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NAVY DEPARTMENT
OFFICE OF NAVAL RESEARCH
WASHINGTON, D. C.

8 October 1953

Report No. 747

(Quarterly)

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01569

**INVESTIGATION OF
LIQUID ROCKET
PROPELLANTS**



Contract N7onr-462

Task Order No. III

Project No. NR 220 023

Aerojet-General CORPORATION

A SUBSIDIARY OF THE GENERAL TIRE & RUBBER COMPANY
AZUSA, CALIFORNIA



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Written by:

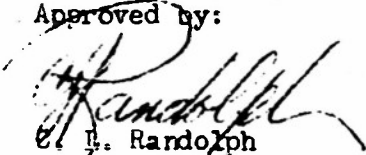
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CONTRACT FULFILLMENT STATEMENT

This quarterly report is submitted in partial fulfillment of Contract N7onr-462, Task Order III, and covers the work done from 1 June through 31 August 1953.

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I. INTRODUCTION

Continued investigations of liquid propellants have yielded outstanding results in several fields.

A. A theory of the action of oxygen added to nitromethane in a rocket motor has been developed, and the general theory of the thermal decomposition of nitromethane has been extended.

B. Attempts to prepare alkyl triazanes by reduction of nitrosohydrazines have been unsuccessful, but preliminary information has been obtained on two other new high-energy fuels.

C. A program to investigate the feasibility of employing acetylide salts as propellant components has been initiated.

D. High specific impulses have been obtained with gasoline burned with mixtures of fluorine and oxygen.

II. KINETIC STUDY OF THE THERMAL DECOMPOSITION OF NITROMETHANE

A. INTRODUCTION

1. During this report period the investigation of the effect of additives on the thermal decomposition of nitromethane at relatively high pressures was continued. The objectives of this phase of the study are two. One is to determine how additives that are known or postulated intermediates in the decomposition of nitromethane affect the course of the reaction. The other is to determine the reason that the addition of 5% or more of gaseous oxygen to nitromethane in a rocket motor lowers considerably the characteristic length and the pressure required for stable operation.

2. During this report period all the decomposition tests were conducted at 355°C, at pressures from 150 to 225 psia, and for various durations of heating.

B. EXPERIMENTAL RESULTS

1. Extent of Decomposition

a. Decomposition tests were carried out with approximately 12% added nitrogen dioxide. The per cent nitromethane decomposed after 2, 5, 15, and 31 min of reaction time, with and without the addition of nitrogen dioxide, is shown in Table I. After 15 and 31 min, there is a decrease in the rate of decomposition in the presence of nitrogen dioxide. In the early stages of the reaction (2 and 5 min) the amounts decomposed with and without nitrogen dioxide are approximately the same. The experimental uncertainties have a relatively greater effect on the reproducibility of the data in the early stages because of the appreciable warmup period (45 sec) and

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the small percentages decomposed. These factors make it difficult to decide whether a difference of one or two percent in the amounts decomposed with and without nitrogen dioxide is caused by the presence of nitrogen dioxide or by experimental variations. Additional tests must be made to solve this problem. The results show definitely, however, that nitrogen dioxide causes no substantial acceleration of the rate, even in the early stages of the decomposition. It was also observed that both nitrogen dioxide and nitric oxide, if present in equal amounts, appear to inhibit the decomposition of nitromethane to the same extent (Table I). This inhibitory action will be discussed in Section C,2.

b. Experiments show that the addition of oxygen does not affect the rate of decomposition of nitromethane for 5, 15, and 31 min of reaction time (Table II). There may be some accelerating effect in the 2-min tests; but again the experimental uncertainties prevent a definite conclusion, and additional tests must be made for confirmation. Even if it is found that the difference in the rates for the 2-min runs is actually caused by the oxygen, it would mean only that in the presence of 13% oxygen approximately 1.7% additional nitromethane is decomposed. This eliminates the possibility that oxygen causes considerable acceleration in the very early stages of the reaction, followed by an inhibition of similar magnitude in the later stages, perhaps because of the presence of certain products of its reaction with nitromethane.

2. Products of the Decomposition

a. In addition to determination of the decomposition rate of nitromethane in the presence of nitrogen dioxide and oxygen, the fate of the additives during the decomposition was determined by analysis of the products. To accomplish this, tests were carried out for 2, 5, and 15 min. For purposes of comparison a similar series was run with ampoules containing only nitromethane. The results are listed in Tables III, IV, and V.

b. It is of interest to note the large percentage of nitrogen bound in C-N compounds in the runs which were made without additives. These results are summarized in Table VI. Although the percentage of C-N compounds shows no trend with the duration of the run, the relative amount of hydrogen cyanide increases in the longer runs, and the amounts of acetonitrile and n-propionitrile diminish. The presence of propionitrile among the decomposition products was previously suspected (Reference 1) and has now been confirmed. A calibration spectrum of n-propionitrile, obtained by means of the mass spectrometer, accounts satisfactorily for the peaks clustered about mass 54. As shown in Tables IV and V, C-N compounds have been virtually eliminated from the decomposition products by the addition of nitrogen dioxide or oxygen to the ampoules. This indicates that at least in the early part of the decomposition, nitrogen dioxide and oxygen behave in a similar manner when added to nitromethane. The significance of these results is discussed in more detail in Section D,2.

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c. The relative percentage of nitric oxide among the decomposition products of samples pyrolyzed without additives is constant for the 2-, 5-, and 15-min runs, and decreased by about half in the 31-min run. This drop in the nitric oxide concentration is accompanied by a corresponding increase in the amount of nitrogen formed. The fact that the concentration of nitric oxide remains constant for a long period before dropping is an indication that the maximum of the curve of the nitric oxide concentration vs time must be rather flat (Reference 2). This conclusion may be compared with the results of Cottrell (Reference 3), which indicate a gradual decrease in the nitric oxide concentration at sub-atmospheric pressures.

d. Another correlation with Cottrell's work is found in the relative amounts of carbon monoxide and carbon dioxide in the runs made without additives. Cottrell found more carbon monoxide than carbon dioxide; however, in the Aerojet study it is found that for the 2-min run the carbon monoxide concentration is twice that of carbon dioxide, for the 5-min run the two concentrations are equal, for the 15-min run more carbon dioxide than carbon monoxide is found, and this trend continues for the 31-min run.

e. The relative concentration of methane decreases somewhat from the 2-min run to the 31-min run.

f. Formaldehyde has not previously been found as a decomposition product in pyrolyses carried out in a static system. In the 2-, 5-, and 15-min runs, the inability to account for a peak at mass 29 led to a tentative assignment of this peak to formaldehyde. It was not possible to make the assignment definite, because the other large peaks in the formaldehyde spectrum (masses 28 and 30) are masked by peaks resulting from other decomposition products. In order to confirm unequivocally the presence of formaldehyde, the reaction products from Run No. 141 (200 psia initial pressure, 5-min duration, 355°C) were tested qualitatively and quantitatively for formaldehyde. The method used involves a specific color reaction for formaldehyde, described by Matsukawa (Reference 4). The maximum of the absorption curve (525 mμ) was used as the means of identification; and a Beer's-law plot, constructed on the basis of samples containing known amounts of formaldehyde, was employed for the quantitative estimation. It was found that 6.6% formaldehyde, based on the amount of nitromethane decomposed, was formed during the decomposition of nitromethane in 5 min. This is in fair agreement with the values determined by the mass spectrometer.

g. The identification of methanol is very uncertain. Again it is based on only one peak (the 31 peak); all other peaks are masked by other decomposition products. Methanol does, however, account for the 31 peak, does not conflict with any other peaks, and appears to be a reasonable product.

h. It was pointed out previously that the addition of both oxygen and nitrogen dioxide caused a marked decrease in the concentration

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of hydrogen cyanide. Similarly, methane, methanol, and formaldehyde are virtually eliminated from the reaction products. The addition of nitric oxide also caused suppression of methane (Reference 1). Another effect of the addition of oxygen is to increase the concentration of carbon monoxide and carbon dioxide (Table V); this was expected, on the basis of the decreased amounts of C-N compounds. The concentration of nitric oxide is also markedly increased, and nitrogen dioxide is found among the decomposition products. The low value for nitric oxide (5.8%) found in the 2-min decomposition run does not conflict with this assertion. After 2 min only about 50% of the added oxygen has been consumed, and it is quite reasonable that a certain amount of the nitric oxide produced in the pyrolysis should react with free oxygen and be converted to nitrogen dioxide. This conclusion is borne out by the high percentage of nitrogen dioxide found in the sample. No free oxygen was found in the 5-min and 15-min runs (see also Section i, below).

i. The influence of nitrogen dioxide on the distribution of the products closely parallels that of oxygen (Table IV). The concentrations of nitric oxide, carbon dioxide, and carbon monoxide are markedly greater than in the samples to which nothing has been added. About 50% of the nitrogen dioxide originally added was recovered in all three runs. The significance of these results is discussed in Section C,2.

j. Although the analysis for nitric oxide and nitrogen dioxide is quite straightforward, there is some uncertainty regarding the actual distribution of these materials among the reaction products at 355°C. Two mutually counteracting reactions may occur in the ampoules after quenching and prior to the analysis.

(1) In the presence of oxygen (which may result from the addition of oxygen, the decomposition of nitrogen dioxide, or pyrolysis of the nitromethane) nitric oxide would form nitrogen dioxide. This reaction is relatively slow at the low pressures at which nitric oxide and oxygen are present: an independent experiment showed that large amounts of oxygen and nitric oxide are still present 3 hr after mixing. Because the ampoules are stored for different periods, the original amount of nitric oxide is therefore uncertain.

(2) An opposing process takes place during the transfer of the gases from the ampoule into the pre-expansion volume of the mass spectrometer, since an analysis of a known nitric oxide--nitrogen dioxide mixture showed a small decrease in the nitrogen dioxide concentration and a corresponding increase in the concentration of nitric oxide after the sample was Toepler-pumped.

k. Difficulties were encountered in the interpretation of certain data in the runs with added oxygen and nitrogen dioxide.

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(1) The samples are fractionated prior to mass-spectrometer analysis, as described previously (Reference 2). A large mass 30 peak appeared in the -50° fraction. Only part of this peak could be attributed to nitric oxide arising from the decomposition of nitrogen sesquioxide (N_2O_3). However, analysis of a known mixture of nitric oxide and nitrogen dioxide showed that more nitric oxide appears in the fraction containing nitrogen sesquioxide than would be expected from the stoichiometry. This is presumably the result of the solubility of nitric oxide in nitrogen sesquioxide, and the mass 30 peak was thus satisfactorily explained.

