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EXPERIMENTAL EVALUATION OF INHIBITED NITROGEN TETROXIDE

L.P. BARCLAY, CAPT, USAF

TECHNICAL REPORT AFRPL-TR-69-61

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AFRPL-TR-69-61

EXPERIMENTAL EVALUATION OF INHIBITED NITROGEN TETROXIDE

Lewis P. Barclay, Capt, USAF

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AIR FORCE ROCKET PROPULSION LABORATORY
DIRECTORATE OF LABORATORIES
AIR FORCE SYSTEMS COMMAND
UNITED STATES AIR FORCE
EDWARDS, CALIFORNIA

FOREWORD

This report covers work done on Project 314803ACI, Inhibited Nitrogen Tetroxide (INTO) Evaluation, by the Exploratory Evaluation Branch in the Propellant Division of the Air Force Rocket Propulsion Laboratory from 1 July 1967 to 30 April 1968. The project engineer was Capt Lewis P. Barclay.

This report has been reviewed and approved.

John W. Marshall

JOHN W. MARSHALL, Chief
Exploratory Evaluation Branch
Propellant Division
Air Force Rocket Propulsion Laboratory

ABSTRACT

Nitrogen tetroxide containing 3 percent FNO_2 by weight, inhibited nitrogen tetroxide, (INTO) was fired in a 1000-lb-thrust engine with hydrazine, MHF-3 and Aerozine-50. The INTO performed essentially the same as neat NTO, as predicted by the theoretical performance computer program.

Two 50-gallon batches of INTO were field-prepared. Severe tank corrosion and iron fluoride precipitation occurred, resulting in clogged feed lines and flowmeters.

Although performance is not degraded by the inhibitor, the corrosion problem and physical properties make the use of INTO impractical for future Air Force applications.

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EXPERIMENTAL EVALUATION OF INHIBITED NITROGEN TETROXIDE

I. INTRODUCTION

Systems using water-contaminated nitrogen tetroxide (NTO) have suffered severe corrosion due to the formation of nitric acid in the propellant. An inhibitor has been found which eliminates that corrosion (Reference 1). Since the proposed concentration of the inhibitor is 3 percent by weight, the possibility of an effect on propellant performance must be considered. Theoretical performance data indicates that the performance difference of inhibited nitrogen tetroxide (INTO) versus normal NTO is less than 1/2 sec of specific impulse with hydrazine family fuels, however, the properties of the inhibitor are such that kinetic effects are possible. Considering this and the value of experimental field handling of the propellant, the Air Force Rocket Propulsion Laboratory (AFRPL) undertook an evaluation program to field-prepare and performance-test INTO a 1000-pound-thrust combustor.

II. DISCUSSION

A. General

The military specification for NTO allows a maximum of 0.1 percent by weight of water in the propellant. Unfortunately NTO absorbs water easily, and during transfer operation and in normal handling will do so to a considerable extent. The water reacts with NTO to form nitric acid as follows:

$$3N_2O_4 + H_2O \longrightarrow 4HNO_3 + 2NO$$

The acid in turn reacts with metal tankage thus:

$$\text{Metal} + 4HNO_3 \longrightarrow Me(NO_3)_2 + 2H_2O + N_2O_4$$

As can be seen, the same amount of water is released at the end of the cycle as is used in the beginning, so that a perpetual cycle is evolved.

A solution to the problem can be considered from two standpoints, that the problem is one of nitric acid or that it is one of water. Solutions to nitric acid problems tend to concentrate on hardware. Because of the nature of technology used in existing systems, a component modification could easily affect other parts of the system so as to reduce mission capability. A solution to a water problem is apt to be chemical in nature, and this was the route chosen.

It was determined (Reference 1) that gaseous fluorine when added to NTO reacts as follows:

$$F_2 + N_2O_4 \longrightarrow 2FNO_2$$

The product in turn reacts with water:

$$2FNO_2 + H_2O \longrightarrow 2HF + N_2O_4 + 1/2\ O_2$$

The oxygen boils off while the hydrogen fluorine remains in solution. The addition of HF was not regarded as harmful since experience with it in inhibited red fuming nitric acid (IRFNA) indicates negligible effects. However, the effects of FNO_2, particularly considering 3 to 5 percent as useful quantities, were unknown. The properties of FNO_2 are not well known, as the only work done on it dates back to 1932. Values of heat of formation, both measured and calculated, differ drastically; none are encouraging. Nitryl fluoride boils at -63.5°C, and thus results in very high vapor pressure mixtures with NTO. In addition, the FNO_2 causes a fluoride passivation coat to form on metal tankage. This was regarded as a benefit in the attempt to inhibit tankage corrosion.

