UNCLASSIFIED

AD NUMBER

AD009863

CLASSIFICATION CHANGES

TO: unclassified
FROM: confidential

LIMITATION CHANGES

TO:
Approved for public release; distribution is unlimited.

FROM:
Distribution authorized to DoD only; Administrative/Operational Use; 10 NOV 1952. Other requests shall be referred to Office of Naval Research, Arlington, VA 22203. Pre-dates formal DoD distribution statements. Treat as DoD only.

AUTHORITY

ONR ltr dtd 28 Aug 1968; ONR ltr dtd 28 Aug 1968

THIS PAGE IS UNCLASSIFIED
THIS REPORT HAS BEEN DECLASSIFIED AND CLEARED FOR PUBLIC RELEASE.

DISTRIBUTION A
APPROVED FOR PUBLIC RELEASE;
DISTRIBUTION UNLIMITED.
TO: Office of Naval Research  
Department of the Navy  
Washington 25, D.C.  

SUBJECT: Investigation of Liquid Rocket Propellants  

CONTRACT: N70onr-462, Task Order III  
Project NR 220 023  

PERIOD COVERED: 1 September through 15 October 1952  

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

AEROJET ENGINEERING CORPORATION  

D. L. Armstrong, Principal Chemist  
Solid Engine and Chemical Division  

NOTE: The information contained herein is regarded as preliminary and subject to further checking, verification, and analysis.
WORK PERFORMED DURING REPORT PERIOD

A. KINETIC STUDY OF THE THERMAL DECOMPOSITION OF NITROMETHANE

1. During this report period additional thermal decomposition tests were made with nitromethane at varying initial pressures (in the range of 200 psi), and at approximately 350°C.

2. An analytical procedure for the polarographic determination of nitromethane was developed and tested. This method was employed in the analysis of samples that had been subjected to thermal decomposition, and data are being assembled to determine the order of the reaction.

3. Several samples that had been allowed to decompose until all nitromethane had disappeared were analyzed mass-spectrometrically. As the data have not yet been completely reduced it is not possible to account for all decomposition products, but it appears certain that the main products are carbon dioxide (25%), water (15%), hydrogen cyanide (10%), acetonitrile (5%), nitrogen (17%), carbon monoxide (15%), and nitrous oxide (5%).* Methane, hydrogen, and unidentified compounds present in small amounts comprise approximately 9% of the total products.

B. IMPROVEMENT OF DINITROGEN TETROXIDE AS A ROCKET OXIDIZER

1. Construction of a freezing-point apparatus incorporating a unique magnetic stirrer capable of operating at high speed has resulted in far more complete solid-liquid equilibrium than was possible with the equipment previously employed. Determination of the complete freezing-point-composition curve for nitromethane and dinitrogen tetroxide indicates some error in the low-temperature data previously reported. With the new apparatus, the eutectic for the system was found at 51 wt% nitromethane at a temperature of -59.0°C.

2. The effect of five additives on the freezing point of dinitrogen tetroxide was noted. The additives were selected so that useful information could be obtained concerning the effect of structure on the degree of deviation from ideality. Results of the freezing-point determinations are briefly noted below. Where possible, the freezing point both at 30 mole% and at the eutectic composition is given: in the case of diethyloxalate, the eutectic appears at less than 30 mole%.

<table>
<thead>
<tr>
<th>Additive</th>
<th>Wt%</th>
<th>Mole%</th>
<th>Freezing Pt, °C</th>
<th>Apparent Solvation No.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Observed</td>
<td>Ideal</td>
</tr>
<tr>
<td>Trinitromethane</td>
<td>33</td>
<td>23**</td>
<td>-18.2</td>
<td>-21.0 (Positive Deviation)</td>
</tr>
<tr>
<td>Tetranitromethane</td>
<td>46</td>
<td>30**</td>
<td>-23.2</td>
<td>-24.5 (Positive Deviation)</td>
</tr>
<tr>
<td></td>
<td>69</td>
<td>52**</td>
<td>-33.0</td>
<td>-37.5 (Positive Deviation)</td>
</tr>
</tbody>
</table>

*The percentages given are only approximate.

**Eutectic not determined.
3. In order to determine the stability of certain solutions of dinitrogen tetroxide to a first approximation, temperatures of the explosive autodecomposition of 1-ml samples were recorded. The samples were placed in a Pyrex liner contained within a stainless steel bomb fitted with a rupture disk, and the temperature of the bomb was then increased approximately 10°F/min until explosion occurred. Abbreviated results of these tests are as follows:

<table>
<thead>
<tr>
<th>Additive</th>
<th>Wt%</th>
<th>Mole%</th>
<th>Observed</th>
<th>Ideal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diethylcarbonate</td>
<td>35</td>
<td>30</td>
<td>-39.0</td>
<td>-24.5</td>
</tr>
<tr>
<td></td>
<td>43</td>
<td>37</td>
<td>-54.0</td>
<td>-28.0</td>
</tr>
<tr>
<td>Diethyloxalate</td>
<td>28</td>
<td>28</td>
<td>-38.0</td>
<td>-23.5</td>
</tr>
<tr>
<td>Diethyl Cellosolve</td>
<td>35</td>
<td>30</td>
<td>-29.4</td>
<td>-24.5</td>
</tr>
<tr>
<td></td>
<td>53</td>
<td>47</td>
<td>-58.5</td>
<td>-34.0</td>
</tr>
</tbody>
</table>

C. RESEARCH ON THE PREPARATION OF NEW ROCKET PROPELLANTS

1. Efforts have continued to prepare N-aminoethylenimine by the reaction:

\[
\begin{align*}
\text{CH}_2=\text{CH}_2 & \xrightarrow{0} \text{HOCH}_2\text{CH}_2\text{NH}_2\text{H}_2 \\
\text{N}_2\text{H}_4 & \xrightarrow{\text{H}_2\text{SO}_4} \text{HOCH}_2\text{CH}_2\text{NH}_2\text{H}_2 \overset{+}{\xrightarrow{\text{H}_2\text{SO}_4}} \text{HO}_3\text{SOCH}_2\text{CH}_2\text{NH}_2\text{H}_2
\end{align*}
\]

Numerous experiments were conducted in an attempt to determine the optimum conditions for the highest yield of the desired product. Although in one case a yield of 85% was obtained, it has been found difficult to reproduce so high a value in subsequent experiments. Work is now in progress to check the hypothesis that the formation of an ether instead of an ester in the second step is the cause of the low yields.

2. Characterization of the product is proceeding concurrently with the synthetic phase of the work.
B. PERFORMANCE EVALUATION OF ROCKET PROPELLANTS

Work is in progress to test "HF-D" hydrocarbon mixture with liquid oxygen in a 100-lb-thrust rocket engine. This fuel is an unsaturated (H/C ratio = 1.19) cracking product, supplied by the Standard Oil Company of Indiana. The test facilities have been completely checked and actual motor runs will begin in the near future.