INTERNAL LETTER

SUBJECT: THE NEXT NTO PROBLEM

April 14, 1961

To: Those Concerned

From: H. V. Button

MEMO

The purpose of this memo is to submit laboratory data and observations that indicate unmistakable danger signals as well as predicate an irrefutable argument for the immediate investigation of this problem.

The work has been performed continuously, over a year's time, on the following programs: Gemini (G.O. 5222, 5249), Apollo (G.O. 8405, 8406), Martin Transstage (G.O. 8460, 8461), and LEM (G.O. 8430).

INTRODUCTION

With an assay of 99.3% N₂O₄ on the 5000 gallon NTO storage tank at the Storage Propellant Area, the last rocketdyne source of NTO at TH and Reno failed to meet Military Specification P26539A for propellant grade nitrogen tetroxide (99.3% min. N₂O₄, 0.1% H₂O max.). This generalized calamity which forced the Gemini, Apollo, and Martin production engine programs to a grinding halt did not just happen spontaneously over the weekend of March 22, 1961. Although the handling weather (with hailstones as big as peas at FPL) did not help the situation, the explanation of the crisis rests more with the nature of the propellant than any meteorological conditions.

This report is an attempt to explain the problem. The solution may be just as simple as ordering more NTO. However, the chemistry of this problem should be investigated so that there is a true definition of the propellant system that is being used. In its own time and place, the realistic appraisal of the NTO system is as critical to the Space Engines program as the definition of the hydrocarbon blend was for RP-1 on the Atlas. Certainly a dismissal of the chemical reactions of this propellant by the Space Engines groups would be a very serious matter.
LOGISTICS: Nitrogen Tetroxide, GFF

<table>
<thead>
<tr>
<th>VENDOR</th>
<th>PURCHASE DATE</th>
<th>AMOUNT: LBS. GALS.</th>
<th>COLOR</th>
<th>TYPICAL ASSAY, MIL SPEC.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hercules</td>
<td>8/15/63</td>
<td>36,410 (~3000)</td>
<td>brown</td>
<td>99.8% N2O</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.07% H2O</td>
</tr>
<tr>
<td>Hercules</td>
<td>8/22/63</td>
<td>34,510 (~3000)</td>
<td>brown</td>
<td>same as above</td>
</tr>
<tr>
<td>Hercules</td>
<td>3/21/64</td>
<td>2 x 1 ton cylinders</td>
<td>green</td>
<td>99.7% N2O4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.1% H2O</td>
</tr>
<tr>
<td>(but obtained from Marquardt)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hercules</td>
<td>3/26/64 to arrive tomorrow</td>
<td>10,000 gallons for PFL and Reno</td>
<td>green</td>
<td>their analysis:</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>100.2% N2O4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.06% H2O</td>
</tr>
</tbody>
</table>

EXPERIMENTAL AND DISCUSSION

As early as October, 1963, it was reported from this laboratory that the MIL SPECS are inadequate when a threshold value of water is present because of the series of reactions that take place. The assay for N2O4 is really only a total acid value. From the analytical chemistry standpoint this means that where the titer is calculated against a milliequivalent weight of 4.6006 for N2O4, actually, when the mixed oxides of nitrogen and their corresponding acids are present (from the reactions with water), the milliequivalent weights should be 6.302 for HNO3, 4.702 for HNO2, 3.801 for N2O3, and 3.001 for NO. However, in the aqueous medium of the titration (NaOH), and under the equilibrium conditions of the reacted sample at the time, various percentages of the mixed oxides and acids may be present to add to or detract from the total acid value calculated as N2O4.

For example:

<table>
<thead>
<tr>
<th>N2O4 really present as HNO3 and HNO2</th>
<th>Water if combined</th>
<th>Analysis by MIL SPEC would give the following result:</th>
</tr>
</thead>
<tbody>
<tr>
<td>99.9</td>
<td>0.1</td>
<td>99.98</td>
</tr>
<tr>
<td>99.7</td>
<td>0.3</td>
<td>99.92</td>
</tr>
<tr>
<td>99.5</td>
<td>0.5</td>
<td>99.80</td>
</tr>
<tr>
<td>99.0</td>
<td>1.0</td>
<td>99.90</td>
</tr>
<tr>
<td>81.0</td>
<td>16.0</td>
<td>97.70</td>
</tr>
</tbody>
</table>

Some analyses of production engine NTO have reflected these reactions by producing assays of 103% NTO and a 0.07% water equivalent (Reno) as well as 98.5% NTO with 0.18% water equivalent (PFL). In essence, then, when the reacting NTO-water
species is evaluated using the MIL SPECS method, the values may change from day to day or analysis to analysis until some generalized equilibrium is reached. The parameters of such an equilibrium are at present unknown to us.