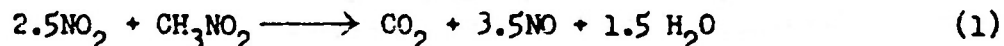
(2) Cyanic acid was prepared in an attempt to assign several smaller peaks, but the spectrograms which were obtained from this substance did not permit assignment; accordingly, a complete interpretation of the results is subject to further investigation. The unidentified substances, however, appear to be present in relatively small concentrations.

C. MECHANISM

1. Introduction

In previous reports several aspects of the mechanism of the thermal decomposition of nitromethane were discussed. These considerations will be extended on the basis of the experiments carried out during this report period.

2. The formation of nitrogen dioxide has been postulated as the first step in the thermal decomposition of nitromethane (Reference 3). If this is true, the following reaction, which was discussed in a previous report (Reference 1), may be important:



In this instance the addition of nitrogen dioxide to nitromethane should result in an increased rate of decomposition. From the results with added nitrogen dioxide (Table I, Section B.1.a) it must be concluded that if nitrogen dioxide is formed in the thermal decomposition of nitromethane this reaction cannot be important. It appears to be difficult to reconcile the fact that nitrogen dioxide does not attack nitromethane with the results obtained by Harnsberger (Reference 5) who reports the rate constant for reaction (1) to be $10^7 \exp(-21,000/RT)$. A comparison of the rate of this reaction with that of the overall decomposition of nitromethane ($k = 10^{14.6} \exp(-53,600/RT)$), according to Reference 3, shows that at zero time the reaction of nitromethane with 12% nitrogen dioxide should be more than 3500 times faster than the decomposition of nitromethane. One reason for the discrepancy may be that the conditions of Harnsberger's experiments were different from the conditions of this investigation. The low pre-exponential factor of 10^7 (second-order reactions usually have a pre-exponential factor of approximately 10^{14}) may suggest the occurrence of heterogeneous reactions or other complicating factors in

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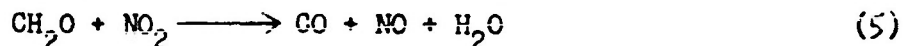
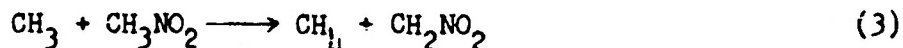
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Harnsberger's work. In this connection, it should be pointed out that the nitrogen dioxide that is added initially may decompose to a large extent before the nitromethane decomposes appreciably, whereas the nitrogen dioxide that may be formed during the decomposition of nitromethane may also react with other reaction products, such as radicals or formaldehyde (the reaction with formaldehyde being extremely fast). It is very likely, therefore, that in the experiments with added nitrogen dioxide (Table IV) the disappearance of cyanides, methane, and formaldehyde is caused by the oxygen formed from nitrogen dioxide and not by nitrogen dioxide itself. It is seen from Table V that the same compounds disappear when oxygen is added, although such disappearance in itself would not be sufficient proof. On the basis of the results obtained thus far it cannot be stated whether nitrogen dioxide is formed during the decomposition of nitromethane; however, if it is formed, reaction (1) must be unimportant.

3. It was noted that both nitrogen dioxide and nitric oxide inhibit the decomposition of nitromethane (Table I). Since the concentration of nitric oxide increases markedly when nitrogen dioxide is added, it is very likely that the inhibitory action of nitrogen dioxide is actually attributable to nitric oxide.

4. In the past, none of the investigators of the thermal decomposition of nitromethane have emphasized the formation of cyanides. The results obtained in this study show that at least under the present experimental conditions the production of cyanides appears to be very important. As shown in Table VI, 40 to 50% of the nitromethane that decomposes forms cyanides. These compounds are produced very early in the reaction and do not seem to be the result of product reactions in the later stages of the decomposition. Graham and Cottrell proposed that the following reactions are important in the decomposition of nitromethane:



In view of the high percentage of C-N compounds there must, however, be other reactions that are more important. In general, there are two ways of forming cyanides: (1) they are produced from nitromethane directly or from a portion of the molecule with the C-N bond intact, or (2) they are formed by reactions of radicals or other intermediate compounds, such as

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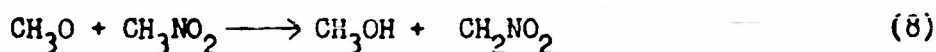
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This reaction does not seem to be very important, since when nitric oxide was added to nitromethane, the concentration of hydrogen cyanide not only did not increase but actually decreased somewhat, although the concentration of methane was reduced to zero. This indicates that methyl radicals reacted with nitric oxide instead of forming methane by reaction with nitromethane, but that the reaction of nitric oxide with methyl radicals apparently does not produce significant amounts of hydrogen cyanide. Of the organic cyanides, there was less acetonitrile but more propionitrile in the presence of nitric oxide; but it is not certain whether nitric oxide is responsible for the formation of propionitrile or whether it inhibits its decomposition. It appears likely, although it has not been proved definitely, that the C-N bond in nitromethane is not broken and re-formed to produce cyanides. In any event, the fact that large amounts of C-N compounds and small amounts of methane are formed conflicts with the reaction scheme of Cottrell and Graham. It is hoped that in an early report a mechanism can be presented that will be in accord with all of the experimental data.

5. Appreciable quantities of formaldehyde have been found during studies in a flow system (Reference 6) and during the photochemical decomposition of nitromethane (Reference 7). However, prior to the identification of formaldehyde in the present study, it had not been detected during experiments carried out by the static method. Formaldehyde may be formed by reaction (4) or by an intramolecular rearrangement. The identification of methyl alcohol is somewhat uncertain. A possible means for its formation would be the following reactions:



D. THE EFFECT OF OXYGEN ADDED TO NITROMETHANE IN ROCKET MOTORS

1. It had been observed that the addition of oxygen to nitromethane in a rocket motor lowers considerably the characteristic length (L^*) and the pressure required for stable operation (Reference 8). Because L^* is related to the time the propellant remains in the motor, it was assumed that the function of oxygen is to increase the rate of decomposition of nitromethane sufficiently to effect complete decomposition in a shorter time than is otherwise possible. If this explanation is valid, one would expect that under the conditions of the present investigation the addition of 13% oxygen should result in a considerable increase in the per cent nitromethane decomposed. Since the results presented in Table II, and discussed in Section B,1,b, show definitely that this cannot be so, another explanation for the action of oxygen is postulated, and is discussed below.

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2. An examination of the mass-spectrometer analyses of the products of the reaction reveals that in the presence of oxygen the distribution of products is altered (Table V). The addition of oxygen appears to produce a very sharp decrease in the concentration of compounds containing C-N, and an increase in the concentrations of carbon monoxide and carbon dioxide. The effect of oxygen in reducing to zero the concentration of compounds containing C-N, or at the most to traces, is considered to be significant, since the cyanides, notably hydrogen cyanide, comprise approximately 50% of the nitrogen (or carbon) compounds formed from nitromethane in the absence of additives (Table VI). On the basis of the results of the rate experiments (Table II) conducted thus far, it appears that the principal action of oxygen is not to cause additional decomposition of nitromethane but to remove hydrogen cyanide and other cyanides after their formation, although the possibility of a slight reaction between oxygen and nitromethane in the 2-min tests cannot be excluded. In addition to these results the mass-spectrometer analyses show that oxygen does not react solely with nitromethane to yield carbon monoxide and carbon dioxide directly, since under these conditions the cyanides would not be reduced completely but only partially.

3. Hydrogen cyanide is thermodynamically unstable by 31.2 kcal and acetonitrile by 21.0 kcal, and the absorption of energy is required for their formation. If a substantial portion of nitromethane is transformed to C-N compounds having an appreciable life before the final products CO and CO₂ are obtained, the realization of the full thermodynamic potential of nitromethane will be delayed. This may be sufficient to cause unstable operation. If the addition of oxygen shortens this time interval by the removal of all or a portion of the cyanides it may bring about smooth operating conditions. Further study of this hypothesis will include an investigation of the distribution of products in the presence of ethylene oxide or other compounds that are known to improve operating conditions in the motor. It should be pointed out, however, that if the cyanides are not removed in the experiments with added ethylene oxide, the hypothesis advanced is not necessarily disproved, since in such experiments the higher volatility of ethylene oxide, which results in easier ignition, may be the controlling factor for stable operation.

4. It is believed that the relatively small percentage of methane among the decomposition products in the absence of oxygen, together with its positive heat of formation (it is thermodynamically stable by 18.4 kcal), make it unlikely that the disappearance of methane is as important as that of the cyanides.

III. RESEARCH OF THE PREPARATION OF NEW ROCKET PROPELLANTS

A. INTRODUCTION

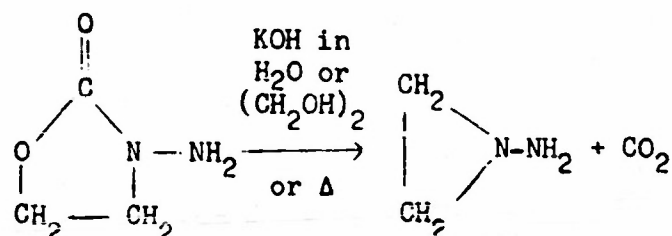
Several new approaches have been initiated during the current report period in attempts to synthesize new high-energy liquid propellants. The synthesis of N-aminoethylenimine by the dehydration of the sulfuric acid

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ester of ethanolhydrazine affords a maximum yield of only about 35% of the crude product (Reference 1). The preparation and decomposition of 3-amino-2-oxazolidone has therefore received attention as a possible alternate method of synthesis. The isolation of N,N,N'-trimethyltriazane from reduction mixtures of nitrosotrimethylhydrazine has not been realized. A more successful approach to the general problem of synthesizing alkyl derivatives of the higher hydro-nitrogens appears to be found in the careful oxidation of a trialkylhydrazine; a reaction of this type has been carried out, but only preliminary results are available at present. In order to determine the suitability of simple dihydrazines as high-energy fuels, an attempt was made to prepare a representative compound through the action of formaldehyde on trimethylhydrazine.

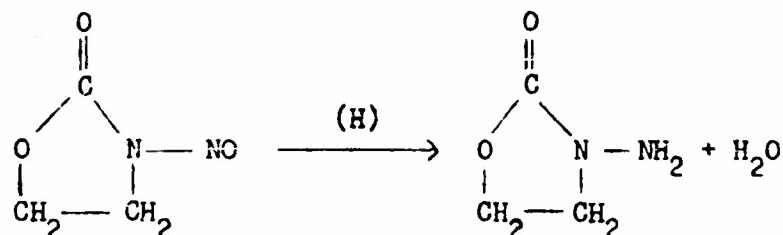
B. THE ATTEMPTED PREPARATION OF 3-AMINO-2-OXAZOLIDONE

1. The thermal and alkaline decompositions of 3-amino-2-oxazolidone have been considered as possible methods of synthesizing N-aminoethylenimine:



Because the required 3-amino-2-oxazolidone is unknown, various methods have been employed in an attempt to prepare it.

