures with other solid propellants.



BOMB FOR IMPETUS MEASUREMENT

FIGURE 7

CATALYSTS FOR THE THERMAL DECOMPOSITION OF HYDRAZINE WHEN USED AS A MONOPROPELLANT OR AS A GAS GENERANT

by

Arthur F. Grant, Jr.
Jet Propulsion Laboratory, California Institute of Technology

Abstract

The use of hydrazine as a monopropellant or as a gas generant involves its adiabatic thermal decomposition. In order to obtain the complete decomposition of hydrazine in reaction chambers of reasonable size and weight, it is necessary to use catalysts which increase the rate of decomposition of the hydrazine. For this purpose, a catalyst consisting of metallic iron, nickel, and cobalt deposited on porous aluminum oxide pellets was developed and tested*. With this catalyst, optimum performance of hydrazine as a monopropellant was achieved with a reaction time of less than 3 millisec. The decomposition gases produced with this catalyst and reaction time contained about 30 mol per cent ammonia and had an average molecular weight of about 14 lb/mol. The temperature of the gases leaving the catalyst bed was about 1850°F.

In the use of hydrazine as a gas generant it is desirable to decrease the molecular weight and temperature of the decomposition gases through the complete dissociation of the ammonia which is formed through the initial thermal decomposition of hydrazine. For this purpose an ammonia decomposition catalyst consisting of Fe_3O_4, K_2O, and Al_2O_3 was developed for use in series with the catalyst described in the paragraph above. With this combination of catalysts using a total reaction time of about 21 millisec it was found possible to generate gases at about 1450°F which contained approximately 12 mol per cent ammonia and had an average molecular weight of 12 lb/mol.

Because of the high freezing point (34°F) of pure hydrazine, its use as a gas generant and monopropellant is greatly limited; however, it has been found possible through the addition of hydrazine nitrate and water to hydrazine to produce mixtures which freeze below -40°F and which may be used as efficient monopropellants and gas generants. These mixtures have been successfully tested with the catalysts described.

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*This paper represents the results of one phase of research carried out at the Jet Propulsion Laboratory, California Institute of Technology, under Contract No. DA-04-495-Ord 18, sponsored by the Department of the Army, Ordnance Corps.

Introduction

Since early 1948, the Jet Propulsion Laboratory has been engaged in the development of hydrazine as a monopropellant and as a gas generant for use in the pressurization of the propellant tanks of rocket vehicles. This paper is a summary of the catalyst-development work which was carried out in connection with this program.

Thermochemistry

The thermal decomposition of hydrazine apparently proceeds in a stepwise manner which may be represented by two consecutive reactions, as follows:

$$3\,N_2H_4(\ell) = 4NH_3(g) + N_2(g) + 80.15 \text{ kcal} \qquad (1)$$

$$4NH_3(g) = 2N_2(g) + 6H_2(g) - 44.00 \text{ kcal} \qquad (2)$$

When the decomposition of hydrazine is carried out adiabatically at moderate pressures (less than 1000 psia), chemical equilibrium favors the completion of both reactions. However, reaction (2) is generally much slower than reaction (1); thus in practical systems in which the residence time is limited by considerations of weight and space, the ammonia cannot be completely dissociated. Therefore reactions (1) and (2) have been combined to give the following expression*, in which X represents the fraction of the ammonia which is dissociated:

$$3N_2H_4 = 4(1 - X)NH_3 + (1 + 2X)N_2 + 6XH_2 + (80.15 - 44.00X) \text{ kcal} \qquad (3)$$

Using this equation the influence of X on the performance of hydrazine as a monopropellant and a gas generant was calculated (Cf. Ref. 1). From Figure 1 it can be seen that the characteristic velocity c^* and specific impulse I_{sp} are virtually constant until about 50 percent of the ammonia has been dissociated. Beyond this point both parameters fall quite rapidly as X increases. Both the adiabatic reaction temperatures T_c and the average molecular weight of the decomposition gases M_g decrease steadily as X increases.

Optimum Performance of Hydrazine

The efficient use of hydrazine in any application requires the completion of reaction (1), whereas the extent of the completion of reaction (2), i.e., the value of X in Equation (3), which is

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*The nomenclature used in this paper is listed in Table I.

TABLE I

NOMENCLATURE

c^* = characteristic velocity (ft/sec)

I_{sp} = specific impulse (sec)

L^* = characteristic length (in)

M_g = average molecular weight of decomposition gases leaving reaction chamber (lb/mol)

p_c = pressure at exit of reaction chamber (psia)

R = perfect gas constant (psi)(cc)/(mol)(°R)

T_c = adiabatic reaction temperature (°R)

V_c = volume of reaction chamber or catalyst bed (cc)

X = fraction of ammonia dissociated

Θ_c = residence time in reaction chamber or catalyst bed (sec)

$\dot{\omega}$ = hydrazine injection rate (lb/sec)

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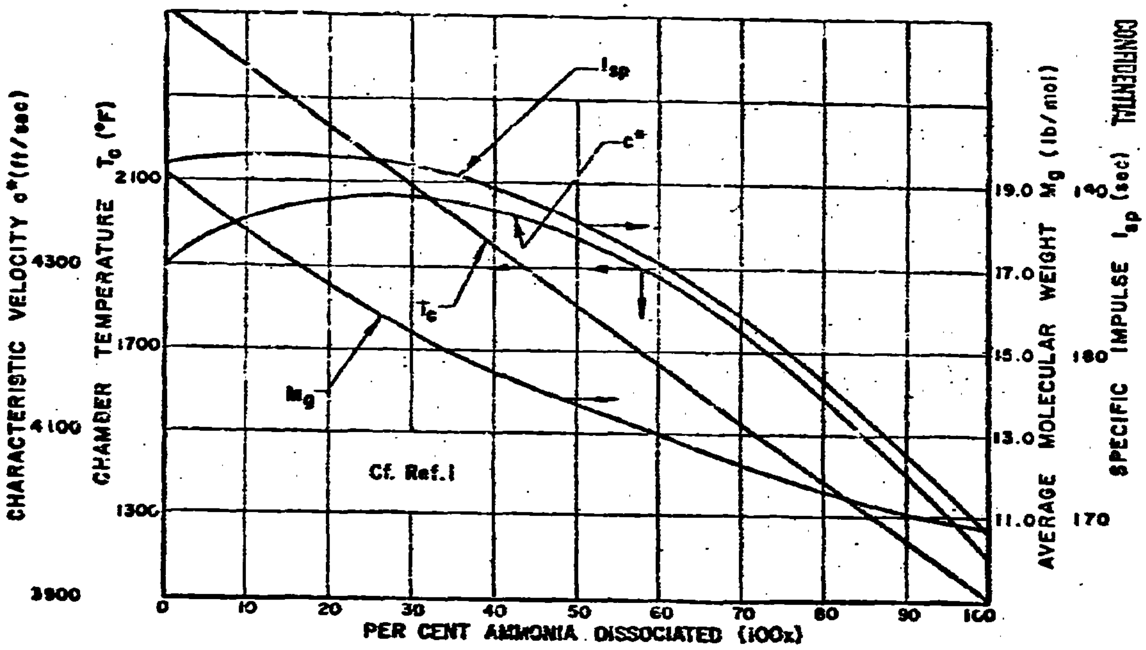

Figure 1. Theoretical Performance of Monopropellant Hydrazine

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required for the optimum performance of hydrazine in a given application, is dependent on the nature of the application. When hydrazine is used as a monopropellant in a rocket motor, it is desirable to operate at as low a chamber temperature as possible and at the same time to obtain near maximum I_{sp}. For this type of application, therefore, it is desirable to dissociate from 30 to 50 percent of the ammonia. When hydrazine is to be used as a source of energy for gas turbines, it is necessary, for mechanical reasons, to reduce the temperature of the gases to 1800°F or less. For such applications, therefore, it is necessary to dissociate at least 52 percent of the ammonia. For high-temperature, isobaric, pressure-displacement systems, e.g., catapults, optimum performance is achieved when M_g/T_c is at a minimum. For pure hydrazine this optimum performance is achieved when about 43 percent of the ammonia is dissociated. In low-temperature, isobaric, pressure-displacement systems (i.e., systems in which the gas temperature must be less than 1100°F as, for example, in propellant tank pressurizing systems in rockets), the maximum efficiency of hydrazine as a gas generant is achieved when all the ammonia has been dissociated so that gases of minimum molecular weight are produced.

Kinetics

The extent to which reactions (1) and (2) can be completed in a given reaction chamber is dependent on the rates of the reactions and the residence time ($\mathfrak{Q}$) provided by the reaction chamber where $\mathfrak{Q}$ may be defined* as follows:

$$\mathfrak{Q} = (p_c/\dot{\omega})(M_g/RT_c)\ V_c \qquad (4)$$

In a specific application p_c and $\dot{\omega}$ are fixed by factors related to the particular application, whereas the value of the ratio M_g/T_c required for optimum performance is determined by the use which is to be made of the decomposition gases. As a result, the residence time can be varied only by varying the volume of the reaction chamber.

In most practical systems, the volume of the reaction chamber must be limited in order to conserve weight and space. Therefore

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*Equation (4) is based on conditions at the outlet of the catalyst bed and on the total volume of the reaction chamber or catalyst bed. However, there are wide variations in T_c, M_g, and to a lesser extent in p_c throughout the reaction chamber; when a catalyst is used, the true gas volume is the volume of the chamber less the volume occupied by the catalyst particles. As a result, Equation (4) gives only an approximation of the true residence time.

[redacted]

the practical attainment of the efficient use of hydrazine as a gas generant or as a monopropellant requires that reactions (1) and (2) proceed quite rapidly.

When the adiabatic decomposition of hydrazine is carried out in the absence of catalysts, reactions (1) and (2) proceed quite slowly; thus a minimum residence time of about 35 millisec is required in order to permit the generation of gases which are free of detectable concentrations of hydrazine, i.e., in order to bring reaction (1) to completion. With this residence time, which in a rocket motor corresponds to an L^* of about 800 inches, chemical analysis of the decomposition gases showed that reaction (2) was less than 30 percent complete. Increasing the residence time resulted in only a slight increase in the amount of ammonia which was dissociated. From these facts it can be seen that the efficient use of hydrazine as a monopropellant or as a gas generant in reaction chambers of moderate size requires the use of catalysts which increase the rates of reactions (1) and (2).

Catalyst Development

Previous studies (Cf. Ref. 2) indicated that the thermal decomposition of hydrazine is a heterogeneous reaction which apparently proceeds for the most part in the vapor phase. The rate of the decomposition reaction was found to be markedly increased by a large variety of surfaces, the extent of the increase in the rate of the reaction produced by a given surface being directly proportional to its area in contact with the hydrazine. Among the materials which were tested, it was found that iron, nickel, and cobalt gave the highest specific surface activities.

Based on these studies, it was concluded that in order to be effective a catalyst would have to meet the following criteria:

1. Have a high unit-surface activity.

2. Expose a large surface per unit volume in order to permit the development of a large surface in a reaction chamber of moderate size.

3. Have a high thermal conductivity so that the rate of the vaporization process could be increased by the transfer of heat through the solid catalyst from the high-temperature regions to the low-temperature inlet regions of the catalyst bed and thence to the incoming hydrazine.

4. Have a sufficiently high melting point to prevent fusion at all temperatures encountered in the adiabatic decomposition of hydrazine.

5. Have sufficiently high mechanical strength to prevent powdering and packing during use.

In order to satisfy the last four criteria, it was necessary to use porous pellets of a refractory material as the catalyst support. For this purpose, porous cylinders of aluminum oxide having a nominal size of 3/16 inch were selected. In order to produce high unit-surface activity, these pellets were impregnated with concentrated aqueous solutions of the nitrates of iron, nickel, and cobalt, either separately or in various combinations. After the saturated pellets had been dried, they were tested in a reaction chamber similar to that shown in Figure 2. Seventeen catalysts of this general type were tested. Of these seventeen, the most satisfactory catalyst consisted of an equimolal concentration of metallic iron, nickel, and cobalt on the alumina support, the reduced catalyst containing a total of approximately 11 weight percent of the free metals. With this catalyst (Cf. Ref. 3) which has been designated H-7, it was found possible to bring reaction (1) to completion with a residence time 2.5 millisec (L^* of about 55 in.).

A. Catalyst Performance

1. Temperature Profile. Figure 3 shows the equilibrium-temperature profile obtained with the H-7 catalyst in a reaction chamber similar to that shown in Figure 4. This profile was measured at a chamber pressure of 300 psia and a flow rate of hydrazine of about 0.30 lb/sec. The curve is a plot of the temperature of the catalyst bed at a given point in the reaction chamber against the residence time provided by the volume of catalyst lying upstream from the point. The temperatures were measured by means of five chromel-alumel thermocouples enclosed in thin-wall thermowells located at 2-inch intervals down the length of the chamber. The total residence time in the chamber was 23 millisec. The residence time in the catalyst volume lying upstream from a given thermocouple was varied through the removal or addition of pellets at the upstream end of the catalyst bed.