The mechanism of the inhibition process involves several steps. When gaseous fluorine is initially added, it begins a passivation coat in the ullage where the F_2/NTO reaction occurs in the vapor phase. After the coat is formed in the ullage, the FNO begins to dissolve into the NTO where it reacts with the water present. When the water is completely removed passivation of the tank below the liquid level occurs. At this point, a buildup of FNO_2 in the NTO occurs. For storage purposes, it is desirable to have 3 to 5 percent present to react with any incoming water.

Reference 1 is the final report on the development and physical properties of INTO.

B. Equipment and Procedures

A schematic of the test system is shown as Figure 1 and a photograph of the system is included as Figure 2. The tankage, pressurization lines, propellant feed lines and valve bodies were 347 stainless steel. The valve seats and flowmeter bearings were Teflon.

The engine was rated at 1000-lb thrust at a chamber pressure of 500 psia. Nine like-on-like doublets admitted the oxidizer while 12 were used for the fuel. Flow was controlled by cavitating venturis.

The inhibited N_2O_4 was prepared in the run tank to simulate field preparation. Fluorine was added through a dip leg until the tank pressure was 50 psi below the K-bottle pressure. The mixture was then monitored while formation and dissolution of the inhibitor occurred. After a day or two a sufficient amount of the fluorine reacted to require another charge.

During the inhibiting process the vapor pressure of the propellant was checked periodically. The vapor pressure of N_2O_4 - FNO_2 mixtures is a strong enough function of FNO_2 concentration to allow it to be used as a crude analytic tool. When the vapor pressure indicated the FNO_2 concentration was within the desired range (3 to 5 percent), an analysis was made by infrared spectrometer.

Because of the extremely high vapor pressure of the FNO_2 as compared with NTO, the FNO_2 rapidly boiled off during venting procedures. Considerable effort was required to maintain the propellant within the desired inhibitor limits.

C. Data Reduction

An instrumentation specification sheet for these tests is included in the Appendix. The data was recorded by a Systems Engineering Laboratory