2. A convenient method for preparing 3-amino-2-oxazolidone should be the reduction of 3-nitroso-2-oxazolidone:



The nitroso compound can be prepared by treating 2-oxazolidone with nitrous acid (Reference 9). Ten grams of the material was dissolved in 62.5 ml of 2N hydrochloric acid at 0°C, and 10 g of potassium nitrite was gradually added. The product separated easily from the solution as a salmon-colored solid. The solution was filtered, and the solid was washed with ice water. The compound was recrystallized from a mixed solvent of ethyl acetate and n-hexane, and gave a solid melting at 49 to 50°C. The yield was 8.1 g, or 60.7% of the theoretical amount. It was found that this compound is extremely sensitive to alkali, and decomposes violently in the presence of even trace amounts.

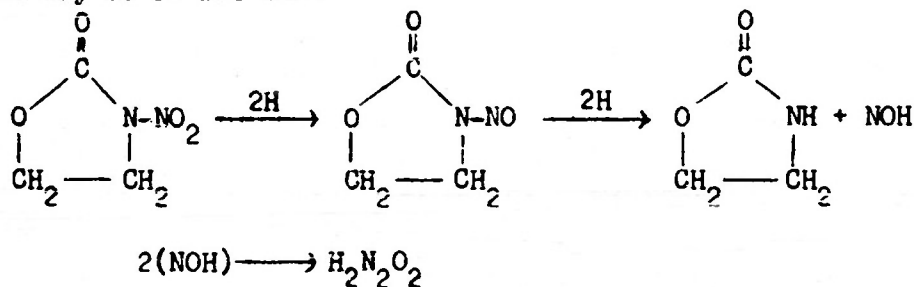
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III Research of the Preparation of New Rocket Propellants, B (cont.)

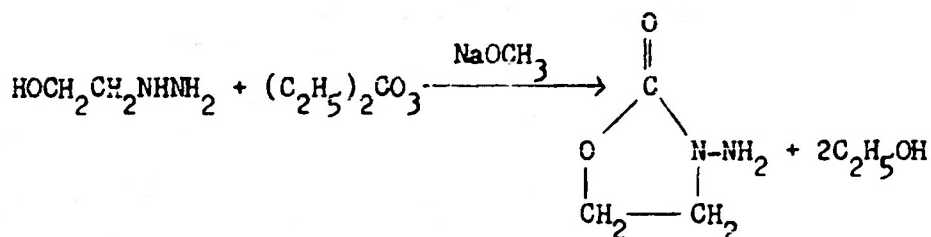
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An attempt was made to reduce the nitroso derivative in neutral aqueous solution by catalytic hydrogenation at room temperature and 1 atm of pressure. However, on contact with the activated catalyst used (10% palladium on charcoal), the nitroso compound slowly decomposed, and no hydrogen absorption was observed. It is probable that the presence of a small amount of the reduced product, 3-amino-2-oxazolidone, may catalyze the decomposition of the nitroso compound. In subsequent preparations of the nitroso compound violent decomposition occurred on removal of the solvent used in the recrystallization. For this reason, other methods of preparation of the desired amino compound were attempted.

3. Because the compound 3-nitro-2-oxazolidone is known to be stable to alkali, a sample was reduced with hydrogen in the presence of 10% palladium on charcoal in glacial acetic acid. Three moles of hydrogen per mole of the nitro compound are required for reduction to the amino compound. Exactly two moles were absorbed; the resulting solution did not reduce iodate, and therefore did not contain any of the desired compound. The course of the reaction may be as follows:



4. An attempt was made to prepare 3-amino-2-oxazolidone directly, by the reaction of diethyl carbonate and ethanolhydrazine:



This reaction is analogous to the preparations of 2-oxazolidone from ethanolamine and diethyl carbonate (Reference 10). The reaction is driven to completion by removal of the ethanol formed. When stoichiometric amounts of ethanolhydrazine and diethyl carbonate were heated at 120°C in the presence of a catalytic amount of sodium methylate no ethanol was collected as a distillate. After heating for 12 hr a small amount of distillate was obtained, but this was found to be diethyl carbonate. The residual diethyl carbonate was distilled from the reactor, and the ethanolhydrazine was removed by distillation.

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Propellants, B (cont.)

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at reduced pressure. The difference in reactivity between ethanolhydrazine and ethanolamine is considered to be due to a difference in the basicity of the nitrogen atoms in these compounds. The effect of substituting an amino group for hydrogen in ethanolamine to form ethanolhydrazine is to decrease the basicity of the nitrogen affected in the substitution. In fact neither nitrogen atom in ethanolhydrazine is as basic as the nitrogen atom in ethanolamine. This follows from the fact that hydrazine itself is less basic than ammonia. Since the formation of the C-N bond in an oxazolidone is a nucleophilic displacement on the carbon atom, it is evident that reaction is favored when the displacing nitrogen atom is especially basic. A similar explanation holds for the fact that the dehydration of the sulfuric acid ester of ethanolamine affords a high yield of ethylenimine, while the dehydration of the analogous ester of ethanolhydrazine results in only a small yield of N-aminoethylenimine.

5. As a possible method for preparing 3-amino-2-oxazolidone the reduction of 3-nitroso-2-oxazolidone will be attempted in an acid medium, in which the nitroso compound is known to be stable. In order to prevent the spontaneous decomposition of this compound during its preparation, it will be kept moist before use with a small amount of the solvent to be used in the subsequent reduction.

C. THE REDUCTION OF NITROSOTRIMETHYLHYDRAZINE

1. The reduction of nitrosotrimethylhydrazine has been carried out as a possible method for the production of N,N,N'-trimethyltriazane (Reference 1). Additional work in this direction has indicated that the desired triazane probably does not form during the reduction. A possible alternative synthesis of compounds of this type is indicated below, in connection with the oxidation of trimethylhydrazine.

2. A sample of nitrosotrimethylhydrazine, b_{10} 43.0°C, was submitted for analysis:

	<u>% C</u>	<u>% H</u>	<u>% N</u>
Found	35.50	8.80	41.50
	35.41	8.83	41.45
Calculated for $C_3H_9N_3O$	34.94	8.80	40.75

Inasmuch as this compound is known to be rather unstable even at low temperatures, these analytical results are considered to be entirely satisfactory.

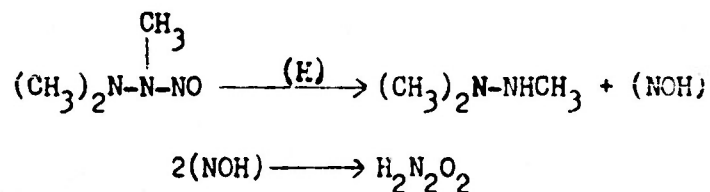
3. A 5 wt% aqueous solution of nitrosotrimethylhydrazine was reduced catalytically at room temperature and 1 atm. Ten percent palladium

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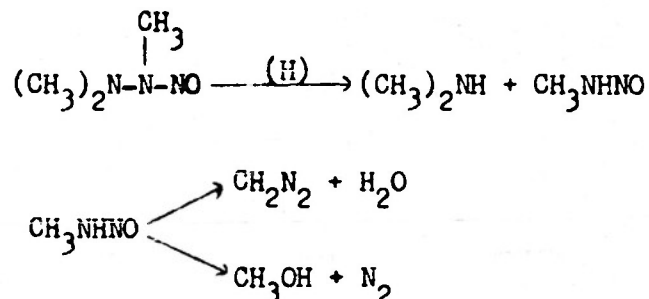
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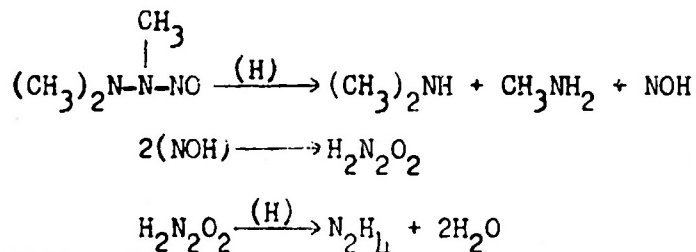
on charcoal was used as the catalyst. Approximately 1.5 moles of hydrogen were absorbed (theoretical amount for the formation of the triazane is 2 moles); the rate of hydrogenation decreased with time and became zero before all of the nitroso compound had been reduced. About 12% of the starting material was recovered and, in addition, a yield of about 35% of trimethylhydrazine was obtained (identified as the picrate, by mixed-melting-point determinations with sample of trimethylhydrazine picrate). Evidently cleavage occurs in the following manner:



4. The reduction of nitrosotrimethylhydrazine was carried out with lithium aluminum hydride in ether at room temperature (Reference 11). A yield of approximately 40% dimethylamine was obtained. This indicates that the course of reaction may have been as follows:



5. The nitroso compound was reduced with 2% sodium amalgam at 0°C in absolute ethanol (Reference 12). The reaction flask was shaken for several hours, and the solution was then filtered. Water was added, and the solution was made just acidic to litmus. When benzaldehyde was added and the flask was shaken, benzalazine separated. Dimethylamine was also isolated in about 30% yield. The observed reduction products may be explained in several ways. The dimethylamine may result from a cleavage, as indicated above for the catalytic reduction



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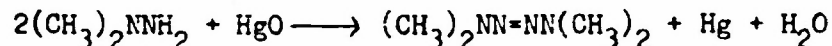
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This sequence also accounts for the formation of hydrazine. It is known that the reduction of certain N-nitroso compounds with sodium amalgam yields hydrazine, provided that the reaction is carried out at low temperatures (Reference 13).

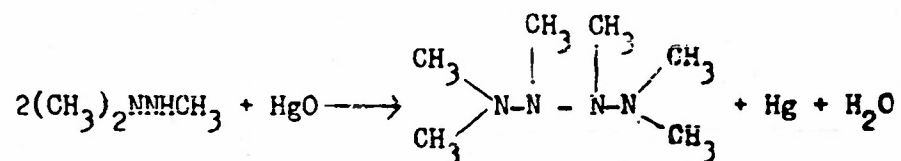
6. Since the desired triazane need not be postulated as an intermediate in explaining the formation of the observed reduction products, as noted above, this method of synthesizing higher alkyl hydronitrogens has been discontinued.