The temperature profile shows that the hydrazine which enters the reaction chamber at room temperature undergoes little thermal decomposition upstream from the catalyst bed. In the catalyst bed, in the region $0<\Theta_c<0.5$ millisec, the temperature of the advancing stream rises rapidly to the boiling point of hydrazine at the existing chamber pressure and then probably remains constant for a short time until all of the hydrazine has been vaporized. It was pointed out previously that the thermal decomposition of hydrazine is largely a vapor-phase reaction. Consequently it has been concluded that in the entrance section

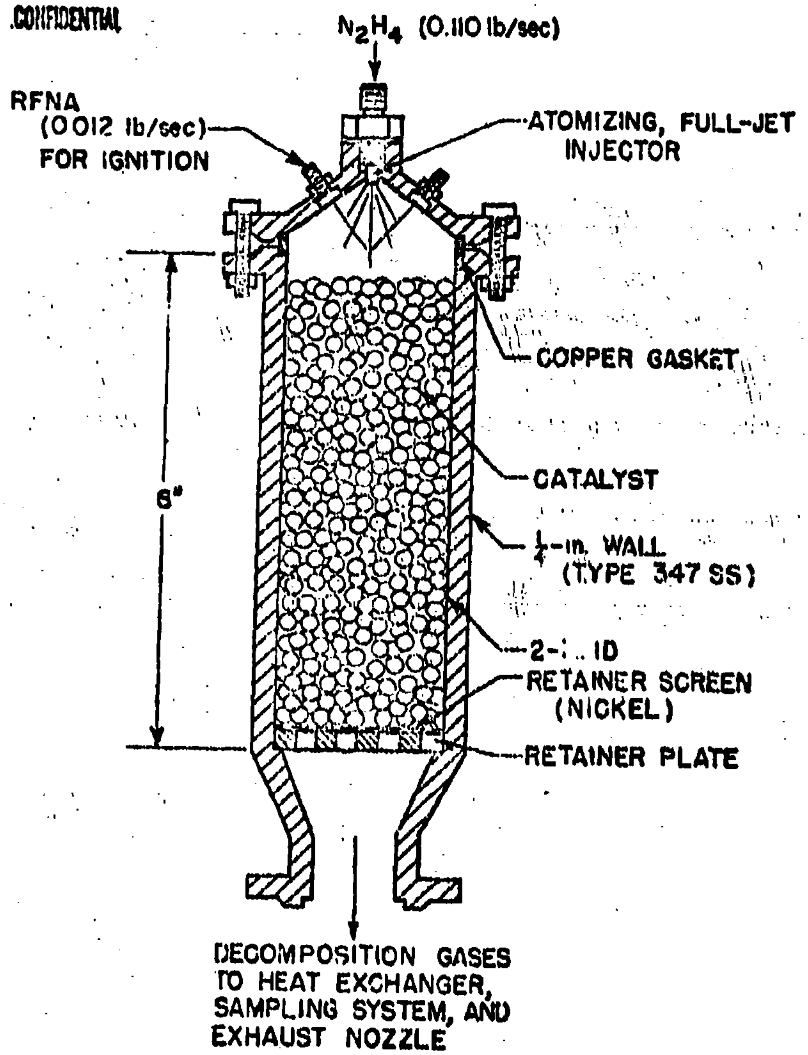

Figure 2. Hydrazine Catalyst Test Chamber

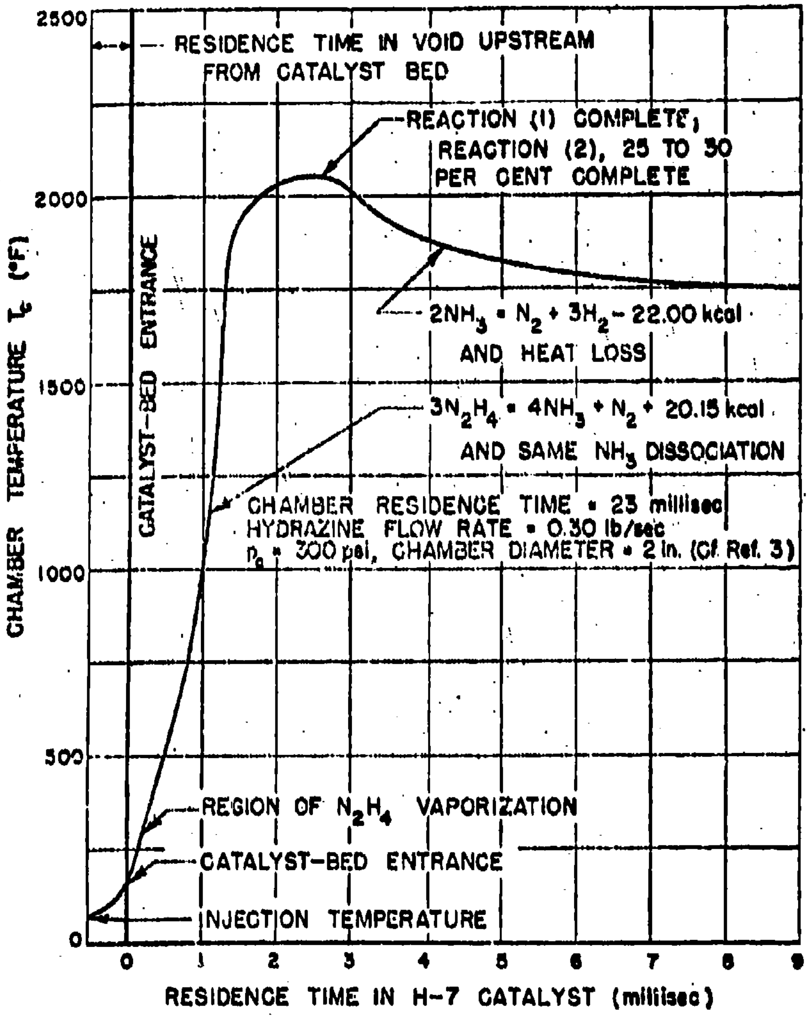

Figure 3. Temperature Profile in Type H-7 Catalyst Bed

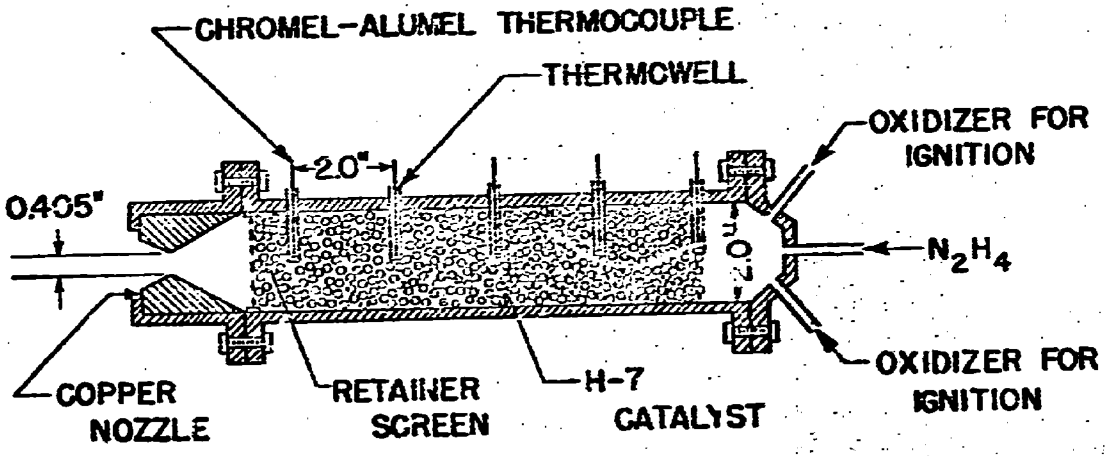

Figure 4. Catalyst Chamber Used in Measuring Temperature Profile

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of the catalyst bed the heat liberated by the thermal decomposition of hydrazine is not sufficient to complete the vaporization process; thus the establishment of equilibrium in this region is dependent on the transfer of heat from the catalyst bed to the hydrazine stream. It is further concluded that this heat is obtained by thermal conduction back through the catalyst bed from the high-temperature regions. In the region $0.5 < \theta_c < 2.5$ millisec, the hydrazine undergoes rapid thermal decomposition accompanied by the dissociation of some ammonia; a maximum temperature of about 2050°F is attained after a residence time of 2.5 millisec. This temperature corresponds to the dissociation of from 25 to 30 percent of the ammonia. As the residence time beyond 2.5 millisec increases, the temperature of the gas stream decreases gradually owing to the endothermic dissociation of the ammonia and to the loss of heat through the walls of the reaction chamber.

2. Variation in the Amount of Ammonia Dissociated with Residence Time in Type H-7 Catalyst. Figure 5 shows the influence of residence time in type H-7 catalyst on the amount of ammonia which can be dissociated in a reaction chamber similar to that shown in Figure 2. The data in this Figure were obtained by chemical analyses of the decomposition gases. The total residence time in the empty reaction chamber was approximately 38 millisec. The chamber pressure was about 500 psia, and the hydrazine was introduced at a rate of about 0.105 lb/sec. The curve is a plot of the amount of ammonia which was dissociated against the equivalent residence time provided by the volume of catalyst in the reaction chamber.

In all cases the upstream surface of the catalyst bed was maintained at a distance of about 1/2 inch from the hydrazine injector in order to permit the attainment of uniform cross-sectional distribution of the hydrazine before it entered the catalyst. The volume of the void upstream from the catalyst bed corresponded to a residence time of about 2 millisec. The residence time in the catalyst bed was varied by changing the total volume of catalyst through the addition or removal of pellets at the downstream end.

It should be noted that in all tests the total residence time in the reaction chamber was 38 millisec. In Figure 2 only the residence time corresponding to the volume of the catalyst bed is plotted. When no catalyst was present in the chamber, only 25 percent of the ammonia was dissociated. As catalyst was added to the chamber, the extent of the ammonia dissociation increased until a volume of catalyst corresponding to a residence time of about 15 millisec in the catalyst was reached, at which point approximately 50 percent of the ammonia was dissociated.

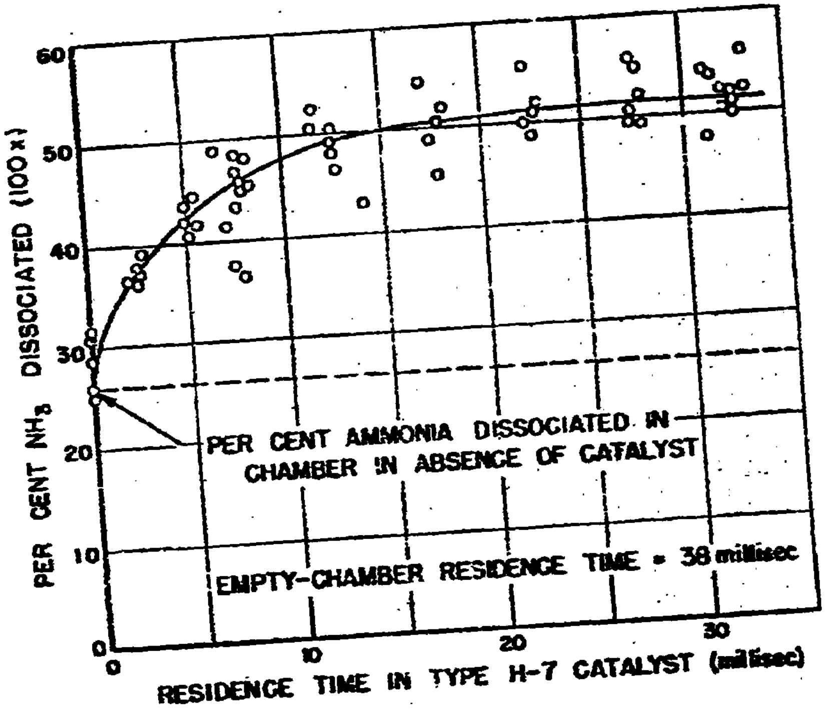

Figure 5. Influence of Residence Time in Type H-7 Catalyst on the Percentage of Ammonia Dissociated

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Increasing the volume of catalyst beyond this point resulted in only a slight additional increase in the amount of the ammonia which was dissociated. It appears, therefore, that from the standpoint of ammonia dissociation the optimum residence time in the H-7 catalyst is about 15 millisec. Tests in reaction chambers of different total residence times show that the extent of the ammonia dissociation which can be achieved with a given residence time in the H-7 catalyst is virtually independent of the total volume of the reaction chamber. For example, in a reaction chamber which provided a total residence time of about 20 millisec, it was found that approximately 50 percent of the ammonia was dissociated when the volume of catalyst in the chamber corresponded to a residence time of 15 millisec.

Ignition

With the type H-7 catalyst, it was not found possible to obtain sustained thermal decomposition until the catalyst bed was heated to over 400°F. For this purpose, electrical heaters were first used. However, this method of ignition was not believed to be satisfactory for practical use. Therefore a bipropellant starting technique was developed. With this method, the decomposition reaction is initiated through the simultaneous injection of hydrazine and an oxidizer (RFNA or N_2O_4) during the first 1/2 second of operation. The mixture ratio (ratio of oxidizer flow rate to hydrazine flow rate) is maintained between 0.2 and 0.3 in order to prevent hard starts (obtained when the mixture ratio is below 0.15) or fusion of the catalyst (obtained when the mixture ratio is above 0.35). The oxidizer is injected in such a manner that uniform mixing with the hydrazine is achieved, thereby preventing local overoxidation and resultant damage to the catalyst. Under these conditions, the bipropellant starting system was found to be reliable and reproducible.

