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Report No. [illegible]

Aerojet ENGINEERING CORPORATION

AZUSA, CALIFORNIA

INFORMAL REPORT OF PROGRESS

Copy No. 13

23 January 1953

TO: Office of Naval Research
Department of the Navy
Washington 25, D.C.

SUBJECT: Investigation of Liquid Rocket Propellants

CONTRACT: N7onr-462, Task Order III
Project NR 220 023

PERIOD COVERED: 1 December 1952 through 15 January 1953

This is the second in a series of informal progress reports, submitted between quarterly reports, in partial fulfillment of the contract.

AEROJET ENGINEERING CORPORATION

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NOTE: The information contained herein is regarded as preliminary and subject to further checking, verification, and analysis.

I. WORK PERFORMED DURING REPORT PERIOD

A. KINETIC STUDY OF THE THERMAL DECOMPOSITION OF NITROMETHANE

1. During this report period, further thermal decomposition tests were made with nitromethane at 355°C in order to confirm the apparent second-order character of the reaction at high pressures.

2. Additional quantities of nitromethane were purified by distillation for use in the decomposition tests.

3. Recent experiments in which nitromethane containing less than 0.05% water (by Karl Fischer titration) was analyzed in the mass spectrometer gave mass peaks corresponding to known decomposition products which were appreciably larger than had been observed previously. These peaks, primarily those due to water and acetonitrile, were reduced considerably after conditioning of the mass spectrometer tube with butene overnight, but they still are not as small as noted earlier in this program. Informal discussions with other workers in the field of mass spectrometry brought out the fact that similar behavior had been noted in earlier attempts to analyze nitromethane. As a new source has been installed in the spectrometer since the earlier work, it is possible that an unexpected decomposition of nitromethane inside the instrument is now occurring. This phenomenon is being investigated as a possible source of information on the primary decomposition of nitromethane.

4. In continuing the work on a mass-spectrometric procedure for the analysis of water, a conditioning procedure was developed to overcome difficulties associated with the adsorption of water in the sample system. It was found that a plot of peak height versus pressure of water is not linear, the ionization efficiency per unit pressure decreasing considerably as the pressure is lowered. A permanent gas such as nitrogen does not exhibit such characteristics. The realization of the existence and magnitude of this deviation from linearity should make it possible to improve considerably the accuracy of the analyses of the decomposition products of nitromethane.

B. RESEARCH ON THE PREPARATION OF NEW ROCKET PROPELLANTS

1. Efforts to synthesize N-aminoethylenimine by the dehydration of ethanolhydrazine have continued. One of the crude reaction products obtained from the dehydration by sulfuric acid was distilled twice at 100 mm, and a middle cut was found by analysis to contain the following:

	% C	% H	% N	Total
Found	42.01	10.65	42.10	94.76
	41.93	10.71	42.22	94.86
Calculated for $C_2H_6N_2$	41.36	10.41	48.23	100.00

If oxygen is assumed to make up the remainder of the sample, these results suggest that ethanolhydrazine may have decomposed to some extent as follows:

$$HOCH_2CH_2NHNH_2 \longrightarrow N_2H_4 + CH_3CHO$$

When an additional quantity of the material used for the analysis was treated with sulfuric acid, hydrazine sulfate precipitated; when the product was treated with 2,4-dinitrophenylhydrazine, acetaldehyde 2,4-dinitrophenylhydrazone precipitated. In investigating the cause of the impurities in the product, it was found that only minor decomposition of the ethanolhydrazine occurs during its purification by distillation at reduced pressure, and that no decomposition occurs in the esterification of ethanolhydrazine. Work is now in progress to confirm the conclusion that decomposition must occur in the removal of the elements of sulfuric acid from the ester.

2. An ampoule of the middle cut of the first distillation of the material analyzed was sealed under its own vapor and stored for 216 hr at 155°F. There was no increase in apparent viscosity of the liquid, and no change in the clarity. Molecular weight determinations by freezing-point lowering in benzene indicate that no polymerization occurs. This stability test will be repeated on a pure sample.

3. Consideration has been given to the preparation of the sulfuric acid ester of ethanolhydrazine by methods which would afford a purer product than by the addition of ethanolhydrazine to sulfuric acid at 110°C. Two such methods have been investigated: the action of sulfur trioxide, in the form of its dioxane complex, on ethanolhydrazine in chloroform solution at room temperature; and the prolonged action of 96% sulfuric acid on anhydrous ethanolhydrazine at room temperature. A solid reaction product has been obtained in both cases, but these have not yet been characterized.

4. It is intended to prepare an oxygen-free dehydration product of ethanolhydrazine for analysis. This will be accomplished by employing less drastic experimental conditions in removing the elements of sulfuric acid from the intermediate ester.

C. PERFORMANCE EVALUATION OF LIQUID ROCKET PROPELLANTS

Delay in receiving gaseous fluorine from the vendor has resulted in a temporary cessation of operations on this program. The fluorine has just arrived and motor tests will soon start for the evaluation of aviation gasoline with an oxidizer of mixed fluorine and oxygen.

D. IGNITION DELAY STUDY OF TRIETHYL TRITHIOPHOSPHITE WITH NITRIC ACID

Results of this program are to be reported in a special report to be issued by 11 February 1953. Problems of toxicity of the fuel, and destruction of pressure pickups by "hard starts" have caused some delay in obtaining results.

E. IMPROVEMENT OF DINITROGEN TETROXIDE AS A ROCKET OXIDIZER

A new series of additives to dinitrogen tetroxide has been suggested by the work so far. It is planned to prepare one or several of the lower γ- trinitro ethers for evaluation, as indications are that the combination of ether linkages and nitro groups in one molecule will give large negative deviations from ideality. In addition, some of the additives previously suggested remain to be examined. Equipment and intermediates for the preparation of nitro ethers have now been assembled.

F. STUDY OF ACETYLIDE SALTS AS ROCKET PROPELLANT COMPONENTS

It is planned to start work on this problem as soon as some additional data are obtained on N-aminoethylenimine. Work should have begun by the next report period.

II. STATUS

The decrease in work output during the last report period was occasioned by the termination of a chemist, Mr. L. K. Moss, to enter graduate school, and the recall of a temporary replacement for him, Dr. S. C. Burket, who was on loan from another department. As a result of a large number of interviews of prospective employees, one new man, Dr. Jacob Silverman, has been hired and will start early in February, and several other experienced men are under consideration. Attempts will be made to add a total of three men to the project, to carry the expanded work load for the remainder of the year. A summary of Dr. Silverman's experience is appended.

Dr. Jacob Silverman

B.S. 1943 - Wayne University
Ph.D. 1949 - Wayne University

1944 to 1945 - U. S. Army Air Force
1949 to 1951 - University of Southern California Post-Doctoral Fellowship
1951 to Present - U. S. Naval Radiological Defense Laboratory, San Francisco

Dr. Silverman's applicable experience includes work on phase relationships in the critical region, and a diversified background in the physical chemistry of solutions.