D. THE OXIDATION OF TRIMETHYLHYDRAZINE WITH MERCURIC OXIDE

1. The oxidation of unsym.-dimethylhydrazine in absolute ether with mercuric oxide is known, and has been found to yield tetramethyltetrazene at 0°C (Reference 14):



In the case of trimethylhydrazine only one hydrogen atom per molecule is available for oxidation, so that the reaction might be expected to afford hexamethyltetrazene:



It has been found, for example, that triphenylhydrazine gives hexaphenyltetrazene when oxidized with lead dioxide in ether at -55°C (Reference 8). Calculations show that hexamethyltetrazene should possess a specific impulse approximately equal to that of hydrazine, while its freezing point should be considerably lower.

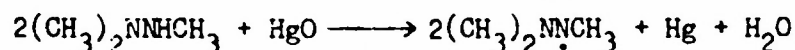
2. Trimethylhydrazine was prepared from unsym.-dimethylhydrazine according to the method of Aston (Reference 16). Anhydrous calcium sulfate and a trace of a saturated solution of potassium hydroxide in absolute ethanol were added to an ether solution of trimethylhydrazine. The solution contained 4 wt% trimethylhydrazine. The calcium sulfate was used to remove the water formed in the subsequent oxidation reaction; the potassium hydroxide solution was added to catalyze this reaction. A twofold excess of yellow mercuric oxide was then added gradually while the solution was stirred. The mercuric oxide served as an internal indicator, since on reduction it appeared gray because of the presence of free mercury. No reaction occurred below room temperature. When reaction did occur the ether solution gradually became intensely blue. When the solution was cooled the color became less intense, and at -80°C it was light blue-green. On warming, the color returned, but the intensity at room temperature was less than that observed before cooling. When the

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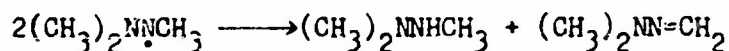
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solution was permitted to stand for several hours in a nitrogen atmosphere at room temperature, the color gradually disappeared, and a light-yellow solution remained. A small sample of the original intensely blue solution was removed with a syringe, and exposed to the atmosphere. This solution gradually became colorless. It was found that if the reaction was carried out as described above, except that the reaction mixture was initially exposed to the atmosphere, no color was observed. A reaction occurred in this case, however, as evidenced by a color change in the mercuric oxide. A possible explanation of these facts involves the assumption of the presence of stable free radicals:



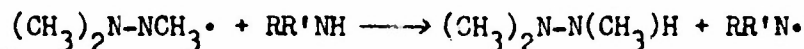
In the oxidation of unsym.-dimethylhydrazine by this method it has also been postulated that free radicals are involved (Reference 17); in this case, however, the radicals are less stable. The gradual disappearance of the blue color under nitrogen is probably the result of a disproportionation of some type--perhaps



The postulated methylene-unsym.-dimethylhydrazine is an isolable intermediate in the preparation of trimethylhydrazine. Because the oxidation of trimethylhydrazine with mercuric oxide was carried out on a two-gram scale, the isolation of products could not easily be accomplished. Only trimethylhydrazine was isolated (as the picrate) and it is not known whether this compound resulted from a disproportionation reaction, or simply represents unreacted starting material. Additional experiments are planned.

3. If trimethylhydrazyl radicals are formed, as is suggested by the above experiment, then considerable importance is attached to the problem of obtaining a solution of these radicals in a suitable high-energy fuel, such as hydrazine. The trimethylhydrazyl radical may be expected to possess a specific impulse somewhat higher than that of hydrazine. If hexamethyltetrazane, $(\text{CH}_3)_2\text{NN}(\text{CH}_3)\text{N}(\text{CH}_3)_2$, possesses a specific impulse approximately equal to that of hydrazine, then the trimethylhydrazyl radical, $(\text{CH}_3)_2\text{NN}(\text{CH}_3)$, must be more energetic than the tetrazane (and hence have a higher specific impulse than hydrazine) because the energy required to rupture the central N-N bond in the tetrazane has already been supplied in forming the radical.

4. If trimethylhydrazyl radicals are actually formed, then a possible method is available for the preparation of alkyl triazanes. If a secondary amine is added to the system, the following reaction may occur:

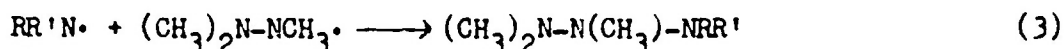
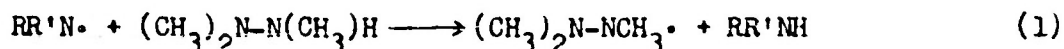


But $\text{RR}'\text{N}\cdot$ represents an unstable radical, and will react rapidly in one of the following ways:

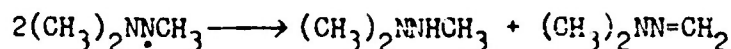
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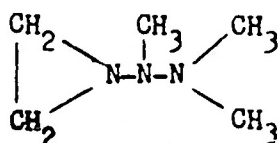
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Reaction (1) is the reverse of the immediately preceding reaction. Reaction (2) can be inhibited through the use of an ether solution of the amine which is dilute with respect to free radicals. Reaction (3) represents the desired reaction, in which a triazane is formed. The stabilization of trimethylhydrazyl radicals in this way will compete with the following reaction, which has already been discussed:



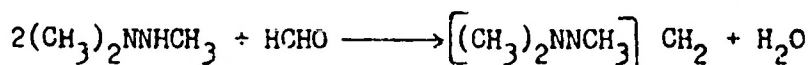
However, the desired reaction possesses the advantage that a hydrogen atom need not be removed from a carbon atom (the difference in bond energy between a C-H and an N-H bond is about 11 kcal/mole). Of special interest is the case in which the secondary amine is ethylenimine. The resulting triazane



may be considered a derivative of N-aminoethylenimine, but it will obviously possess a superior specific impulse because of the triazane linkage.

E. THE REACTION OF TRIMETHYLHYDRAZINE WITH FORMALDEHYDE

1. Although simple dihydrazines are at present unknown, it has become a matter of interest to attempt to prepare a compound of this type for evaluation as a high-energy liquid fuel. The simplest member of the class of compounds under discussion is methylenedihydrazine, $H_2NNHCH_2NHNH_2$. But methylenediamine, $H_2NCH_2NH_2$, is unstable, and presumably methylenedihydrazine would be also. The completely methylated dihydrazine derivative $[(CH_3)_2NNCH_3]_2CH_2$, should be stable, since analogous amine derivatives are stable (Reference 18). This compound should result from the reaction of trimethylhydrazine and formaldehyde:



2. Trimethylhydrazine was treated with a stoichiometric amount of 40% aqueous formaldehyde, while the temperature was kept below 30°C. A

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product was salted out when solid sodium hydroxide was added to the solution, the temperature again being kept below 30°C. The product was distilled at atmospheric pressure, and boiled at 92 to 94°C. This material is now being characterized.

IV. PERFORMANCE CALCULATIONS FOR HIGH-ENERGY ROCKET PROPELLANTS: TRIAZANE AND N,N,N'-TRIMETHYLTRIAZANE

A. Because of the presence of two N-N bonds in triazane, NH_2MHNH_2 , it was estimated that this compound would possess a substantially higher specific impulse than hydrazine. In like manner, alkyl triazanes should have correspondingly higher specific impulses than analogous alkyl hydrazines. Detailed calculations show that triazane possesses a maximum theoretical impulse of 289 lb-sec/lb under conditions such that the corresponding impulse for hydrazine is 274 lb-sec/lb.

B. Calculations were made of the specific impulse to be expected when triazane was burned with liquid oxygen as the oxidizer. For this purpose it was assumed that equilibrium of the exit gases was established during the expansion process in an ideal rocket motor at 300 psia chamber pressure. The method of calculation used has been previously outlined (Reference 19). The maximum value of the specific impulse for the triazane-oxygen system is 289 lb-sec/lb, and occurs at a mixture ratio of 0.53.

1. The values of specific impulse, chamber temperature, and exhaust temperature over the range of mixture ratios from 0.45 to 0.85 are shown in Figure 1. Values of characteristic velocity, coefficient of thrust, and mean specific heat ratio are shown in Figure 2.

2. The thermodynamic data used for the combustion gases were based on those published by the National Bureau of Standards. The heat of formation of liquid triazane was calculated by the method of Kharasch (Reference 20).

3. The calculation of the theoretical specific impulse of triazane permits rapid estimation of the specific impulse for triazane derivatives. On this basis the specific impulse for N,N,N'-trimethyltriazane should be approximately 274 lb-sec/lb. Triazane was chosen in preference to a triazane derivative in carrying out the detailed performance calculations because its estimated heat of formation is probably more accurate than the estimate for a derivative. This is because of the nature of the method used for estimating heats of combustion, in which there is some uncertainty in estimating the contributions of substituent groups. From the observed freezing points of ammonia and hydrazine it seems likely that triazane itself would be a solid at room temperature, and the value calculated serves principally as a base for estimating impulses of derivatives.

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V. STUDY OF THE FEASIBILITY OF EMPLOYING ACETYLIDE SALTS AS PROPELLANT COMPONENTS

A. INTRODUCTION

1. In a continuing search for materials that will depress the freezing point or vapor pressure of existing propellants without simultaneously lowering the specific impulses, a study has been initiated to determine the feasibility of employing certain acetylide salts as propellant components. By the proper selection of the cation, it should be possible to produce salts that are both stable and possess relatively high energy. The method of preparation of these salts could involve a metathetical reaction, of the general type:



where

M = a metal, e.g., sodium

B = a nitrogen-containing base

X⁻ = a suitable anion, e.g., a halide.

It is obvious that proper conditions of base strength, solubilities, and ionization constants must be met before the desired acetylide salts can be isolated.

2. The study was initiated with attempts to prepare guanidine acetylide and tetramethylammonium acetylide.

B. GUANIDINE ACETYLIDE

The preparation of guanidine acetylide was attempted by reaction of sodium acetylide with guanidine sulfate in liquid ammonia. Stoichiometric quantities of the two dry reagents were mixed in a three-necked flask fitted with a mercury-sealed stirrer and a Dry Ice reflux condenser, the system first being flushed with dry nitrogen. As liquid ammonia was pumped onto the solids from a Dewar flask, gas was evolved; when this gas was passed through ammoniacal silver nitrate solution, a precipitate of silver acetylide formed. This formation of free acetylene indicates that the acetylide ion has a stronger affinity for a proton than does the guanidinium ion, and hence a stronger base than guanidine will have to be employed.