Catalysts Which are Active at Room Temperature

In the course of the investigation of various catalysts, an attempt was made to develop catalysts which would be sufficiently active to initiate the thermal decomposition reaction at room temperature. Two catalysts of this general type were found. The first consisted of a modification of the type H-7 in which a concentrated solution of the metal nitrates saturated with ammonium dichromate was used to impregnate the aluminum oxide pellets. The pellets were then heated to about 250°F for four hours. When hydrazine was brought into contact with this catalyst at room temperature, ignition occurred within 10 millisec after the introduction of hydrazine into the chamber. However, after the catalyst had been stored in airtight containers for several weeks, it was found that its activity had declined to a point where over 50 millisec was required to initiate reaction.

As a result, when ignition occurred, the reaction was extremely violent owing to the large accumulation of hydrazine in the reaction chamber. For this reason, further development of this catalyst was abandoned. A catalyst consisting of metallic cobalt deposited on coconut-charcoal pellets and promoted with platinum was found to be capable of initiating the thermal-decomposition reaction at room temperature. However, the ignition properties of this catalyst were erratic, and its physical properties were not found suitable for prolonged use. Neither of these two catalysts was found to be spontaneous on re-use although the platinum-cobalt catalyst could be regenerated by heating for several hours at about 150°F in air. With both catalysts, it was evident that the ignition properties resulted from an oxidation reaction rather than from true catalysis. On the basis of these studies, therefore, it appeared desirable to use the bipropellant starting technique.

Catalysts for the Dissociation of Ammonia

Although the iron, cobalt, nickel, and alumina catalyst (type H-7) previously described is capable of producing optimum performance of hydrazine as a monopropellant in rocket motors of moderate L*, it is not suitable for use in low-temperature pressurization systems where it is desirable to dissociate the ammonia as completely as possible. Therefore an investigation of catalysts for the acceleration of reaction (2) was undertaken. This study was divided into two parts:

In the first part, which was unsuccessful, an attempt was made to develop a catalyst which would increase the rates of reactions (1) and (2) to the same extent or else cause the decomposition of hydrazine to nitrogen and hydrogen to occur directly without the intermediate formation of ammonia. For this purpose, over 70 different catalysts were tested. These catalysts, which were prepared in a variety of ways, incorporated one or more of the following: iron, nickel, cobalt, platinum, silver, copper, manganese, cerium, molybdenum, vanadium, chromium oxide, aluminum oxide, potassium oxide, sodium oxide, barium oxide, magnesium oxide, and tungsten oxide. These materials were supported on carriers of alumina, silicon carbide, zirconium oxide, kieselguhr, fuller's earth, filtrol, or charcoal. For the most part these catalysts were inferior in activity to the iron, nickel, cobalt, and alumina catalyst, and in the few cases where a superior activity was observed, the physical properties of the catalysts were not suited for practical use.

In the second part of this study an attempt was made to develop a catalyst which would be active in the dissociation of the ammonia formed in the decomposition of the hydrazine over the iron, nickel, cobalt, and alumina catalyst. For this purpose, many of the catalysts developed for the first phase of this study were tested in series with the type H-7 catalyst. However, with the best of these catalysts, only a slight increase in the amount of ammonia which could be dissociated in a given residence time was observed. Therefore several industrial ammonia-synthesis catalysts were tested. Of these, the most satisfactory from the standpoint of activity and physical properties was Aero catalyst, type FM produced by the Chemical Construction Corporation. With this catalyst, which consists of Fe_3O_4 promoted and stabilized with K_2O and Al_2O_3 and is supplied in the form of 3x6-mesh grains, it was found possible to dissociate up to 75 percent of the ammonia with a residence time of 21 millisec. (An additional residence time of about 10 millisec in the iron, nickel, cobalt, and alumina catalyst was provided for the completion of reaction 1.)

The influence of residence time in type FM catalyst on the extent of ammonia dissociation is shown in Figure 6. The data in the figure were obtained through the analysis of the decomposition gases. The catalyst bed was arranged in the manner shown in Figure 7. The hydrazine was first brought into contact with type H-7 catalyst in order to bring reaction (1) to completion before the gases entered the type FM catalyst. For this purpose, a residence time of approximately 10 millisec was provided in the type H-7 catalyst. With this residence time, approximately 48 percent of the ammonia was dissociated before the gases entered the FM catalyst (Cf. Fig. 4). The residence time in the type FM catalyst was varied in the same manner as described in connection with Figure 4. From Figure 6, it can be seen that the FM catalyst increases the rate of dissociation of the ammonia quite markedly; thus with a total residence time of 30 millisec, approximately 75 percent of the ammonia is dissociated. When the residence time is increased beyond this value, only a small additional increase in the amount of the ammonia dissociation is obtained. The decrease in the rate of decomposition of ammonia as Θ_0 increases is attributed to two factors: the decreasing concentration of ammonia in the gases and the lower gas temperatures. From Figure 6 it can be seen that the optimum residence time for FM catalyst is about 30 millisec. The large scatter in the data results from the fact that many of the points were obtained under widely varying conditions of pressure and flow rate. An attempt is currently being made to determine the influence of pressure, mass flow rate, and chamber diameter on the activity of the catalysts.

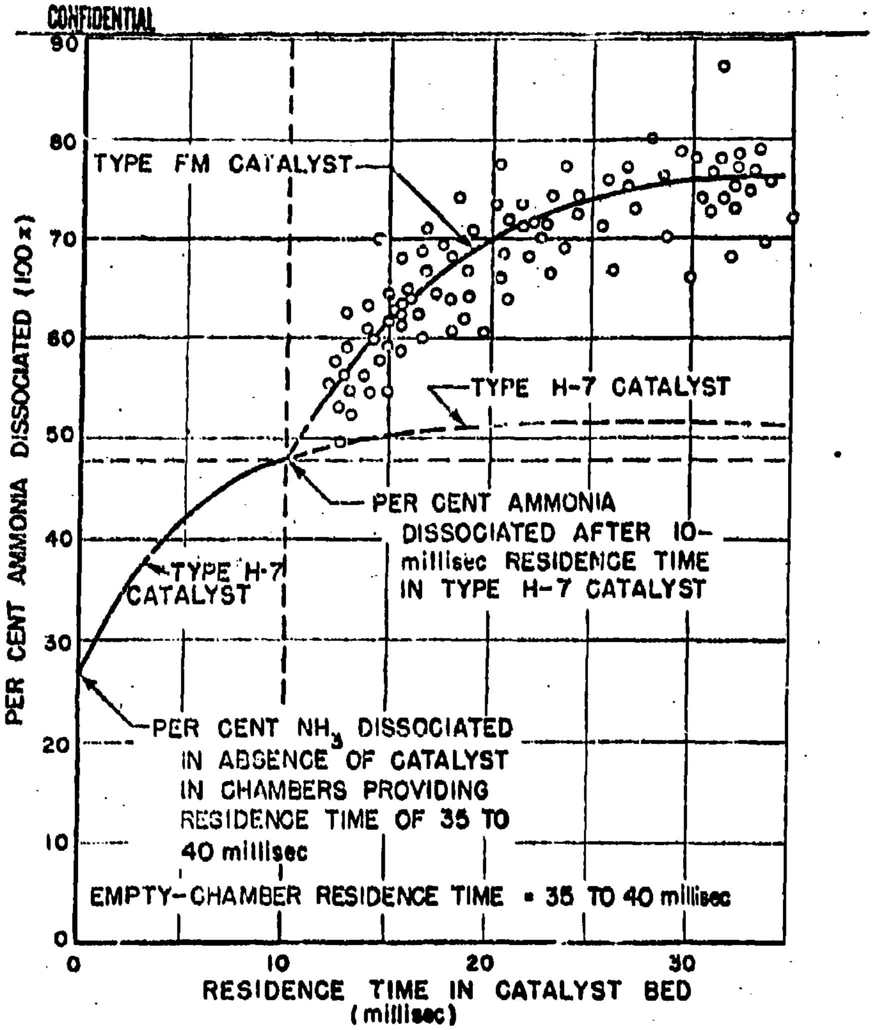

Figure 6. Influence of Residence Time in Type FM Catalyst on Per Cent Ammonia Dissociated

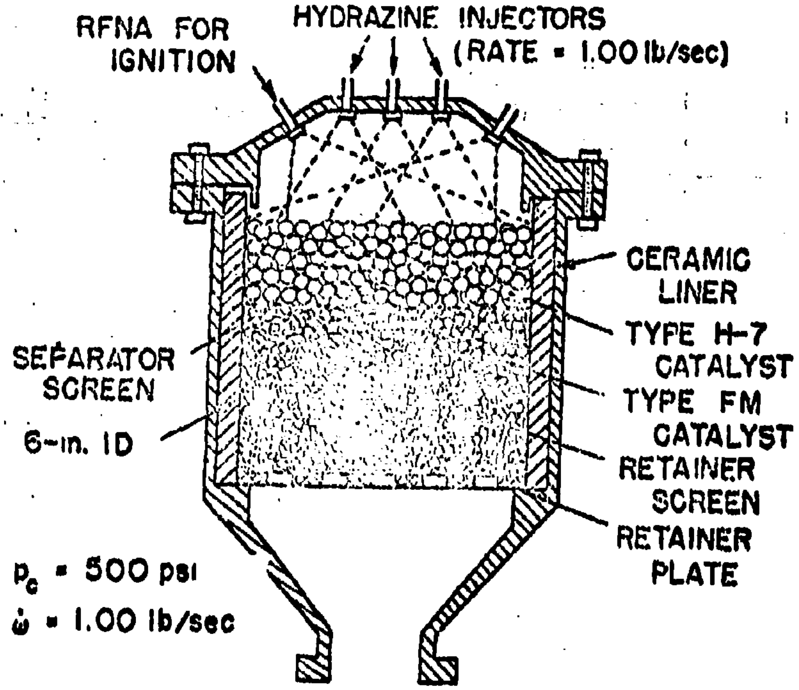

Figure 7. Arrangement of Two-Phase Catalyst Bed in Reaction Chamber

Low-Freezing Mixture of Hydrazine, Hydrazine Nitrate, and Water

Because of the high freezing point of pure hydrazine (34°F), its use as a gas generant and monopropellant is greatly limited. However, it has been found possible, through the addition of hydrazine nitrate and water to hydrazine, to produce mixtures which freeze below -40°F and which may be used as efficient monopropellants and gas generants.

In connection with the development of hydrazine as a gas generant for use in the pressurization of the propellant tanks of the Corporal flight vehicle, it was found that the presence of ammonia in the decomposition gases of hydrazine was active in causing an explosive reaction when these gases were used to pressurize the RFNA tank of the vehicle. Small-scale tests showed that the probability of explosive reaction between the decomposition gases and RFNA decreased as the concentration of ammonia in the gases was decreased.

When the concentration of ammonia was less than 5 mol percent, the probability of explosion was extremely low. However, using pure hydrazine and presently developed catalysts, it was not found possible to produce gases which contained less than 12 mol percent of ammonia. Therefore, in order to reduce the ammonia concentration to a safe value, it was necessary to add nitric acid (in the form of hydrazine nitrate) to the hydrazine. For this purpose, a mixture consisting of 74 percent hydrazine, 20 percent nitric acid, and 6 percent water by weight was selected. The theoretical performance parameters for this mixture are shown in Figure 8. Using this mixture, which freezes at -40°F, and a residence time of 12 millisec in the type H-7 catalyst followed by 20 millisec in type FM catalyst, it was found possible to produce gases which contained approximately 4.0 mol percent of ammonia ($X = 0.86$ in Fig. 8).

The chief disadvantage encountered in the use of the hydrazine-hydrazine nitrate mixture (hydrazine containing lesser amounts of nitric acid behaved similarly) was in connection with its tendency to detonate when brought into contact with the catalyst bed at low temperature. On three occasions, when an attempt was made to start monopropellant operation in a catalyst chamber, the oxidizer starting valve failed to operate, and the hydrazine mixture alone was introduced into the chamber. Although the hydrazine flow was stopped within 0.3 second, nearly 0.2 pound of the mixture had entered the chamber. This hydrazine detonated within 20 seconds after the flow had been stopped. Under similar conditions, no reaction was observed with pure hydrazine.