Water Equivalent

The water equivalent determination seems satisfactory and reproducible for "good" NTO, but once the reactions in the system have taken place such that the water is tied up as other than HNO₃, the method becomes unrealistic. The vendor, Hercules Corp., has suggested to the Air Force that the evaporation technique as now used be abandoned in favor of the cloud point determination originally pur forth by Allied in 1958. This is more tedious, the apparatus is more delicate, and the test would be longer, but Hercules claims it is an improvement. The premise used for the cloud point determination is that water and N₂O₄ are miscible only within certain limits. In concentrations of up to 1.6% wt. water, the two components form a homogeneous solution, while between 1.6% wt. water and 16.9% wt. N₂O₄, two phases are present. These limits are valid at 0°C. They are not significantly affected by slight changes in temperature. These facts make it possible to determine the H₂O content of liquid N₂O₄ with good accuracy, they say, by evaporating the latter until the mixture just separates into 2 phases, which at 0°C must result in obtaining the 1.6% water mixture.

Color and Consistency

BROWN NTO

The color and consistency of the August, 1963 supply of NTO has been used for the Go/NoGo method of analysis as long as the original material was the color and consistency of Pepsi-cola. When this was so, a greenish color presaged a rising water equivalent (due to the production of blue N₂O₃ which combined with the brown-amber N₂O₄ to give the green) and a lessening of the opacity which has been postulated to indicate a loss of NO₂ with possible conversion to HNO₃ which would, in some cases, lower the assay.

GREEN NTO

At the immediate present (3/25/64) there is no method for the screening of the green NTO that is comparable to the Go/NoGo test for brown NTO. This green NTO will be arriving from Hercules momentarily. One of their chemists explained that the process department had been under attack for the green color since other people also found that water in NTO would produce the green. Hercules claims that their present process (what their process was in 1963 is unknown) includes having about 1% NO in the NTO. The NO combines with the NO₂ to give the emerald green coloration associated with the reaction between N₂O₄ and N₂O₃. They also cite that their material will analyze (using the MIL SPECS) at 100.2% N₂O₄ which is very consistent with our interpretation of the chemical reactions. They
claim that the NO can be removed, if it is so desired, by using gaseous nitrogen
since the vapor pressure of NO is greater than that of NO₂. This particular
phenomenon has been evidenced in our laboratory; upon evaporation proceedings,
the green NTO becomes brown.

An Aerojet report (Storable Liquid Propellants, LRP 198, June, 1962) states some
other interesting facts: NTO turns green or blue when it is cold. During the
winter months N₂O₄ turns green in shipping containers, handling equipment, and
storage tanks because of the low ambient temperatures. The green color, they
agree, is caused by the presence of N₂O₅, a blue compound which exists only in
the liquid and solid phase. The gaseous phase dissociates into brown NO₂ fumes.
They mention that the NO content of N₂O₄, and therefore the N₂O₃ content is
related to the amount of water present but that the color cannot be used as a
reliable indication of water content. (We have lately found this to be so....
on the initially green material.) However, if N₂O₄ is green at normal room
temperatures, they cite, it is safe to assume that it contains an excessive
amount of water, for it takes relatively large amounts of N₂O₃ to influence the
dark brown color of warm N₂O₂. On this point, in our laboratories we have added
as much as 50% N₂O₃ to dark brown NTO and get the same green color that the
Marquardt NTO had (analyzed 99.7% N₂O₄, 0.1% water equivalent).

REACTIONS

When NO is either present from the reaction between N₂O₄ and H₂O, or from the
process, then,

\[ 3 \text{NO}_2 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3 + \text{NO} \]

and,

\[ \text{NO} + \text{NO}_2 \underset{(brown)}{\longrightarrow} \text{N}_2\text{O}_3 \]

It should be remembered that N₂O₃ in the gaseous state is almost completely
dissociated into nitric oxide and nitrogen dioxide, and in the gaseous state
the equilibrium would go to the left.

Other known reactions are:

\[ (\text{N}_2\text{O}_4 + \text{H}_2\text{O}) \rightarrow \text{HNO}_3 + \text{HNO}_2 \]
\[ 2 \text{HNO}_2 \rightarrow \text{H}_2\text{O} + \text{NO} + \text{NO}_2 \]
\[ 3 \text{NO}_2 + \text{H}_2\text{O} \text{ (liquid)} \rightarrow 2 \text{HNO}_3 \text{ (aqueous)} + \text{NO} \]

This is the overall reaction when NO₂ gas is brought to equilibrium with liquid
water. The purely gas phase reaction between NTO and water does not occur to
any appreciable extent.
REFERENCES


4. TITAN II Storable Propellant Handbook, Bell Aerosystems, EAFB, California, Contract AF04 (611)-6079.


ACKNOWLEDGMENTS

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