C. TETRAMETHYLAMMONIUM ACETYLIDE

Under conditions similar to those described above, tetramethylammonium chloride and sodium acetylide were agitated in liquid ammonia for 2 hr, and the resulting mixture was extracted with ammonia in a Soxhlet extractor. No acetylene-containing gas was generated, but no clear-cut separation was obtained, because of the solubility of sodium chloride in

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ammonia. An extraction with dioxane likewise did not result in the desired separation. It became obvious at this point that quantitative information on the solubilities of tetramethylammonium salts in liquid ammonia would be necessary if the proper salts were to be chosen for the metathetical reaction.

D. SOLUBILITY OF TETRAMETHYLAMMONIUM SALTS IN LIQUID AMMONIA

1. Reagent grade tetramethylammonium chloride was dried at 100°C for 12 hr, and then analyzed for chloride ion by titration with silver nitrate. Results indicated a purity of 99.1%.

2. Tetramethylammonium nitrate was prepared by titration of a solution of tetramethylammonium chloride with silver nitrate to the dichlorofluorescein end point. After filtration, the solution was evaporated to dryness, and then purified by recrystallization twice from a mixed solvent of ethanol and water. A nitrogen determination indicated that the purity was 99.1%.

3. The apparatus for the determination of the solubilities consists of an unsilvered Dewar flask fitted with a stopper containing a mercury-sealed stirrer, a thermometer, a fitting for a drying tube, and a stainless steel rod onto which is fastened a calibrated volumetric cup. The liquid, containing an excess of the salt to be tested, is stirred for a sufficient time to produce a saturated solution. The solution is then permitted to settle, and the volumetric cup is submerged beneath the surface of the liquid. It is then raised above the solution, where it is permitted to remain until all of the ammonia has evaporated. After being dried in an oven, the outside is wiped thoroughly, and the tube is weighed to determine the amount of salt originally present in the solution contained in the volumetric cup.

4. The results to date are as follows:

Solubilities in Liquid Ammonia at -30°C

<u>Salt</u>	<u>g/100 ml Sol'n</u>
$[(CH_3)_4N]Cl$	0.81
$[(CH_3)_4N]NO_3$	0.40
$[(CH_3)_4N]Br$	0.05
$NaC\equiv CH$	5.12
$[(CH_3)_4N]I$	0.08

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VI. ENGINE TESTING: GASOLINE WITH MIXTURES OF FLUORINE AND OXYGEN

A. INTRODUCTION

It has been found that high specific impulses may be obtained when aviation gasoline is burned with mixtures of fluorine and oxygen. Complete results and details of the test program are being issued as a special report, and only a brief summary is presented here.

B. RESULTS

1. Previous tests (Reference 21) and those made during this program indicate that performance values comparable to experimental values obtained with an ammonia and fluorine mixture (Reference 22) may be obtained when gasoline is burned with fluorine diluted as much as 67 mole% with oxygen. A maximum specific impulse of 272 lb-sec/lb and a characteristic velocity of 6720 ft/sec were obtained in the 100-lb-thrust rocket motor shown in Figure 3. A summary of the data is presented in Table VII and curves of the experimental performance parameters in Figures 4, 5, and 6; tie lines join the values corrected and uncorrected for heat transfer in these curves. Results obtained previously are given in Table III.

2. A plot of maximum specific impulse for each of the several mixtures of fluorine and oxygen vs percentage of fluorine in the mixture produces an "S"-shaped curve, performance increasing from 0% fluorine to 33%, decreasing from 33% to 50%, and then increasing with 67% fluorine. Such a phenomenon can be explained on the basis of injector efficiency, since only one injector was used for the many different conditions of fuel and oxidizer flow. If theoretical specific impulse increases with increasing percentages of fluorine (or even drops off somewhat at high concentrations), and injector efficiency is not high in the mid-ranges of fluorine concentration, such an "S"-shaped curve would result. Only a thorough injector study would show the maximum performance possible with each oxygen-fluorine mixture.

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TABLE I

EFFECT OF NITROGEN DIOXIDE AND NITRIC OXIDE ON THE
THERMAL DECOMPOSITION OF NITROMETHANE

Temperature: 355°C

Run No.	Initial Pressure of Nitromethane psia	Additive mole %	Duration min	Amount Decomposed %
128	190	-	2	1.5
132	195	-	2	0.7
140	201	12.4 NO ₂	2	2.7
118	227	-	5	6.0
144	227	-	5	7.0
141	217	11.9 NO ₂	5	5.6
153	192	11.7 NO ₂	5	4.8
145	175	-	15	14.4
157	211	-	15	16.0
146	221	12.0 NO ₂	15	10.9
156	182	12.1 NO ₂	15	8.8
-	200*	-	31	26.9
116	192	11.1 NO ₂	31	20.5
122	230	12.1 NO ₂	31	19.2
123	188	12.0 NO	31	18.5
124	181	11.3 NO	31	20.8

* Value taken from Figure 1 of Reference 1.

Table I

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TABLE II

EFFECT OF OXYGEN ON THE
THERMAL DECOMPOSITION OF NITROMETHANE

Temperature: 355°C

<u>Run No.</u>	<u>Initial Pressure of Nitromethane psia</u>	<u>Additive mole %</u>	<u>Duration min</u>	<u>Amount Decomposed %</u>
128	190	-	2	1.5
132	195	-	2	0.7
127	152	13.6 O ₂	2	3.5
131	156	12.4 O ₂	2	2.1
118	227	-	5	6.0
144	227	-	5	7.0
155	182	13.5 O ₂	5	5.8
130	188	13.5 O ₂	5	3.2
145	175	-	15	14.4
157	211	-	15	16.0
129	210	13.2 O ₂	15	17.0
150	207	13.1 O ₂	15	15.8
154	200	13.7 O ₂	15	16.3
-	200*	-	31	26.9
125	203	14.0 O ₂	31	27.0
126	183	6.0 O ₂	31	25.9

* Value taken from Figure 1 of Reference 1.

Table II

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TABLE III

PRODUCTS OF THE THERMAL DECOMPOSITION OF NITROMETHANE

Temperature: 355°C

Product	Product Formed, %			
	Run 138 178.8 psia 2 min	Run 96 233.8 psia 5 min	Run 119 259 psia 15 min	Run 92 310.0 psia 31 min
C_2H_5CN	2.0	0.8	0.6	-
CH_3CN	2.3	0.3	0.8	1.6
HCN	16.0	14.1	21.8	17.2
N_2O	0.9	0.5	0.1	1.1
NO	18.7	17.8	18.0	10.5
N_2	1.9	2.1	2.5	4.2
CO_2	3.8	7.7	7.4	12.4
CO	7.8	7.9	3.5	4.8
CH_4	4.2	4.9	2.0	1.9
H_2O	38.9	42.3	42.6	46.4
CH_2O^*	2.8	1.0	2.0	-
CH_3OH^{**}	0.4	0.1	0.6	-

* Confirmed qualitatively by chemical anal is.

** Identified only tentatively.

Table III

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TABLE IV
EFFECT OF NITROGEN DIOXIDE ON
THERMAL DECOMPOSITION OF
NITROETHANE

Temperature: 355°C

Product	Product Formed, %		
	Run 152* 178.5 psia 11.9% NO ₂ 2 min	Run 135 218.2 psia 16.2% NO ₂ 5 min	Run 151 194.7 psia 11.8% NO ₂ 15 min
C ₂ H ₅ CN	-	-	0.1
CH ₃ CN	-	-	0.04
HCN	0.07	0.5	1.1
N ₂ O	-	2.2	0.6
NO	47.8	58.7	32.2
N ₂	1.4	0.5	5.1
CO ₂	12.3	12.0	9.4
CO	5.3	4.7	9.8
CH ₄	-	-	0.3
H ₂ O	32.9	21.2	41.0
CH ₂ O**	0.3	0.08	0.3
CH ₃ OH**	-	-	-

* About 50% of the added NO₂ was recovered in the samples.

** Identified only tentatively.

Table IV

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TABLE V

EFFECT OF OXYGEN ON THERMAL DECOMPOSITION OF NITROMETHANE

Temperature: 355°C

Product	Product Formed, %		
	Run 137 205.4 psia 14% O ₂ [†] 2 min [‡]	Run 148 204 psia 14% O ₂ [‡] 5 min [‡]	Run 149 210 psia 13.9% O ₂ [‡] 15 min [‡]
C ₂ H ₅ CN	-	-	-
CH ₃ CN	-	-	-
HCN	0.2	-	0.8
NO ₂	22.8	11.6	10.7
N ₂ O	-	0.3	-
NO	5.8	36.7	18.4
N ₂	1.5	2.9	4.6
CO ₂	11.1	14.5	6.4
CO	32.3	14.7	8.1
CH ₄	-	-	0.05
H ₂ O	26.2	19.0	51.6
CH ₂ O*	0.2	-	0.01
CH ₃ OH	-	-	-

* Identified only tentatively.

† About 50% of the added oxygen was recovered as elemental oxygen.

‡ No oxygen found in samples.

Table V

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TABLE VI

FORMATION OF C-N COMPOUNDS DURING
THERMAL DECOMPOSITION OF NITROMETHANE

Temperature: 355°C

Run No.	Duration min	moles Nitromethane Decomp. moles C-N compounds Formed x 100*	moles Nitromethane Decomp. moles HCN Formed x 100*
138	2	45.5	35.9
96	5	39.8	36.9
119	15	50.0	47.0
92	30	47.1	43.1

* These values were computed on the basis of

$\frac{\text{moles N in products}}{\text{moles C-N compounds}} \times 100$ and $\frac{\text{moles N in products}}{\text{moles HCN compounds}} \times 100$, respectively.