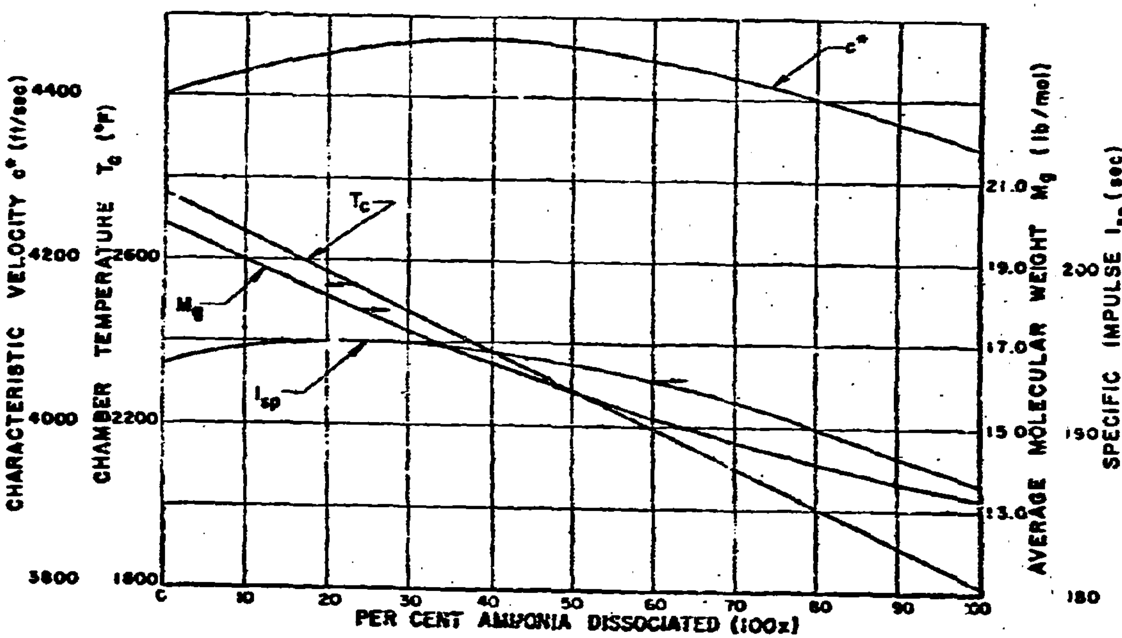

Figure 8. Theoretical Performance of Mixture Containing 74 Per Cent N_2H_4, 20 Per Cent HNO_3, and 6 Per Cent H_2O By Weight

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EXPERIENCE WITH HYDRAZINE AS A ROCKET FUEL AT THE M. W. KELLOGG COMPANY

by

R. J. Thompson
The M. W. Kellogg Company

Abstract

Theoretical performance calculations indicate an advantage for hydrazine over most common rocket fuels with the principal oxidizers. Experimental work initiated at The M. W. Kellogg Company in 1946 confirmed this conclusion. Hydrazine has been tested with nitric acid, liquid oxygen, chlorine trifluoride, and hydrogen peroxide at thrust scales varying from 50 to 1500 lb with generally favorable results. The calculated and experimental performance data are summarized.

Other favorable characteristics of hydrazine include good ignition with several oxidants and convenient gas generation by thermal decomposition. Results of ignition and gas generation studies are reported briefly.

Other physical properties, handling experience, and the freezing point depression problem are mentioned.

In conclusion, it is urged that more attention be given to the problem of producing hydrazine at a sufficiently low cost so that its potentialities as a superior rocket fuel may be realized in practice.

* * *

When The M. W. Kellogg Company embarked on a rocket development program for the Air Force in 1946, our attention was early directed to the potentialities of hydrazine as a rocket fuel for aircraft and missile applications. Both the German developments during World War II and the theoretical performance calculations then available made this material appear quite attractive. A part of our first major job was to survey the rocket propellant field and compile performance and physical property data. In the course of this work we extended the performance calculations of hydrazine with several oxidizers over a range of mixture ratios, pressures, and concentrations of reactants and compared the results with those for other fuels. In each case hydrazine yielded higher performance in terms of both specific and density impulse than the common carbonaceous propellants (hydrocarbons, alcohols, and amines) at about the same or somewhat lower chamber temperature. This may be illustrated by a tabulation of typical values calculated for full expansion at 20.4 chamber-to-back-pressure ratio (300 psia at sea level), displayed in Table I.

A similar advantage in performance of hydrazine over the carbonaceous fuels can also be shown for the fluorine base oxidants.

From consideration both of impulse and of physical and chemical properties, it appeared to us that hydrazine offered the most promise for application in the near future of any rocket fuel capable of yielding higher performance than the gasoline type or other common organic fuels, and should receive serious attention. Our experimental work, which was among the earliest in this country, was directed toward this end. Some six years later, we still feel that this was a sound decision.

Hydrazine has been test fired at The M. W. Kellogg Company with several oxidants including nitric acid, liquid oxygen, chlorine trifluoride, and hydrogen peroxide.

The bulk of our performance experience is with white fuming nitric acid (WFNA) as the oxidizer and with three fuel compositions: 97 percent hydrazine, hydrazine hydrate, and an approximately 75 percent hydrazine-25 percent water composition designed to freeze below -40°F. Tests of all three compositions were carried out at 50 lb and 500 lb thrust levels and of the latter composition only at 1500 lb thrust.

The 50 lb thrust chamber was used for exploratory studies and for determination of characteristic velocity as a function of mixture ratio, as well as for ignition studies. Uncooled steel chambers with copper nozzles were used in runs of about 5 to 10 sec duration. The injectors were of the simple pair or triplet impingement type; characteristic lengths varied from about 60 to 135 inches. Chamber pressures were in the range 300 to 400 psia. In both these tests and in the larger thrust chambers, nitric acid lead flow was provided to ensure smooth spontaneous ignition. Because of its small size and relative simplicity, the 50 lb thrust chamber has proved a most valuable tool in this and subsequent programs for rapid and relatively economical propellant evaluation prior to larger scale thrust firings and for ignition and combustion studies. With reasonably good injectors, characteristic velocities of over 90 percent of theoretical may be obtained consistently. In addition to about 100 nitric acid performance firings, about 25 performance tests were made of hydrazine hydrate with 90 percent hydrogen peroxide. The mixture ratio range covered in these tests was from 2.0 to 0.6 with nitric acid-hydrazine and 3.0 to 0.5 with hydrogen peroxide-hydrazine. The

TABLE I

CALCULATED PROPELLANT PERFORMANCE, PRESSURE RATIO 20.4

Oxidizer	Fuel	Optimum Mixture Ratio, O/F	Mixture Density, lb per cu ft	Calculated Specific Impulse, sec	Calculated Density Impulse, lb sec per cu ft	Calculated Chamber Temp. °R
Oxygen	Hydrazine	0.68	66	267	17,600	5580
	Gasoline	2.4	61	257	15,700	6080
	Ethanol	1.5	61	245	14,900	5720
Nitric Acid	Hydrazine	1.2	77	242	18,700	5120
	Gasoline	4.5	80	227	18,200	5330
	Aniline	2.8	84	221	18,600	5310
90 Percent Hydrogen Peroxide	Hydrazine	1.7	77	240	18,500	4680
	Gasoline	7.0	79	227	17,900	4750
	Methanol	3.2	74	220	16,300	4600

results of these 50 lb thrust scale firings may be briefly summarized by a tabulation of maximum characteristic velocity values obtained, displayed in Table II.

Testing at the 500 lb thrust scale was accomplished in a water cooled unit of conventional design in which the injector and characteristic length could be varied. Several types of injectors were tested including unlike pair impingement, spray nozzles, intersecting cones, impinging and non-impinging showerheads, and splash. Only the annular splash plate, or Enzian type proved superior to the simple unlike pair configuration, and the superiority of the latter over all other injectors tested, particularly at low L*, was very marked. This is shown by the comparative data, expressed in terms of percent of theoretical displayed in Table III. Good consistency was obtained for two to twelve test points at each condition. Now, these injectors were made quite early in our rocket experience and undoubtedly both the impingement and other types could be designed for better performance today. However, the striking improvement achieved merely by adding the annular splash plate to the impingement injector illustrates the advantage of this injector type for propellant combinations and thrust levels where it can be used safely. This safety depends on the combustion reaction being sufficiently rapid so that a dangerous accumulation of unburnt propellant cannot be trapped upstream of the splash ring; in general, we have found it satisfactory for fuels which exhibit rapid spontaneous ignition with nitric acid. The action of the splash ring is not fully understood but is probably at least two fold; it improves the liquid mixing and provides a high degree of turbulence at its downstream edge.

The balance of the 500 lb thrust firings was devoted primarily to a study of the variation of specific impulse with chamber pressure in the range 250 to 500 psia when operating near the optimum mixture ratio. These tests were made with 74 percent and 96 percent hydrazine, using both the splash plate and impinging stream injectors. The results and further data on the test conditions are shown in Figures 1 through 3. The increase in performance, relative to the theoretical, with increasing pressure is typical of most porpellants and is presumably due to more rapid mixing and combustion at the higher pressures. Only a few runs were made with hydrazine hydrate at this scale since its performance was not high enough to be of much interest. An average specific impulse of 196 sec and characteristic velocity of 4650 ft per sec were obtained at 420 psia chamber pressure.

The 1500 lb thrust chambers were designed for regenerative cooling with the acid and were used to check the thermal design as well as to confirm the performance on a somewhat larger scale. The extent of testing at 1500 lb thrust was limited because of the

TABLE II

EXPERIMENTAL PERFORMANCE DATA, 50 LB THRUST CHAMBER

Oxidant	Fuel	Mixture Ratio, O/F	Chamber Pressure, psia	Characteristic Length, L* in.	Characteristic Velocity, c*, ft per sec
90 Percent Hydrogen Peroxide	Hydrazine hydrate	1.4	310	60	4600
WFNA	Hydrazine hydrate	1.0	320	135	4650
WFNA	79 Percent Hydrazine 21 Percent Water	1.0	330	135	4850
WFNA	96 Percent Hydrazine	1.1	310	135	5120

TABLE III

EFFECT OF INJECTOR AND L* ON PERFORMANCE, 500 LB THRUST CHAMBER

Oxidant	Fuel	Mixture Ratio, O/F	Characteristic Length, L* in.	Injector Type	Chamber Pressure psia	Percent of Theoretical Impulse
WFNA	74 Percent Hydrazine 26 Percent Water	1.0	106	Impingement	220-350	88-90
			60	Impingement	300	82
			49	Splash Plate	290-350	89-93
			32	Splash Plate	300	89
WFNA	96 Percent Hydrazine	1.2	106	Impingement	270-350	89-92
			60	Impingement	300	79
			49	Splash Plate	470	94-96

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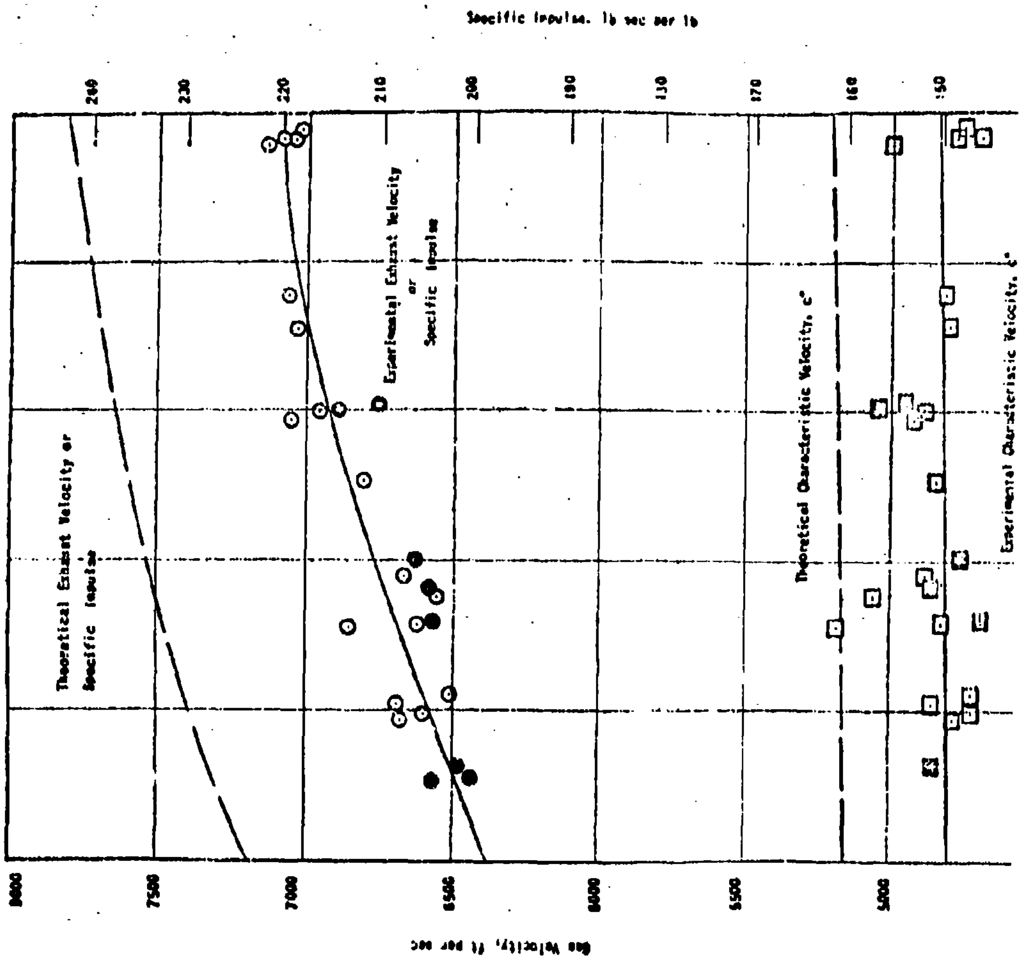