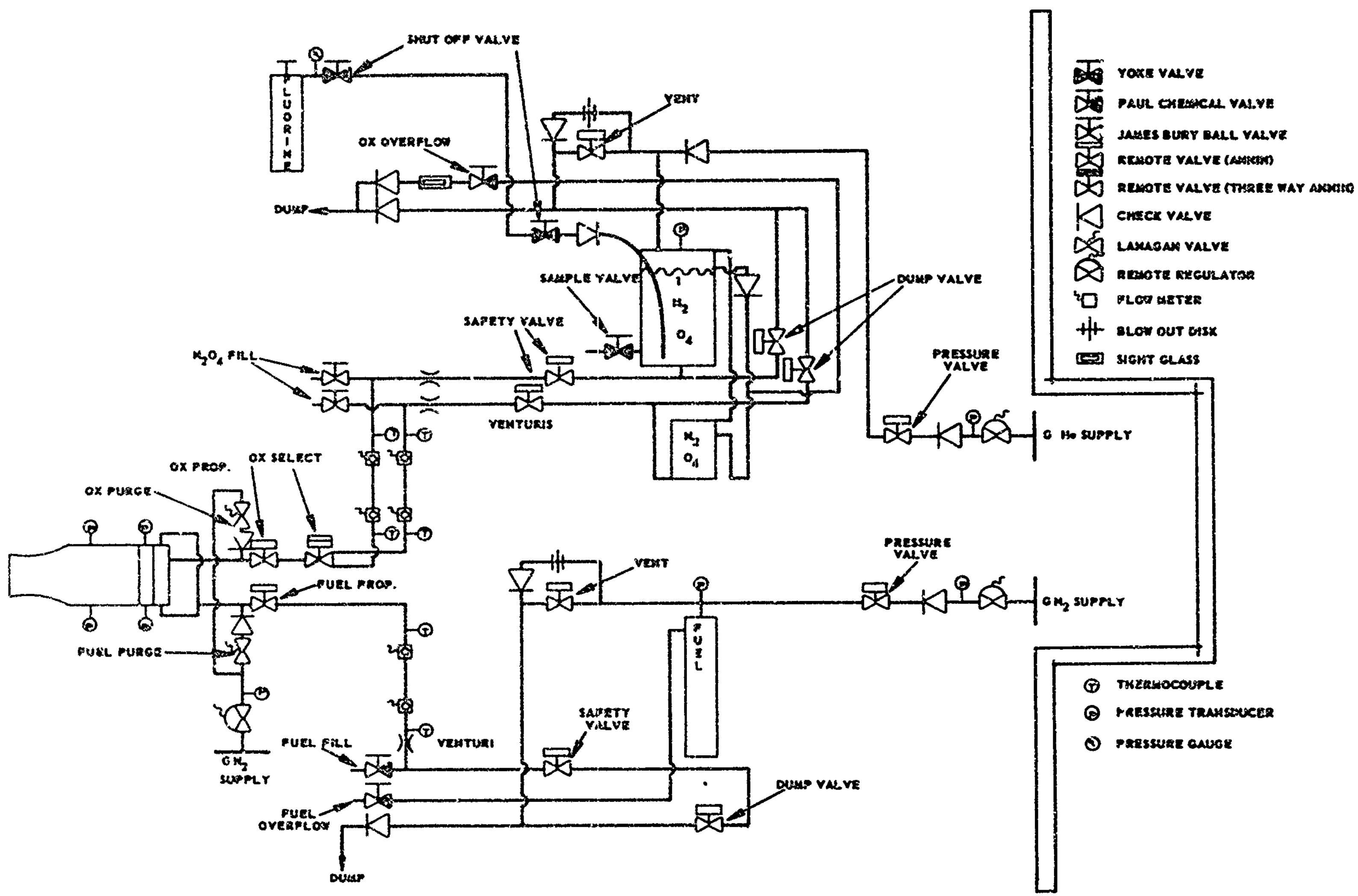

Figure 1. Test System Schematic

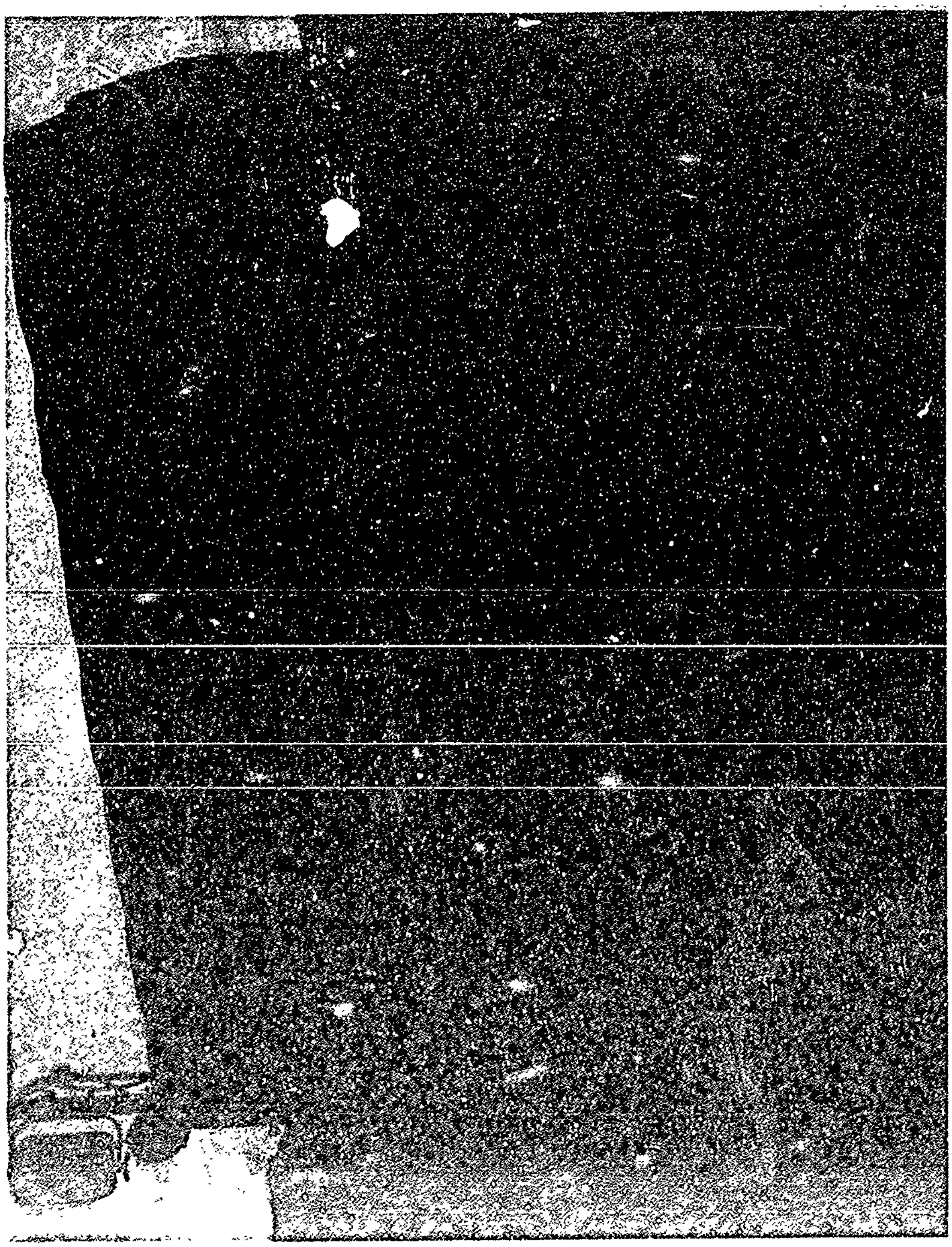

Figure 2. Test System

Analog to Digital unit (SEL 600). Data reduction was done by computer, by Computing and Software, Inc., under Air Force contract.