Table VI

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TABLE VII

ALDO TEST-GENERAL CORPORATION - PROOVING GROUNDS
TEST DATA SUMMARY SHEET

PROPELLANT EVALUATION OF MIXED LIQUID FLUORINE AND OXYGEN WITH AVIATION GASOLINE

M.O.	-	28010012	Test Series	-	D-45-LP
Injector	-	AR-20278-Modified	Thrust Chamber	-	AR-3395

TEST NUMBER	DATE - 1953	DURATION SECONDS	FUEL	Oxidizer				THROAT DIAMETER INCHES	L *	CHAMBER PRESSURE PSIA	T-BUST TEMP	$\dot{w}_0$, lb/sec	$\dot{w}_1$, lb/sec	$\dot{w}_2$, lb/sec	MIDTUBE RATIO $\dot{w}_0/\dot{w}_1$	C_F , CALCULATED	C_F , CALCULATED	C_F , CALCULATED	I_{sp} , CALCULATED	C_F , CORRECTED FOR HEAT TRANSFER	C_F , CORRECTED FOR HEAT TRANSFER	Q_0 , CORRECTED FOR HEAT TRANSFER	Q_1 , BTU/SBC	AVERAGE HEAT TRANSFER	REMARKS	TEST NUMBER	
				MOLE % F_2	MOLE % O_2	WT % F_2	WT % O_2																				
1	6-2	8.50	Av. Gas	0	100.0	0	100.0	.552	130	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	Satisfactory Start and Run - Equilibrium Conditions not Reached.	1	
2	6-4	9.30	Av. Gas	0	100.0	0	100.0	.550	130	299	105	.3068	.1264	.4332	2.4225	1.448	524.3	7760	241	1.49	5330	7920	146	.43	2.149	Satisfactory Start and Run.	2
3	6-5	8.30	Av. Gas	0	100.0	0	100.0	.549	130	288	97	.2931	.1188	.4119	2.470	1.442	5329	7561	235	1.43	5450	7770	241	179	2.500	Satisfactory Start and Run	3
4	6-10	4.50	Av. Gas	0	100.0	0	100.0	.550	130	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	Rough Start, Oxidizer Flow Apparently Stopped about the Time H_2O_2 Flameout.	4	
5	6-11	4.30	Av. Gas	0	100.0	0	100.0	.550	130	253	82	.2820	.1363	.4183	2.070	1.4	4627	6993	196	1.36	4680	6387	195	78.15	0.915	Satisfactory Start and Run.	5
6	6-24	1.20	Av. Gas	100.0	0	100.0	0	.550	130	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	Malfunction of Main Propellant on Start. Apparently Injector Burnt After Malfunction of Oxidizer in Line.	6	
7	7-10	13.00	Av. Gas	52.2	47.8	56.5	43.5	.550	130	259	83	.3219	.0643	.3862	5.000	1.35	5130	6930	215	1.35	5459	7380	279	207.68	2.354	Satisfactory Start and Run.	7
8	7-15	3.50	Av. Gas	50.6	49.4	54.9	45.1	.551	130	-	81	.3237	.0742	.3979	4.352	-	-	-	205	-	-	-	-	-	-	Satisfactory Start. H_2O_2 Flame On During Run .	8
9	7-16	5.00	Av. Gas	49.6	50.4	54.0	46.0	.550	130	267	86	.3404	.0763	.4167	4.467	1.35	4895	6608	205	1.36	5001	6829	219	122.71	1.440	Satisfactory Start and Run.	9
10	7-17	5.50	Av. Gas	49.6	50.4	54.0	46.0	.550	130	284	85	.3705	.0697	.4402	5.320	1.26	4933	6190	192	1.27	5165	6509	202	109.64	1.286	Satisfactory Start and Run	10
11	7-20	2.70	Av. Gas	32.6	67.4	36.5	63.5	.550	130	338	-	.3481	.0894	.4385	3.893	-	5897	-	-	-	-	-	-	-	-	Satisfactory Start and Run. No Oscillograph Record.	11
12	7-22	5.00	Av. Gas	32.6	67.4	36.5	63.5	.550	130	345	105	.3194	.0937	.4131	3.409	1.28	6389	8178	254	1.31	6120	8760	272	189.31	2.221	Satisfactory Start and Run.	12
13	7-24	5.60	Av. Gas	32.6	67.4	36.5	63.5	.550	130	303	102	.3029	.0948	.3977	3.194	1.42	5829	8277	256	1.43	6045	8649	269	163.71	1.921	Satisfactory Start and Run.	13
14	7-27	4.60	Av. Gas	32.6	67.4	36.5	63.5	.550	130	295	97	.3275	.0872	.4147	3.758	1.38	5442	7532	234	1.39	5543	7683	239	151.82	1.781	Satisfactory Start and Run.	14
15	7-28	5.00	Av. Gas	22.8	77.7	26.0	74.0	.551	130	313	104	.2922	.1112	.4034	2.629	1.39	5956	8279	258	1.39	5070	8460	263	120.77	1.417	Satisfactory Start and Run.	15
16	7-29	5.50	Av. Gas	22.8	77.7	26.0	74.0	.551	130	317	100	.3080	.1024	.4104	3.009	1.32	5929	7826	245	1.33	6237	8303	258	145.00	1.701	Satisfactory Start and Run.	16
17	7-31	-	Av. Gas	65.2	34.8	71.1	28.9	.550	130	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	Malfunction. Oxidizer Valve Failed to Open.	17	
18	8-4	5.60	Av. Gas	65.2	34.8	71.1	28.9	.550	130	270	85	.3184	.0599	.3783	5.305	1.32	5460	7207	225	1.35	5759	7850	244	107.82	1.265	Satisfactory Start and Run.	18
19	8-5	4.00	Av. Gas	66.7	33.3	70.4	29.6	.551	130	274	84	.3242	.0643	.3684	5.042	1.29	5396	6961	216	1.32	5574	7335	228	106.79	1.253	Satisfactory Start and Run. Fairly Heavy Carbon Deposits on Chamber and Walls.	19
20	8-6	6.60	Av. Gas	20.0	80.0	22.9	77.1	.550	130	311	94	.3160	.0916	.4076	3.450	1.27	5838	7414	231	1.28	6255	7981	248	163.66	1.923	Satisfactory Start. Hydraulic Pressure Apparently Dropped Off at Midpoint to Gave Low Flow. Carbon Deposits on Chamber Walls.	20
21	8-7	3.10	Av. Gas	20.0	80.0	22.9	77.1	.551	130	318	100	.2903	.1199	.4102	2.420	1.32	5951	7855	244	1.33	6257	8326	259	123.74	1.569	Satisfactory Start. Apparent Chugging during Run.	21
22	8-10	3.80	Av. Gas	33.3	66.7	37.2	62.8	.551	130	317	101	.3174	.0872	.4046	3.640	1.34	6014	8059	250	1.35	6264	8470	262	148.96	1.748	Satisfactory Start and Run. Slight Carbon Deposit on Nozzle.	22
23	8-12	3.20	Av. Gas	31.3	68.7	36.5	63.5	.551	130	320	103	.3337	.0816	.4155	4.079	1.35	5912	7981	248	1.36	6448	8336	259	116.79	1.370	Satisfactory Start and Run.	23
24	8-13	5.50	Av. Gas	31.2	68.7	36.5	63.5	.551	130	302	97	.3172	.0850	.4022	3.730	1.35	5764	7781	241	1.37	6035	8260	257	181.52	2.130	Satisfactory Start and Run.	24
25	8-14	2.30	Av. Gas	100.0	0	100.0	0	.551	130	-	-	.3600	.0506	.4106	7.160	-	-	-	299	-	-	-	-	-	-	Satisfactory Start. Turbulent Burnt Out During Run. Apparently H_2O Flow Reduced.	25

* Heat Transfer Corrections Unreliable.
* Specific Impulse Values Approximate Only.

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TABLE VIII

AVIATION GASOLINE AND MIXTURES OF LIQUID FLUORINE AND LIQUID OXYGEN

SUMMARY OF PERFORMANCE DATA

Test No. PP-15-1-	Fuel	Oxidizer				Chamber Pressure psia	M.F. (w_{ox}/w_f)	C_p (Corr. for Heat-Trans.)	I_{sp} (Uncorr.) lb-sec/lb	c^* , ft/sec (Corr. for Heat-Trans.)	I_{sp} , lb-sec/lb, (Corr. for Heat-Trans.)	Molar Mixture Ratio
		Mole%		Wt%								
		F ₂	O ₂	F ₂	O ₂							
1	← Aviation Gasoline →	50.7	49.3	55.0	45.0	225	2.57	1.34	192	4708	196	8.29
2		50.7	49.3	55.0	45.0	330	3.82	1.46	244	5541	252	12.32
3		—	100	—	100	241	2.51	1.32	198	5016	206	8.86
4		50.3	49.7	54.6	45.4	319	5.85	1.43	242	5665	252	18.88
5		50.3	49.7	54.6	45.4	322	4.62	1.43	253	5884	261	14.91
6		50.3	49.7	54.6	45.4	316	4.87	1.43	243	5736	255	15.72
7		66.7	33.3	70.4	29.6	321	4.62	1.41	247	5991	262	14.50
8		66.7	33.3	70.4	29.6	305	3.87	1.42	237	5648	249	12.15

Table VIII

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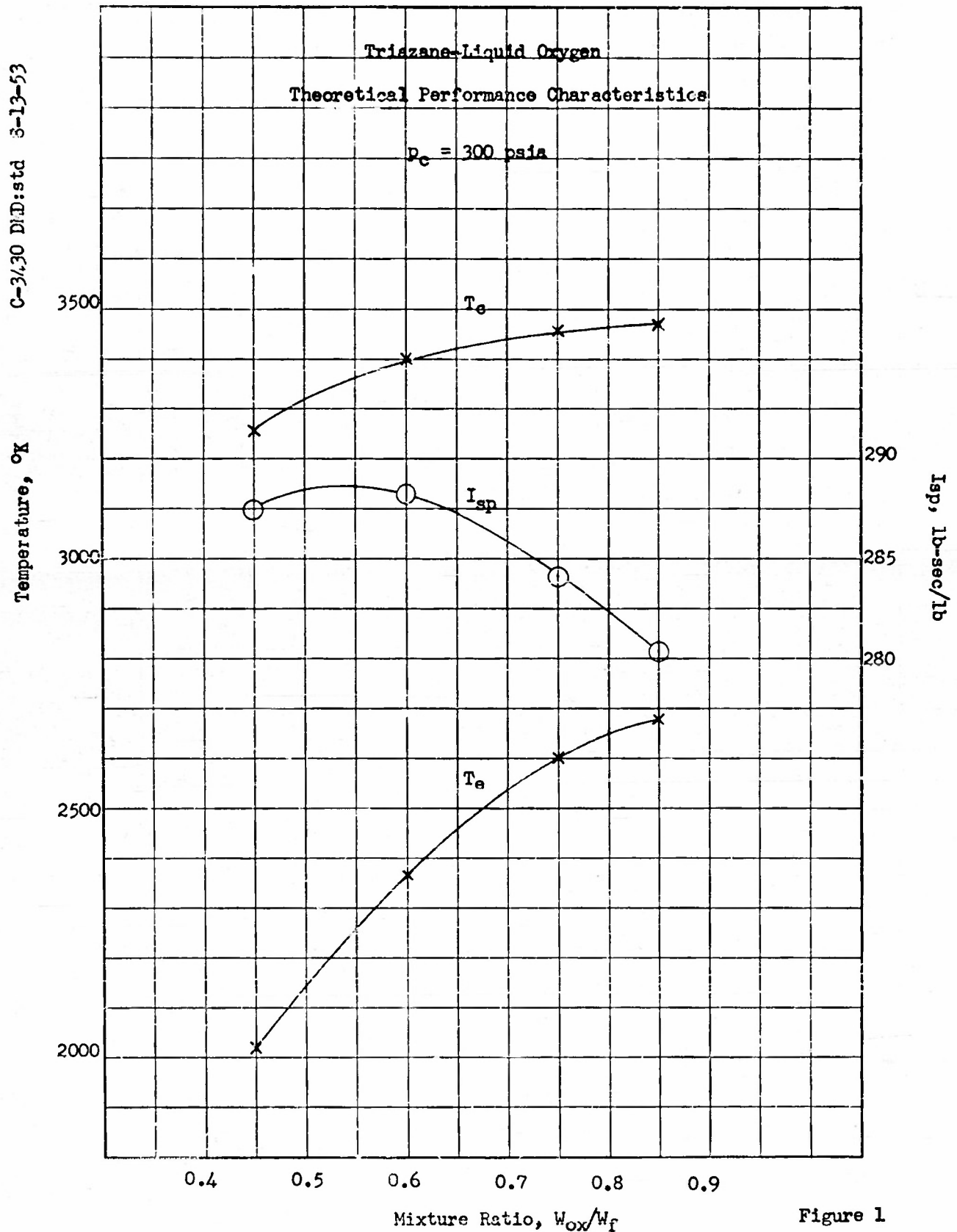