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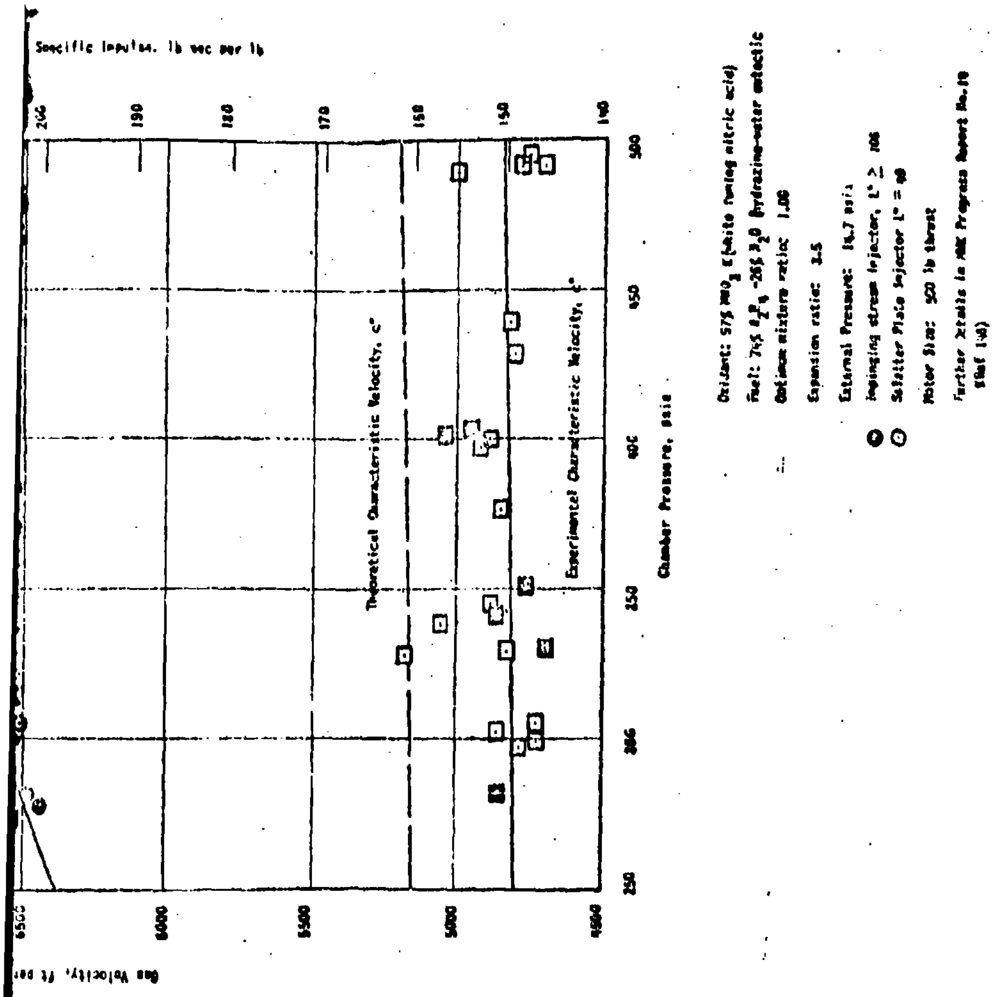

VARIATION OF EXHAUST VELOCITY (SPECIFIC IMPULSE) AND CHARACTERISTIC VELOCITY WITH CHAMBER PRESSURE; HYDRAZINE-WATER EUTECTIC AND WFNA

FIGURE 1

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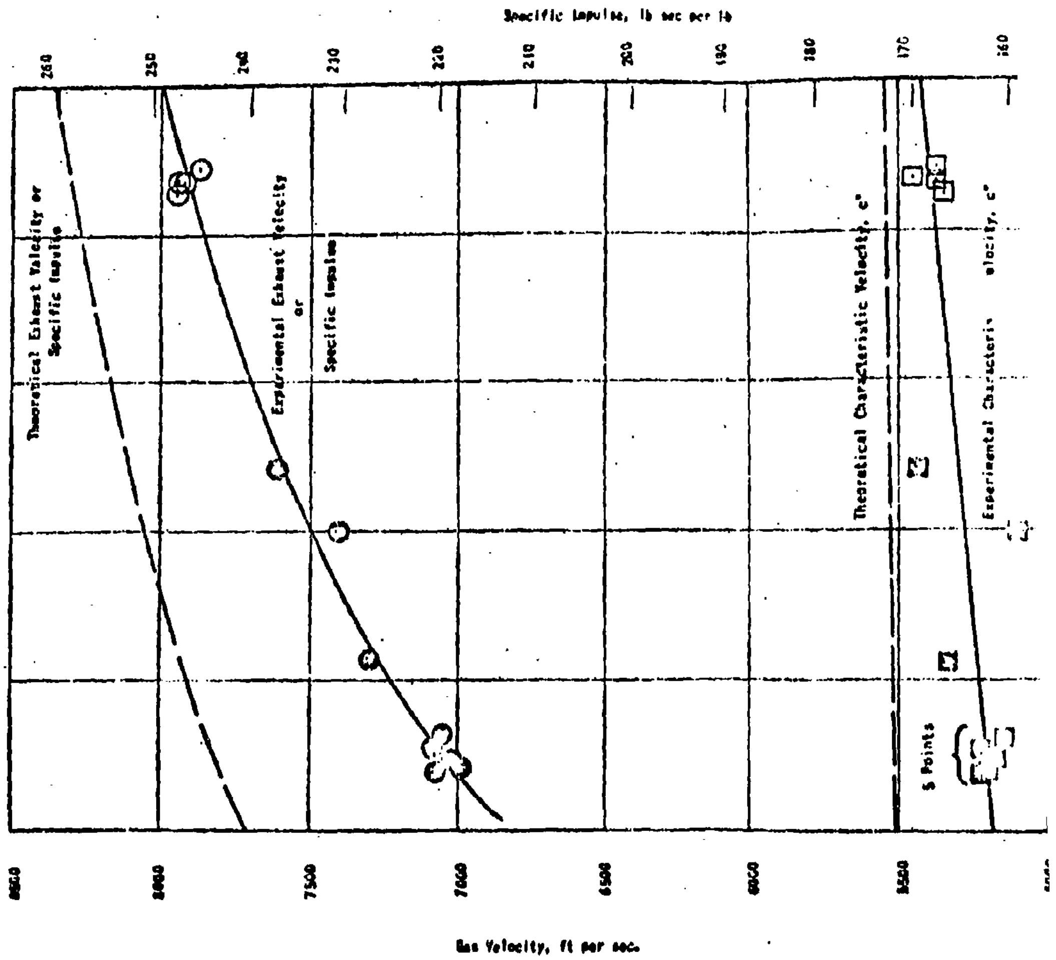

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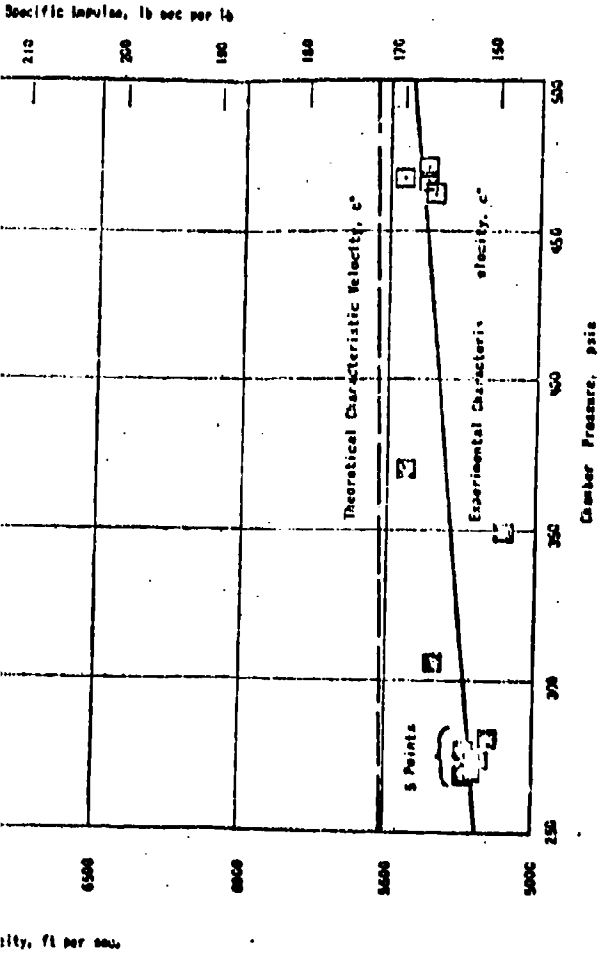

Oxidant: 97% HNO_3 (white fuming nitric acid)

Fuel: 98% N_2H_4 (anhydrous hydrazine)

Catalyst: None

Optimum mixture ratio: 1.20

Expansion ratio: 3.5

External pressure: 14.7 psia

⊡ Impinging Stream injector, L* = 105

⊙ Splatter Plate Injector, L* = 90

Motor Size: 500 lb Thrust

Further details in RMC Progress Report No. 88 (ref 196)

VARIATION OF EXHAUST VELOCITY (SPECIFIC IMPULSE) AND CHARACTERISTIC VELOCITY WITH CHAMBER PRESSURE; ANHYDROUS HYDRAZINE-WFNA

FIGURE 2

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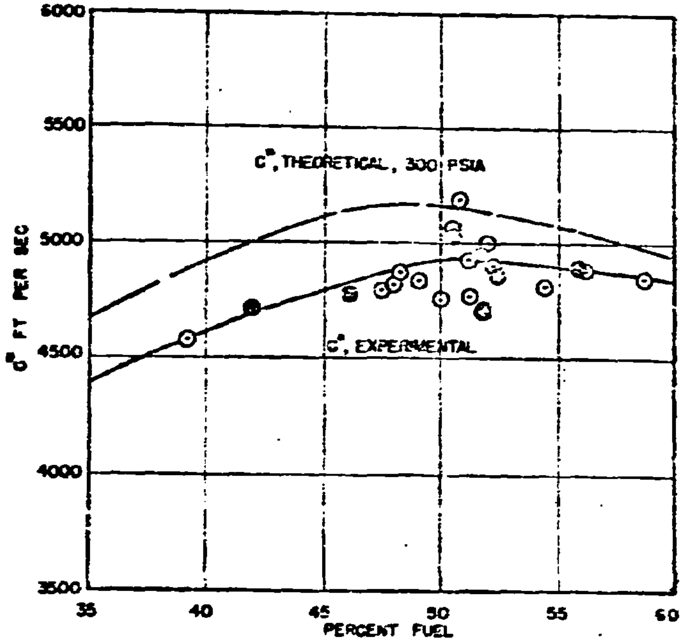
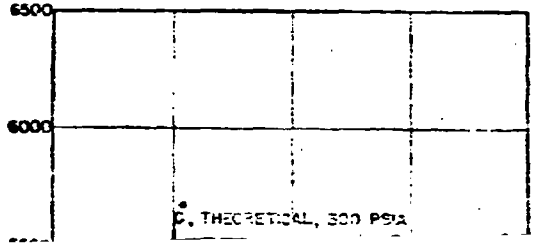
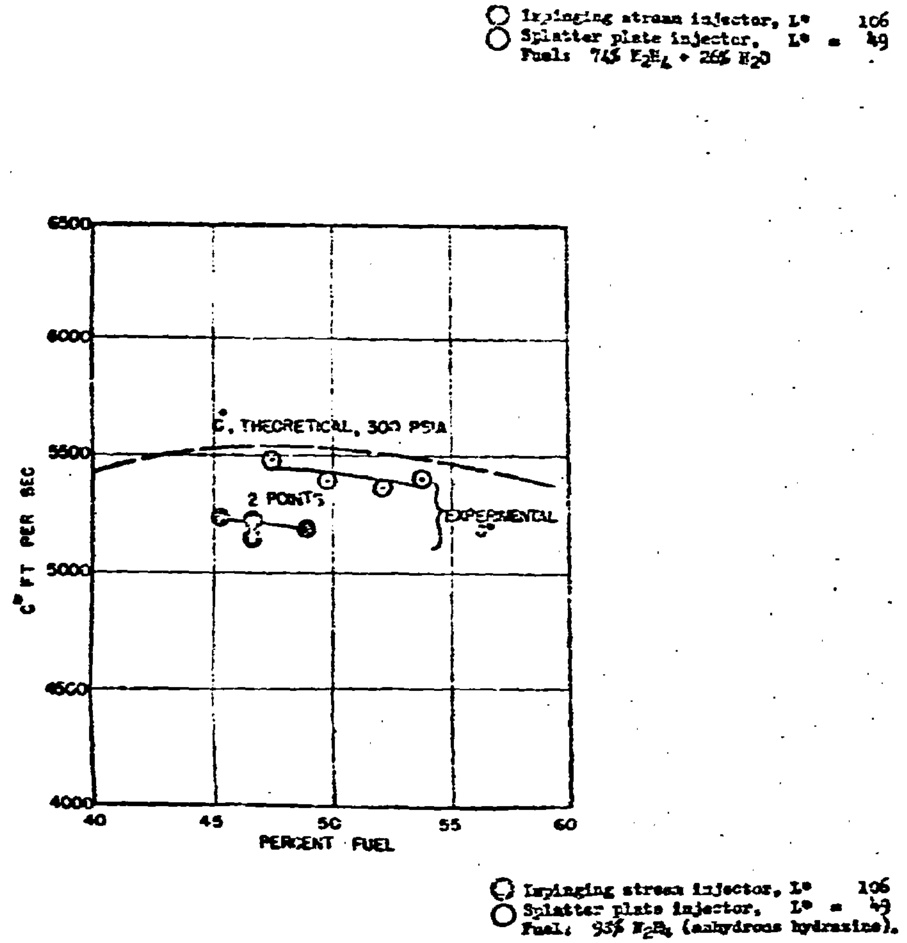


● Impinging stream injector, L* = 106
○ Splatter plate injector, L* = 49
Fuel: 74% N_2H_4 + 26% H_2O



EXPERIMENT



EXPERIMENTAL PERFORMANCE DATA, 500 LB THRUST CYLINDER

FIGURE 3

high cost of the fuel. The splash plate injector proved successful at this thrust also and the results obtained near 300 psia chamber pressure substantiated those obtained at lower thrust.

Performance data on hydrazine-liquid oxygen were obtained in nominally 200 lb thrust uncooled steel chambers with copper nozzles over a chamber pressure range from about 225 to 330 psia. Maximum specific impulse and characteristic velocity values were 242 seconds and 5700 ft per sec, respectively, at a mixture ratio of 0.67 and 330 psia chamber pressure. This corresponds to 90 percent of theoretical impulse at the optimum mixture ratio, which is considered reasonably good performance for a small motor. No extensive injector development was undertaken. The best results were obtained with simple assemblies of intersecting solid cone sprays. Specific impulses above 230 sec were measured over a mixture ratio range from 0.85 to 0.50, as shown in Table IV.

Since this combination is not spontaneous, several methods of ignition were tried. Pyrotechnic ignition was used in the bulk of the tests; this was satisfactory when spray nozzle injectors and oxygen lead flow were employed. With either fuel lead or solid stream injection, hard starts sometimes resulted. The hard starts with solid stream injection were probably related to delayed atomization and vaporization, since no flow staging was provided. Hard starts or explosions with hydrazine lead flow are generally experienced with all oxidizers and probably result from the exothermic decomposition of the hydrazine itself. Ignition was also accomplished by:

a. Separate injection of a stream of nitric acid to establish a flame by spontaneous ignition with the hydrazine prior to oxygen entry,

b. Chromic acid crystals in the chamber,

c. Electrically heated glow plug.

It appeared that oxygen-hydrazine is relatively easy to ignite.

As a part of an experimental study of high performance propellants, chlorine trifluoride was fired with hydrazine, ammonia, gasoline, and ethanol in a nominally 200 lb thrust motor at about 300 psia chamber pressure. Due to the unusually hazardous nature of the oxidant, special safety precautions were taken. Once proper handling procedures were worked out the program proceeded smoothly, quickly, and without difficulty. Best results in terms of high performance without injector burning were obtained with a "buried impingement" splash injector -- that is, the streams struck the splash plate before impinging on each other. When the splash plate was moved downstream of the impingement

TABLE IV

PERFORMANCE OF LIQUID OXYGEN-HYDRAZINE, 200 LB THRUST CHAMBER

Oxidant	Fuel	Chamber Pressure, psia	Mixture Ratio, O/F	Characteristic Velocity, ft per sec	Specific Impulse sec
Oxygen	95 Percent Hydrazine	320-340	0.85	5500	230
			0.80	5580	235
			0.74	5690	240
			0.67	5700	242
			0.59	5630	240
			0.55	5550	235
			0.50	5500	230

point, burning of the splash plate resulted. A summary of the results obtained with chlorine trifluoride is shown in Figure 4. Hydrazine gave the highest performance of the fuels tested, although the advantage in performance over ammonia was not great, and both hydrazine and ammonia were significantly better than the carbonaceous fuels, jet fuel, and ethanol. With nitric acid and oxygen, on the other hand, the performance of ammonia and jet fuel are nearly equal. Figure 5 presents an interesting comparison of the experimentally determined maximum characteristic velocity values with both chlorine trifluoride and nitric acid of hydrazine, ammonia, and jet fuel.

Thus far we have discussed primarily performance as measured by specific impulse, mixture density, and combustion temperature. Hydrazine has been seen to be generally more favorable in the first two respects and comparable in the third to the common carbonaceous fuels. These propellant properties are germane to all rocket applications. There are, of course, other properties which may be of equal or even greater importance in determining the usefulness of a material as a rocket propellant for a specific application. The importance of these physical and chemical properties varies, however, with the application. Some properties, such as thermal instability, may even be favorable for one application and unfavorable for another. Some of the propellant properties which affect the safety, reliability, usefulness under extreme environmental conditions, complexity, weight, and cost of the rocket include:

a. Ignition and combustion characteristics,

b. Thermal and mechanical stability,

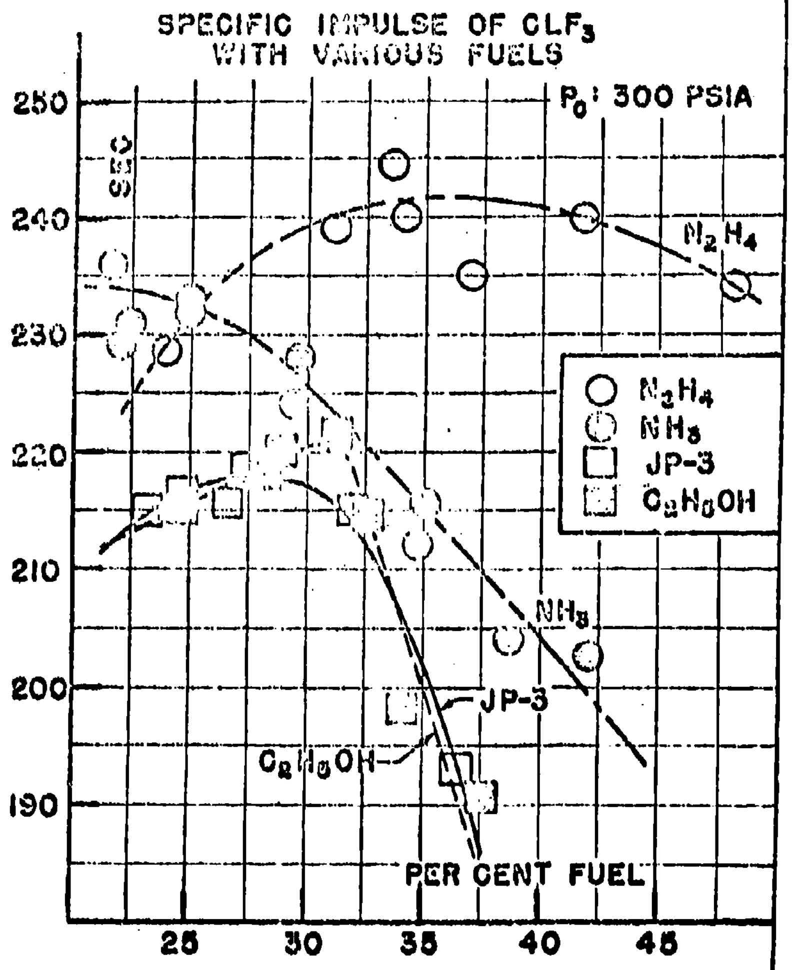
c. Corrosiveness,

d. Toxicity,

e. Physical properties: freezing point, vapor pressure, viscosity,

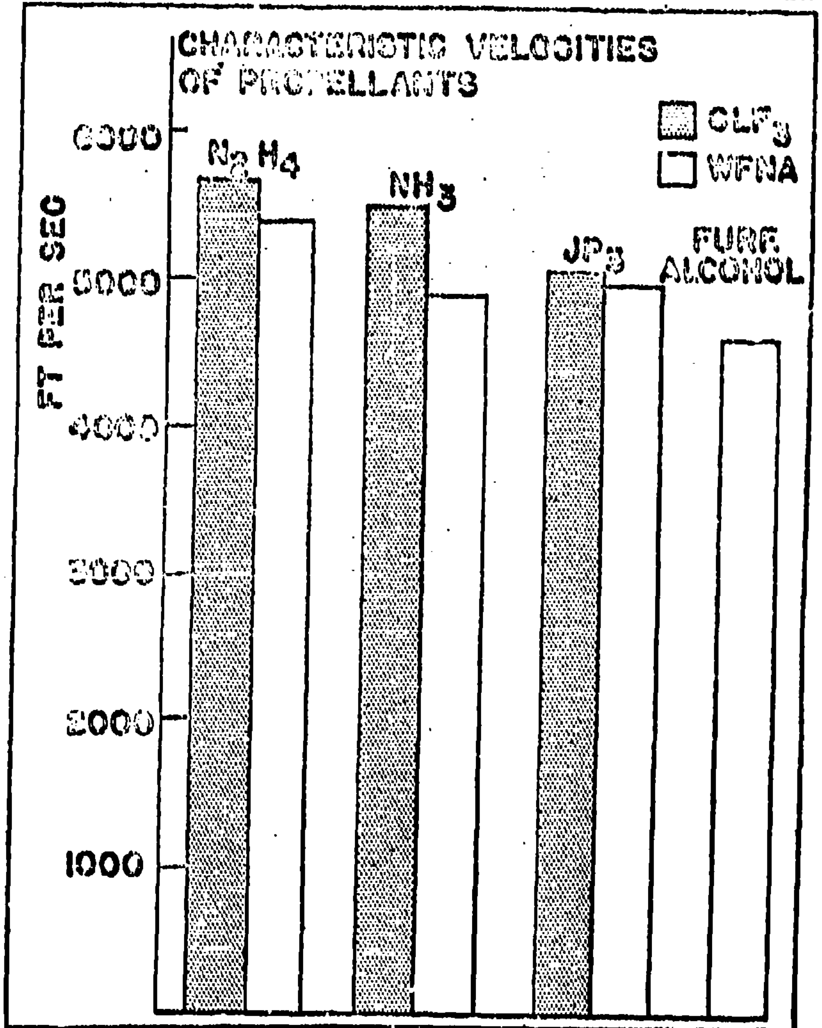
f. Economic factors: availability and cost.

The primary requirement for a rocket ignition system is to ensure that the rate of reaction of the propellants at all times during the starting transient is great enough to prevent a dangerous accumulation of unburnt propellants within the chamber. A second requirement in many rocket applications is that the "ignition delay time" from closing the firing switch to attainment of full thrust be short, accurately known, highly reproducible, and insensitive to environmental conditions. Application of these requirements to propellants which are relatively difficult to



SUMMARY OF EXPERIMENTAL SPECIFIC IMPULSE VALUES

FIGURE 4



CHARACTERISTIC VELOCITIES OF ClF_3 AND OF WFNA WITH SEVERAL FUELS

FIGURE 5

ignite results in ignition and flow staging systems of considerable complexity. Thus, safety is ensured only at the expense of complexity, increased weight and cost, and an extensive development program to attain reliability under all environmental conditions. This is particularly true of starting systems which must be designed for repeated operation without servicing. The difficulties encountered in development of the nitric acid-jet fuel system largely relate to this problem. It is also found that propellants which are hard to ignite or exhibit a long "ignition delay" are more subject to unstable or incomplete combustion under the same conditions of chamber volume and pressure, compared to the fast spontaneously igniting combinations.

The use of spontaneously igniting propellants offers, in many respects, the most desirable ignition method. One of the best spontaneous combinations is hydrazine-nitric acid. Hydrazine-hydrogen peroxide is somewhat less favorable since a catalyst is required. This property can be used advantageously even when hydrazine is not the primary fuel by employing it as a starting fuel or liquid primer for a main fuel, such as gasoline, which is not spontaneous. The quantity of starting fuel need only be sufficient to provide flame for a fraction of a second prior to entry of the main fuel. Such a starting system has proved highly satisfactory in hundreds of test firings with nitric acid-jet fuel at The M. W. Kellogg Company. It is our belief that a hydrazine starting system with appropriate valving, made up as a packaged unit suitable for perhaps 100 repeated firings, may be competitive or superior in size, weight, cost, reliability, and speed of operation to an electrical ignition system for nitric acid-jet fuel.

A considerable part of our early work with hydrazine was devoted to study of its ignition characteristics, employing both drop test and small rocket motors. The most useful technique for both ignition and combustion studies in small units has proved to be the transparent motor, in which a glass or clear plastic chamber is provided with an injector and nozzle, and the propellant entry, mixing, ignition, and subsequent combustion are recorded by high speed photography. It was confirmed that the appearance of visible flame and beginning of pressure rise were simultaneous within a fraction of a millisecond. The drop test is considered a useful screening tool, but not sufficiently similar to actual rocket conditions for quantitative reliability.