Figure 1

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O-3431 DMD:std 8-13-53

c^* , ft/sec

C_F

$\bar{\gamma}, C_p/C_v$

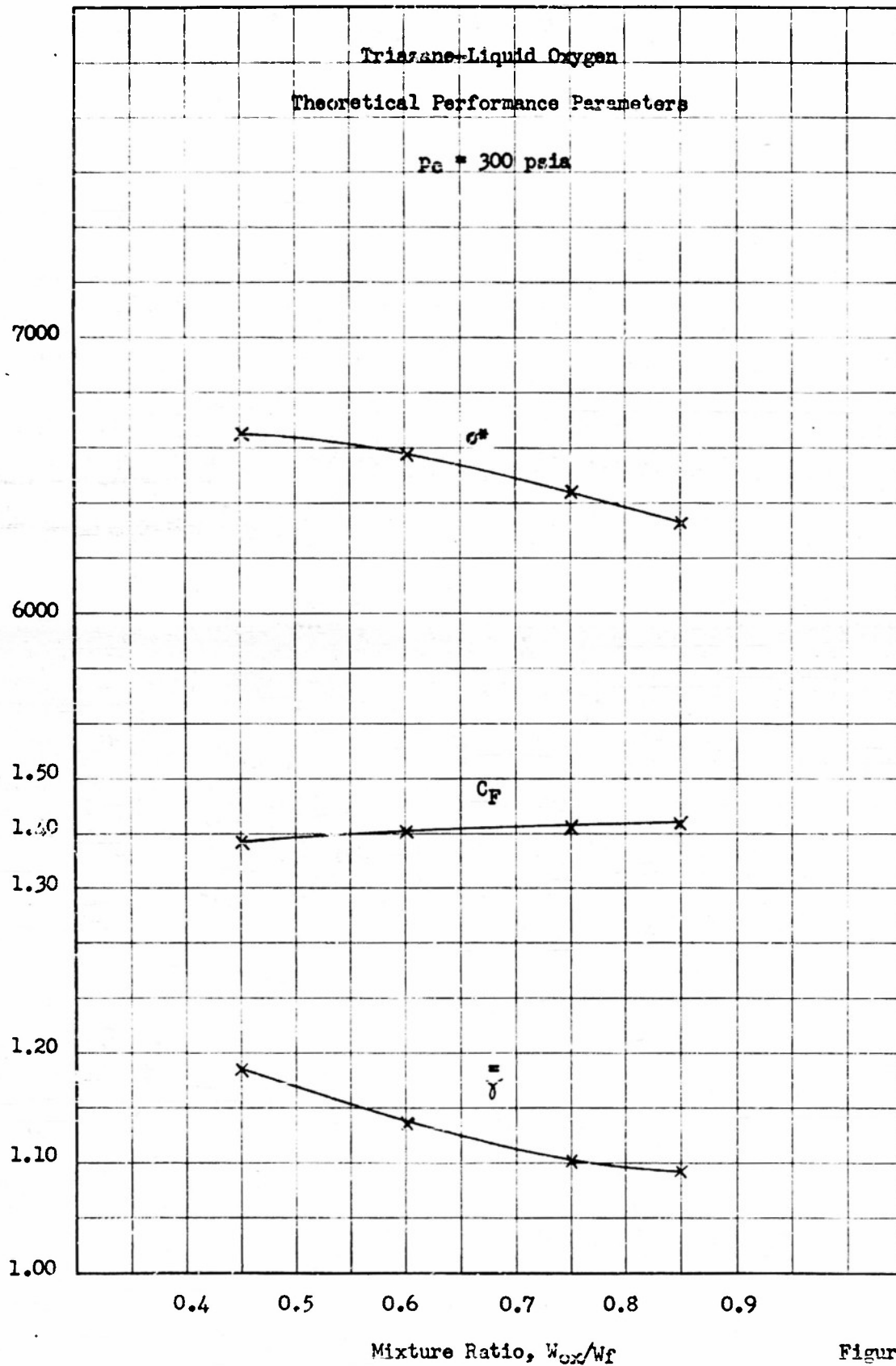


Figure 2

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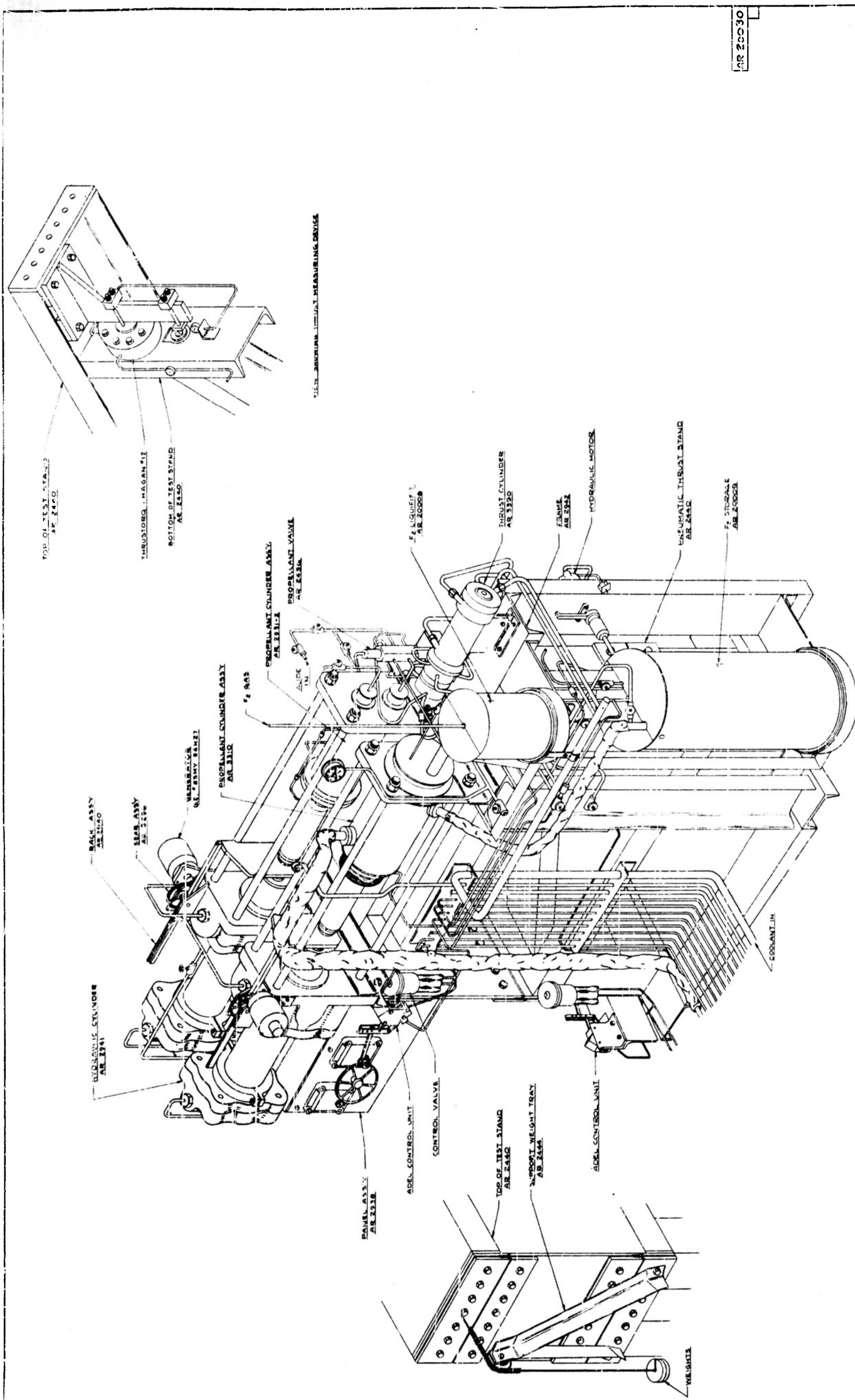