Drop tests were made at room temperature of hydrazine-water and hydrazine-methanol solutions containing a copper catalyst (potassium cuprocyanide) with 90 percent hydrogen peroxide. The ignition delay of the former increased almost linearly with water contents varying from 5 to 70 percent. The hydrazine-methanol solution, on the other hand, maintained a low and nearly constant delay up to 60 percent methanol, and then rose steeply. Spontaneous ignition still occurred, although with long and erratic delays, at 90 percent methanol-10 percent hydrazine. These results illustrate that satisfactory spontaneous ignition can be obtained from mixed fuels in which hydrazine is the minor component. The German "C-Stoff," which is 32 percent hydrazine, 48 percent methanol, 21 percent water by weight exhibits good ignition with peroxide.

Quite a large number of transparent motor tests were made with 90 percent hydrogen peroxide at ambient temperature and with nitric acid at ambient and low temperature with varying fuel compositions. The test conditions and average results for some of these tests are shown in Table V. In brief, hydrazine hydrate and "C-Stoff" with catalyst and anhydrous hydrazine without catalyst all gave satisfactory ignition with 90 percent hydrogen peroxide at ambient temperature, with delays in the neighborhood of 20 millisec. Hydrazine hydrate would not ignite satisfactorily without catalyst. The ignition delay of anhydrous hydrazine with catalyst was less than one millisec. Anhydrous hydrazine, hydrazine hydrate, and intermediate compositions ignite satisfactorily at temperatures above 0°F with both WFNA and RFNA; most of those data are omitted from the table. A low freezing composition of 75 percent hydrazine-28 percent water ignites reliably with RFNA, but not with WFNA, at temperatures from -40° to -55°F.

Hydrazine is thermally unstable. The rate of the exothermic decomposition is dependent on specific catalytic surface effects as well as on the temperature. Experiments both at The M. W. Kellogg Company and elsewhere indicate that hydrazine heated in a stainless steel bomb decomposes rapidly and sometimes explosively at temperatures in the neighborhood of 500°F. Hydrazine vapor can be ignited and decomposed by a spark or hot wire but the decomposition does not propagate into the liquid at normal temperature. Extensive tests made early in our program and subsequently confirmed by others showed that liquid hydrazine is stable to severe mechanical shock and will not propagate a detonation initiated by means of an explosive charge. The vapor is, of course, combustible and hydrazine soaked rags, waste, or filter surfaces may ignite spontaneously in air if not soaked with water.

The thermal instability of hydrazine militates against its use as a regenerative coolant. On the other hand, this property may be advantageously used for generation of turbine drive or pressurizing gas, as will be discussed later.

The corrosiveness of hydrazine toward materials commonly used in rockets has not been serious in our experience. Neither

TABLE V

SUMMARY OF IGNITION DELAY TEST RESULTS IN TRANSPARENT MOTOR

Oxidant	Fuel	Mixture Ratio, O/F	Catalyst*	Temperature, °F	Average Ignition Delay, millisec	Comments
90% Hydrogen Peroxide	Anhydrous Hydrazine	2.0	None	70	20 ± 8	
90% Hydrogen Peroxide	Anhydrous Hydrazine	2.0	0.08%	70	1	Too fast to measure by this method
90% Hydrogen Peroxide	Hydrazine Hydrate	1.5	0.02-0.03%	70	20 ± 5	No apparent affect of catalyst concentration
90% Hydrogen Peroxide	Hydrazine Hydrate	1.5	None	70	250	Violent explosion on start
90% Hydrogen Peroxide	C-Stoff**	1.5	0.04%	70	14 ± 2	
WFNA	Anhydrous Hydrazine	1.33 2.17	None None	75 75	18 11	
WFNA	72% Hydrazine 28% Water	0.98	None	75 -40 to -58	33 22-268	Erratic. Eight ignitions in eleven attempts
WFNA	72% Hydrazine 28% Water	1.53	None	-55	37	One ignition in four attempts
RFNA	72% Hydrazine 28% Water	1.01 1.16 1.57	None None None	-55 -58 -55	24 ±4 51 22 ±3	No failures One time only No failures
WFNA	Hydrazine Hydrate	1.38	None	70	75 ±10	

did we find its toxicity to be a significant problem, although this is apparently at variance with the experience of others. No worse effects than superficial eye and upper respiratory irritation from the vapors and mild skin blistering from liquid spillage were encountered. To our knowledge, no systemic effects were produced in any of our test personnel. In general, it was found that hydrazine could be handled without difficulty by observing normal safety precautions for flammable and toxic chemicals.

The physical properties of hydrazine are satisfactory except for its high freezing point (34.5°F), which is unsatisfactory for some rocket applications. The simplest additive for freezing point lowering is water; it is also the cheapest since anhydrous hydrazine need not be produced. The minimum freezing point is -60°F at 22 percent water, according to our measurements; the corresponding reduction in both calculated and experimental specific impulse is about 8 percent. The addition of water lowers the combustion temperature about 450°F, which eases the combustion chamber cooling problem considerably.

Several other additives have been proposed and tested as hydrazine freezing point depressants, including various alcohols, weak acids such as H_2S or HCN, ammonia, and hydrazine or ammonia salts. For the same freezing point depression, none of these yields significantly higher impulse than the hydrazine-water solution. Their cost is higher since they involve anhydrous hydrazine, and other properties such as storage stability, vapor pressure or density are frequently poorer. We believe that when temperature conditioning cannot be provided water is, all things considered, the best practical additive now available. However, the search for practical additives which exert a lesser effect on the impulse should be continued.

Returning briefly to the subject of gas generation from hydrazine, this can be accomplished in two ways: by very fuel rich bipropellant combustion or by catalytic decomposition of hydrazine alone. Primarily because of the lower molecular weight of its products, hydrazine is superior to hydrogen peroxide as a gas source. Bipropellant gas generation by 74 percent hydrazine-nitric acid at a mixture ratio of about 0.05 (5 percent oxidizer) was successfully demonstrated in a practical unit suitable for driving a 100 hp turbine at The M. W. Kellogg Company in 1947. Near stoichiometric combustion of the acid with part of the hydrazine provided a heat source for thermal decomposition of the balance of the hydrazine. Satisfactory operation was obtained with a characteristic velocity of 3800 ft per sec at a gas temperature of 1000°F, which is about 40 percent higher performance than that of hydrogen peroxide monopropellant at the same temperature.

A practical hydrazine monopropellant gas generator depends on development of a catalyst of sufficient activity for cold self-starting which is also sufficiently durable for the sustained high temperature service required. The M. W. Kellogg Company investigated this problem in 1948-1949. Several metal-metal oxide catalyst compositions were developed which appeared to initiate the decomposition satisfactorily but failed physically under continued testing. In addition, a unit designed to exchange heat from the decomposition gases to the influent hydrazine could sustain operation indefinitely on a preheated thermal decomposition bed, but only at a low flowrate. Since this latter unit is rather large and heavy for its throughput and requires preheating, the development of a more active and durable catalyst is the preferred solution. Considering the degree of success achieved in our quite limited program, it is believed that this problem could be solved.

The limited availability and high cost of hydrazine have been the principal impediments to its widespread use as a practical rocket fuel in this country. We discontinued large scale development work in 1948 and practically all development work in 1950 for just this reason. We believe that the overall rocket development program of the country has been retarded by the non-availability of hydrazine and that insufficient attention has been given to this problem. While such development of a cheaper and more efficient method of production than the Raschig process is admittedly difficult, the American Chemical Industry has solved many difficult problems before when sufficient incentive was supplied. Development of a superior production process is the most important single problem to be solved if hydrazine is to realize its potentialities as a superior rocket fuel.

DISCUSSION

DR. E. H. SEYMOUR (Office of Naval Research): I was thinking about the picture that shapes up out of the discussion of the last two days. I think with reference particularly to the first part of the program on the processes for making hydrazine that to get the whole picture we should give some thought to what wasn't said here as well as to what was said. There was quite a bit of work not reported here on the processes, that which was reported by the military services, at such places as the Olin Industries, and associated groups, Battelle and the Edwal Laboratories.

I think probably most of you are familiar with this but a lot of work has been done. Some of the approaches seem to be good. There is still work going on in addition to that mentioned here under direct sponsorship such as the work of the University of Illinois, and I believe work is also being done by the Bureau of Mines, and we in ONR are carrying on a study of the use of the electric discharge which could not be put in a paper to present here.

I could sum it up by saying we are in a position analogous to the chemical work which Dr. Gunning reported on. You are fighting a problem with a low percentage of conversion where power is also your prime raw material. This makes it difficult, but still worth looking at, we feel, and both in the past and in the present there has been, I think, a varying amount with sometimes small, sometimes large amounts of work done by various private interests on their own. This, of course, has not been reported on publicly and you can only guess as to where it is, what it may consist of, but it is a factor.

I think that an encouraging thing is the development of the Raschig Process. It has been pushed along by the Mathieson people and has shown promise of giving us a process which will meet our needs quite well.

I think we should also consider we may have great enthusiasm in one of the various research areas on another system which will give us something closer to the ultimate process which one of the speakers sort of hinted at when he pointed out the basic materials that go into this are cheap and plentiful.

I think there are two other thoughts on the whole program that occur. One is that hydrazine is not only unique, hydrazine is versatile. I think if you think of the applications discussed during the past day or so you can see that it is so. If it had been only for rocket propellants or gun propellants it might have dropped out of the picture because of its high cost and limited availability several years ago, but it is a very unique sort of chemical for military purposes as well as the many other purposes.

I think the third thing to give a little thought to is that this work that has been reported is just part of the work really on an attempt to exploit one compound and when you think that there are maybe 20 or 30 active contenders for propellant applications in the liquid field today, I think it tells us a little bit the answer to the question often asked about, "Why can't people settle on one and say that is it and go to work on it?"

MR. RALPH BLOOM, Jr. (Buffalo Electro-Chemical Company, Inc.): I would like to ask Mr. Grant about the pellet size in his chambers and whether or not smooth operation resulted from the use of these pellets.

MR. GRANT: The type H-7 catalyst originally was used in the form of 3/16 x 3/16 inch cylinders. However, it was found that the edges of the cylinders tended to break off and cause partial clogging of the catalyst bed. For this reason we changed over to quarter inch spheres which eliminated the problem of catalyst disintegration. In most of the tests which we have made, the operation of the reaction chambers was quite smooth. In a few tests we observed a form of pressure fluctuation which was found to be caused by a vibrational coupling between the reaction chamber and the hydrazine feed system. We have always been able to eliminate that phenomenon by adjusting the size and length of the hydrazine feed lines. The majority of the oscillographic records of reaction chamber pressures showed smooth operation. The type FM catalyst is obtained in the form of 3 x 6 mesh granules. We generally screen this catalyst in order to eliminate all fines.

DR. LIEBER: I would just like to say a few words about the meeting in general following Dr. Seymour who has capably given us an overall picture in a few minutes.

The amazing thing to me is that so often work is going on on this simple compound comprising only two nitrogen and four hydrogen. While interestingly enough some of the work has been reported here there has been unreported work going on all over the country. It is rather incredible to think what has come out of the discovery of Theodore Curtius in 1887 and even not too many years ago -- let's say ten or fifteen -- it would have been hard indeed (these remarks are directed to our colleagues) it would have been rather difficult indeed to have obtained such large sums of money for contracts on hydrazine researches.

I think we owe a debt of gratitude to all of the authors of the papers of this meeting and their presentations. We also owe a debt of gratitude to our audience who have come from all parts of the country, without which a stimulating meeting would have been impossible. I think we will all agree that this has been a very stimulating meeting indeed.

THE CHAIRMAN: I think the tone of this meeting is quite an improvement over the meetings that were held years ago on rocket propellants, and that it seemed that it seemed the authors were all very modest in their claims for their particular systems.

Thank you very much, gentlemen. The meeting is adjourned.

OFFICE OF THE ASSISTANT SECRETARY OF DEFENSE
Washington 25, D. C.

Research and Development

2 November 1953

MEMORANDUM FOR THE RECIPIENTS OF THE REPORT ON THE PROCEEDINGS OF THE SYMPOSIUM ON HYDRAZINE AND ITS APPLICATIONS, FRO 205/3

SUBJECT: Declassification of paper (appendix), "The Toxicology of Hydrazine - A Review"

1. In compliance with the request of the author, Dr. Stephen Krop, Army Chemical Corps Medical Laboratories, the subject paper (page 388, FRO 205/3 dated September 1953) is downgraded to Unclassified.

Robert A Ide
FOR DONALD B. BROOKS
Executive Director
Committee on Fuels and Lubricants

APPENDIX

THE TOXICOLOGY OF HYDRAZINE - A REVIEW

by

Stephen Krop
Army Chemical Corps Medical Laboratories

Appreciation of the versatility of hydrazine as a reagent in the synthesis of large numbers of organic compounds and in its usefulness as a propellant fuel brings an ever-increasing number of personnel in contact with hydrazine and, hence, the exposure of greater and greater numbers of personnel to the toxic hazards of hydrazine. Although derivatives of hydrazine had been widely known and studied intensively by chemists by the year 1875, pure hydrazine was unknown until about 1894 (Ref. 1).

The delay in isolation of the pure material postulated for so long may possibly have been due to its great reactivity. One of the early fruits of the reactivity of hydrazine and its derivatives with carbonyl groups may be found in the work of Emil Fischer on the structure of sugars. It may be recalled that Fischer found the reaction between phenylhydrazine and the carbonyl group in sugars of great usefulness in his study of the structure of sugars concerning which so little was understood until that time. The hydrogen attached to the nitrogen in hydrazine and its derivatives is extremely reactive with oxygen, chlorine, and other negative elements in organic compounds and it is by virtue of this fact that hydrazine combines so readily with a large variety of organic compounds by condensation. Its versatility in reacting with a wide variety of organic compounds (Ref. 2) perhaps bears a relationship to its injurious effects on living matter. Therefore, it is perhaps not surprising that hydrazine and its derivatives have a variety of biological effects including considerable toxicity.

Even before the isolation of hydrazine in pure form, it was recognized by those who worked with hydrazine in solution that vapors coming from the solution were highly irritating to the nose and throat (Ref. 3). The preparation of hydrazine in high degrees of purity soon brought reports that the eyes were affected by hydrazine vapors and also, of course, with hydrazine in solution if splashed into the eye. Although damage to the eye is said to be temporary after vapor exposure, the injury is nonetheless disabling, and with concentrated solutions or liquid hydrazine, permanent injury to the eye may result. It is fortunate that the irritating ammoniacal odor of the vapors is such as to prevent the inhalation of dangerous amounts of hydrazine by personnel making and handling the material (Ref. 2). However, it is possible to sustain serious kidney and liver damage by skin contact with the concentrated solutions of hydrazine, and by ingestion. In addition, severe skin injury can result from liquid hydrazine contact with the skin possibly by virtue of the basicity of hydrazine (Ref. 7). Hence, penetrating burns may be produced by formation of soluble alkaline metaprotein as contrasted with the hard, crusty insoluble acid metaprotein which is characteristic of acid burns and which hinders deep penetration of most acids.

In recognition of the foregoing, the following review is presented on the toxicology of hydrazine in higher animals. No attempt has been made to present a complete bibliography; rather, reference is mainly made to observations which seem to summarize bout the present knowledge of particular features of the mechanism of toxic injury, of the control of hazard, and of the treatment of poisoning.

1. Toxicity: Acute and Chronic

Hydrazine appears to be toxic to all forms of life. Amongst the higher animals, there appears to be no marked species difference in sensitivity to the toxic actions of hydrazine. It is toxic by all routes of administration and does not appear to differ markedly from other compounds in the difference in toxicity observed by different routes of administration to any given species (Refs. 4, 5, 7). Tables I and II summarize the toxicity data. Anorexia, weight loss, muscle tremors, weakness, and vomiting are the chief symptoms of chronic inhalation exposure of concentrations producing minimal pulmonary pathology (Ref. 4).

2. Pharmacological Actions in Higher Animals

a. Central Nervous System: Toxic amounts given intravenously to cats, dogs, and other animals result in excitement and convulsions after a latent period of fifteen to twenty minutes, or longer with smaller doses. Shortly after intravenous injection, hyperpnoe appears, followed by excitement and tonic-clonic convulsions sometimes accompanied by opisthotonus. The pupils are often dilated during the convulsive stages. After large doses, dyspnea and cyanosis supervene. Such central nervous system stimulation is, of course, controllable by common central nervous system depressants such as barbiturates (Refs. 6, 8).

TABLE I

SUMMARY OF ACUTE TOXICITY OF HYDRAZINE IN ANIMALS

Species	Route	LD_{50} or LC_{50}	Remarks
Mice	Intraperitoneal	163[(a)] mg/kg	
Rats	Intraperitoneal	102[(b)] mg/kg	
Rabbits	Intravenous	34[(a)] mg/kg	
Rabbits	Intravenous	20-25[(b)]	Hyperpnea, tonic-clonic convulsions opisthotonus, death
Cats (anesthetized)	Intravenous	(150-225 in divided doses was lethal; LD_{50} not given)[(b)]	Initial dyspnea and hyperpnea, vomiting[(b)]
Dogs (anesthetized)	Intravenous	(250-300[(b)] in divided doses was lethal; LD_{50} not given)[(b)]	Similar to cats[(b)]
Rats	Inhalation	109-400 mg/m³ (c)	16 to 83% mortality in 14 days after a 4 hour exposure; pathology in trachea and lungs
Rats	Inhalation	128-576 mg/m³ (c)	0 to 50% mortality in 14 days after a 2 hour exposure
Rats	Inhalation	106-831 mg/m³ (c)	16 to 33% mortality
Rats	Percutaneous	0.2 ml/total (a)	
Rabbits	Percutaneous	91 mg/kg (d)	

(a) Thienes et al, North American Aviation, Inc., Report No. AL731, 1 June 1948.
(b) Kunkel, et al, Chemical Corps Medical Laboratories Research Report No. 83, September 1951.
(c) Comstock, Lawson, Green and Oberst, Chemical Corps Medical Laboratories Rsch Rpt, to be published.
(d) R. G. Horton and L. W. Conn, personal communication

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TABLE II

SUMMARY OF CHRONIC TOXICITY OF HYDRAZINE BY INHALATION(a)

Species	Concentration	Mortality Percent	Remarks
Rats	6 mg/m^3	None	Exposed for six months; lung injury
Rats	18 mg/m^3	90	Lt50, 27 ± 5 days(b); lung injury
Dogs	6 mg/m^3	None	Anorexia
Dogs	18 mg/m^3	50	Death after 13th and 74th exposure; no pathology attributable to hydrazine

(a) Comstock, Lawson, Green and Oberst, Chemical Corps Medical Laboratories Research Report, to be published; McGrath, Comstock and Oberst, Fed. Proc., 11, 374, 1952; Comstock and Oberst, Fed. Proc., 11, 333, 1952.

(b) Lt50 = time to death of 50% of animals exposed.

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b. Heart and Circulation: If convulsions are prevented by barbiturates or other central nervous system depressants, effects upon the circulation may be observed readily. Convulsive doses produce a precipitous drop in blood pressure which is transient, returning to normal and then again falling over a period of time to shock levels. The pacemaker of the heart and auriculo ventricular conduction are depressed. With very large doses, the contractility of the heart itself is decreased and terminally ventricular fibrillation may supervene (Ref. 6).

c. Gastrointestinal Tract: Effects observed upon the smooth muscle of the gastrointestinal tract include vomiting, which occurs in unanesthetized animals, and an increase in tone of the gut. This effect, however, may possibly be due to a central nervous system effect, since isolated intestinal strips do not respond in a comparable fashion (Ref. 5).

d. The Liver: Hydrazine has striking effects upon the liver as was noted very early in the century by Underhill and Kleiner (Ref. 9), by Wells (Ref. 10), and later by Bodansky (Ref. 11), and others (Ref. 4). Superficially, the effects upon the liver resemble those of phosphorus but differ in an important respect in that the parenchymatous cells of the liver alone seem to lose their cytoplasm to a large degree in hydrazine poisoning, sometimes leaving behind practically denuded nuclei whenever the cells are fragmented; however, the conspicuous feature about the hydrazine-poisoned liver is the great fatty replacement or "fatty degeneration" that occurs throughout, starting principally at the central portions of each lobe. The blood vessels and biliary tract are very little affected. If the doses are not too large and provided a sufficient number of functional cells remain to tide the poisoned animal over the critical period, the effect on the liver is reversible (Ref. 9). In further contrast to phosphorus, it appears that the greatest visible injury by hydrazine is confined to the liver, whereas phosphorus injury is more uniformly distributed among organs.

e. The Kidney: Although azotemia has not been reported as a terminal feature in hydrazine poisoning in animals, urinary abnormalities may be observed. Some of these may arise from effects elsewhere, viz., on the liver and upon the blood. However, the appearance of protein in the urine in the absence of extrarenal urinary tract involvement must be considered to be due to injurious effects upon the kidney. Histological changes in the kidney have been reported (Refs. 10, 12).

f. Effects Upon Metabolism: The hypoglycemic action (Ref. 9) of hydrazine stimulated a number of studies on its metabolic effects. Underhill and associates (Refs. 13, 17)

[redacted]

concluded that increased glucose oxidation was the primary cause of hypoglycemia, basing their belief on the rise in respiratory quotient during one period of the course of poisoning, on the fall in liver glycogen and on allegedly increased combustion of administered glucose by hydrazinized animals. However, heat production was not increased and hence, the hypothesis of increased oxidation of carbohydrate to explain the hypoglycemia was open to question. Moreover, the effects of fasting or inanition appear not to have been completely accounted for, inasmuch as increased allantoin excretion, for example, was ascribed by Underhill and collaborators to inanition.

Subsequently Lewis and co-workers (Refs. 12-19) and others (Ref. 18) demonstrated accumulation of amino acid nitrogen in plasma of poisoned dogs, with a reduced ability of the liver to convert administered glycine and glucose to glycogen. Parenterally and orally administered lactate did not result in increased glycogen deposition in hydrazinized animals, and the blood sugar response to lactate was exaggerated. Izume concluded that the injured liver was unable to produce glycogen from non-carbohydrate (fat and protein) materials as well and thus the blood sugar level could not be sustained (Ref. 19); mobilized fat accumulated in the liver. Hydrazine did not affect tissue protein levels on rabbits (Ref. 20) or acetone body production of phlorhizinized, fasting rats (Ref. 21). It appears certain, therefore, that in addition to preventing deamination, hydrazine interferes critically with reactions important to the utilization of carbohydrate material possibly at the three carbon residue level. The protective effective of pyruvate reported by Cole (Ref. 8) and the toxic effect of glucose to hydrazinized animals claimed by Underhill (Ref. 15) seem to add support to this idea.

The rise in plasma pH, CO_2 combining power and Na/Cl ratio during one stage of poisoning is believed by some (Ref. 18) to be accounted for by loss of acid in vomiting; however, the chloride loss does not appear to account for all of the alkalosis and hence, an additional and perhaps deeper-seated cause for the acid-base imbalance must exist.

3. Hazards to Man:

The recent literature contains little information on the hazards of hydrazine and its salts to production plant personnel and other handlers beyond general statements in publications primarily directed to chemical and production problems (Refs. 2, 22). The effects of brief and of prolonged exposure of man have not been described in sufficient clinical and laboratory detail to determine the extent of qualitative and quantitative similarity to the effects on other animals. Vapor inhalation, and liquid eye and skin contact are the major routes for injurious exposure, and effects may be local, systemic, or both. Dermatitis after skin contact has been reported (Ref. 22). The ammoniacal odor of hydrazine and effective ventilation combined should reduce inhalation hazard adequately, and prompt flushing of skin and eye with copious quantities of water should reduce the hazard of alkali-like skin burn and of percutaneous absorption of toxic amounts. If results of animal experiments can be applied to man, complete vaporization of one-half ounce in an unventilated room, 20 x 10 - 8 feet, would result in approximately 400 mg/m^3, a dangerous concentration, if none were adsorbed by the walls, furnishings, fabrics, etc.; the ratio of adsorbed to hydrazine vapor form would determine the amounts of spillage expected to be dangerous. However, adsorbability of hydrazine is potentially serious, since brief flushing of a room with air after a spill may lead to a false sense of security inasmuch as the walls, furnishings, etc., could subsequently give off sufficient hydrazine to produce a hazardous situation. Possibility of such a hazard should be ascertained in each situation by suitable study.

4. Personnel Protection and Treatment of Poisoning:

Aside from the provisions relative to ventilation and washing of liquid contact with water implied in Section 3 above, adequate respirators, eye-glasses, rubber aprons, gloves, etc., should be provided wherever there is risk of exposure and particularly in the unusual circumstance of insufficient ventilation and lack of water. Treatment of casualties is, at the present state of knowledge, empirical and symptomatic, and no single symptom is diagnostic of hydrazine intoxication.

Convulsions characteristic of acute intoxication may be controlled by judicious use of a barbiturate such as pentobarbital or thiopental by a physician, with due regard for the central nervous system depression which often follows a convulsive episode of any origin.

Skin and eye burns should be treated as are those produced by heat or by any other alkali. Dyspnea or other signs of pulmonary damage should be managed with oxygen inhalation, and liver and kidney injury should be treated by conventional methods for renal and hepatic insufficiency to the degree required by the extent of injury sustained. This should be determined by kidney and liver function tests, particularly carbohydrate tolerance and plasma amino acid nitrogen level following amino acid administration. Additional treatment may include ascorbic acid administration, if results of treatment of acute intoxication reported in some animals are applicable to other species (Ref. 23). The protective effect of pyruvate alluded to earlier (Ref. 8) may be considered in severe poisoning, and caution in the use of glucose should be observed (Refs. 8, 15). In severe acute poisoning, intravenous administration of fluids should be considered.

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