Figure 3

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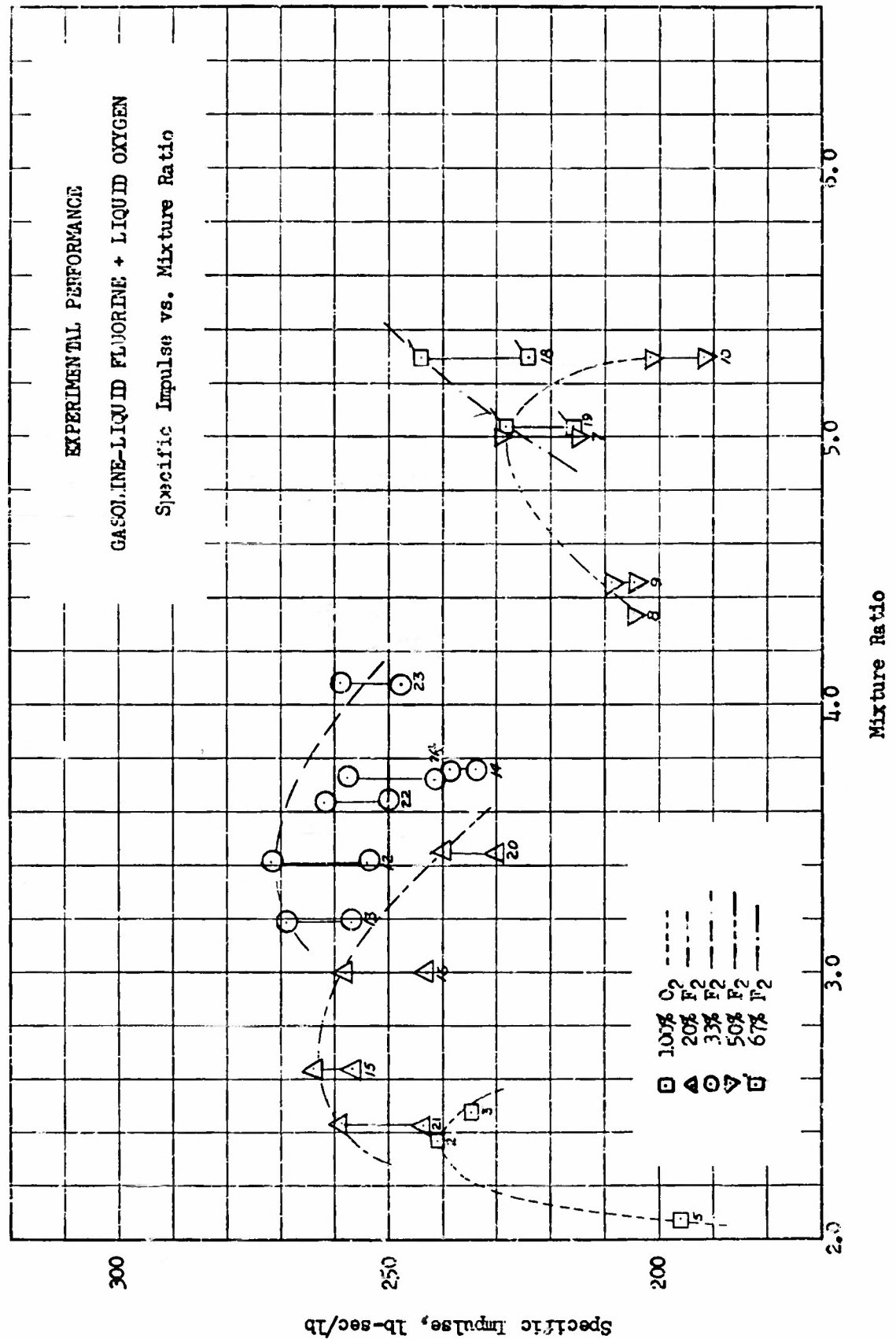


Figure 1

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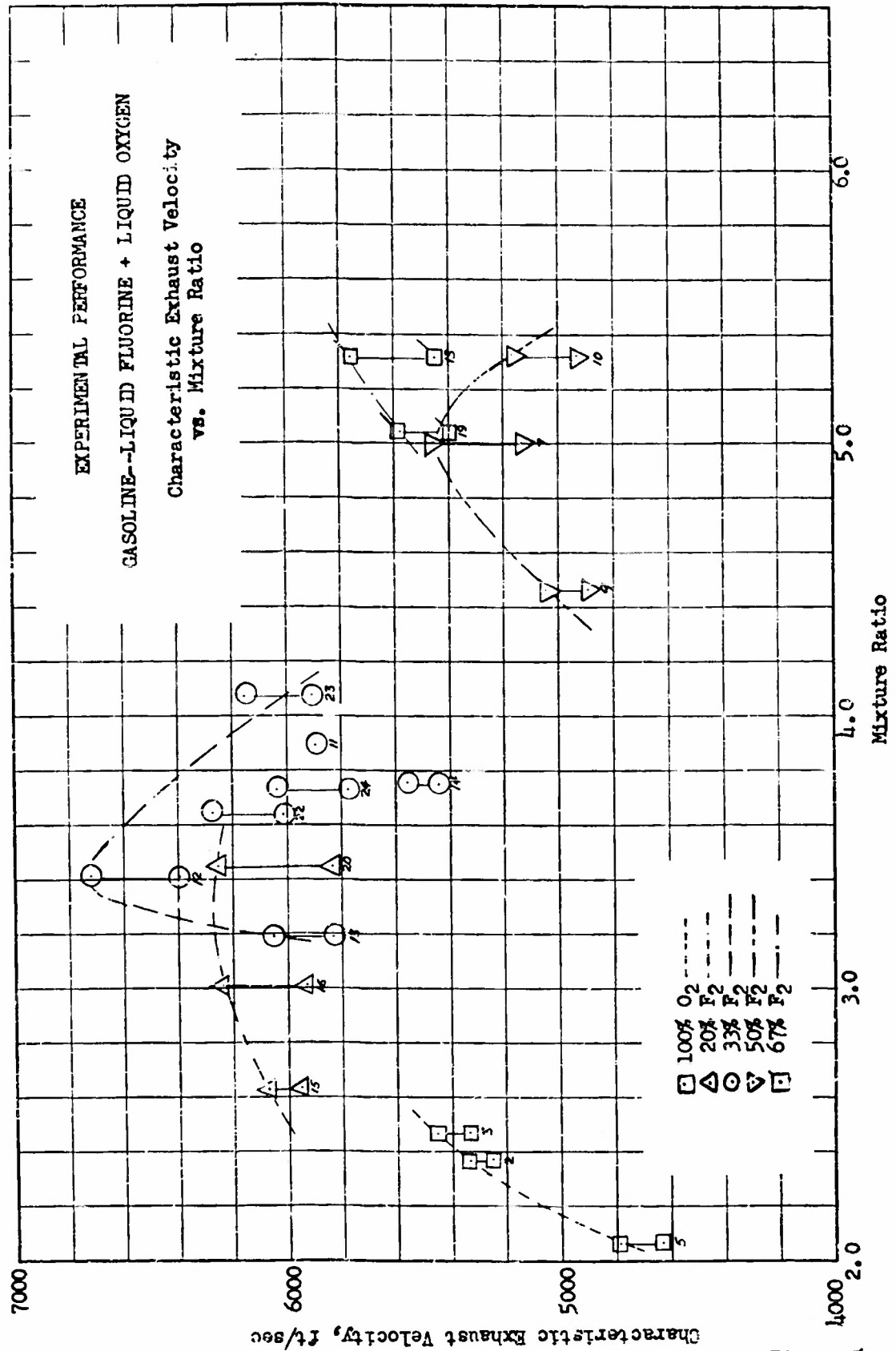
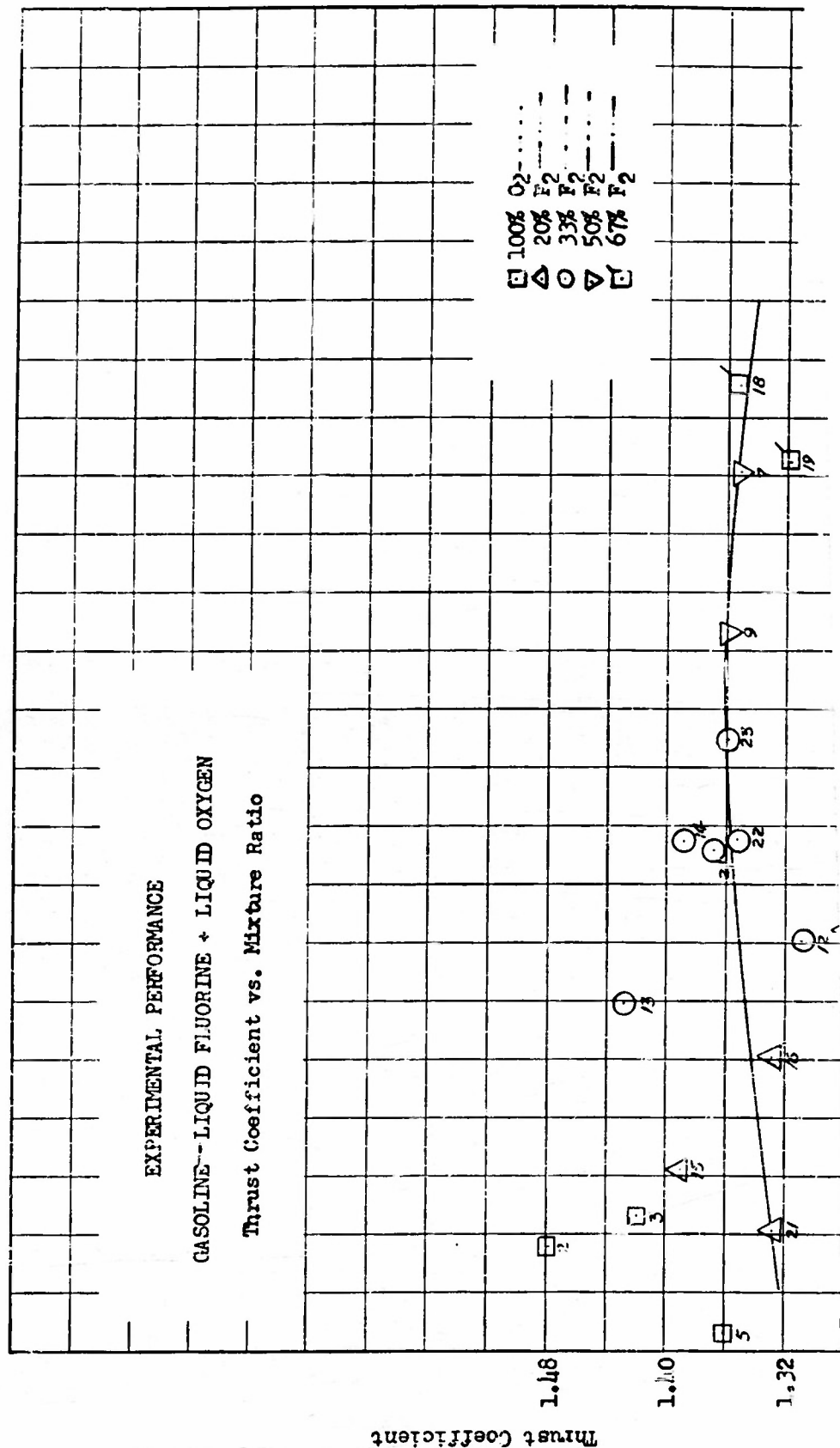


Figure 5

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C-3440 EMW:17 9-10-53



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