Because of variations in the chamber pressure from run to run and because a 30 degree cone nozzle was used, the reduction program employed two corrections for specific impulse.

Specific impulse is determined as follows:

$$Isp = \frac{C_f C^*}{g} = \frac{F}{gP_c A_t} \times \frac{P_c A_t g}{\dot{w}} = \frac{F}{\dot{w}}$$

Where:

F	=	thrust
$\dot{w}$	=	total propellant flow rate
C_f	=	thrust coefficient
C^*	=	characteristic exhaust velocity
P_c	=	chamber pressure
A_t	=	nozzle throat area
g	=	32.176 ft/sec^2

While C_f is a strong function of pressure, C^* is not, so that for small variations in pressure the following ratio may be written assuming that C^* is constant:

$$\frac{(Isp)REF}{(Isp)ACT} = \frac{(C_f)REF}{(C_f)ACT}$$

(Isp)REF = corrected specific impulse at reference conditions
(P_c = 500psia
P_e = 13.2psia)

(Isp)ACT = actual specific impulse calculated as $\frac{F}{\dot{w}}$

(C_f)ACT = actual thrust coefficient calculated as $\frac{F}{P_c A_t}$

(C_f)REF = theoretical thrust coefficient at reference conditions (P_c = 500 psia, P_e = 13.2 psia)

The above correction is valid if the actual chamber pressure is within 10 percent of the reference pressure. A more complete discussion of the above can be found in Reference 2.

An added correction was made for nozzle divergence angle since the theoretical impulse calculations are made for a zero divergence angle.

$$(Isp)corr = \frac{(Isp)ACT}{\lambda}$$

Where: $\lambda = 1/2\ (1 + \cos\beta\ )$

and $\beta = 15^{\circ}$ the nozzle divergence half angle. The above can be found in Reference 3.

Test data was recorded at a rate of 58 samples per second through a 3-second test at each mixture ratio. Five slices of 10 consecutive samples each were taken during steady operation at approximately equal time intervals. Calculations as described above were made from the average values obtained from each data slice. Data tables are included in the Appendix. The five slices were further averaged and curves plotted as specific impulse versus mixture ratio. These curves are displayed as Figures 3, 4 and 5 and follow the discussion of propellant performance.

The thrust measurement was accurate within 0.50 percent while the pressures were accurate to 0.25 percent. However, the turbine flowmeters can only be considered accurate to 3 percent.

III. RESULTS AND INTERPRETATION

A. Propellant Performance

The impulse efficiencies achieved were 90 percent and above with all combinations tested. The impulse/mixture ratio curves for the hydrazine tests were shifted very slightly to lower mixture ratios as were the curves for the MHF-3 tests. The curve for the Aerozine-50/NTO baseline tests have positive curvature, that is, where the maximum Isp should occur there is a minimum. Several series of tests were made with the latter fuel and in all cases the curves were inverted. The explanation is probably related to flowmeter accuracy. The curves are offered only as a point of interest.

Because of the 3 percent flowmeter accuracy, the curves can be said to be essentially the same. From a thermodynamic standpoint, this was to be expected. The theoretical performances are within 0.5 sec impulse of each other.

B. Iron Fluoride Problem

A rather severe problem was encountered with iron fluoride with the first 50-gallon batch of INTO that was made. Feed lines, flowmeters and injector manifold were coated with iron fluoride during the first test runs. Line pressure drops became excessive and the flowmeters were completely clogged within approximately 1 second of propellant flowing conditions. When the lines were drained and opened the coat dried rapidly but could be washed off with water easily. The coat was 1/16 inch thick over most of the feed lines which were 3/4 inch in diameter. The flowmeters received such a heavy coat as to sometimes completely stop propellant flow.

After several tests the problem cleared up of its own accord. Following the test series, when the run tank was to be drained, the dump line was found to be completely clogged. Visual inspection of the tank showed it to be severely corroded, especially at the top. Because of the construction of the tank, no pictures were possible, and no quantitative analysis of the corrosion could be made. The flowmeters were out of calibration although the portions of lines that were clogged were as good as new when cleaned; there was no evidence of corrosion.

It would appear that the GF_2/NTO reaction is of such a nature as to disrupt the normal passivation process. Apparently the passivation coat, especially in the tank ullage, flaked off repeatedly until finally a strong enough fluoride coat was formed.

A second batch of INTO was made in the same tank. After the batch was completed it was run through a 10-micron filter. No iron fluoride deposited on the filter element nor on the feed lines is subsequent tests.

This effect was also discovered at Rocketdyne and is reported in Reference 2.

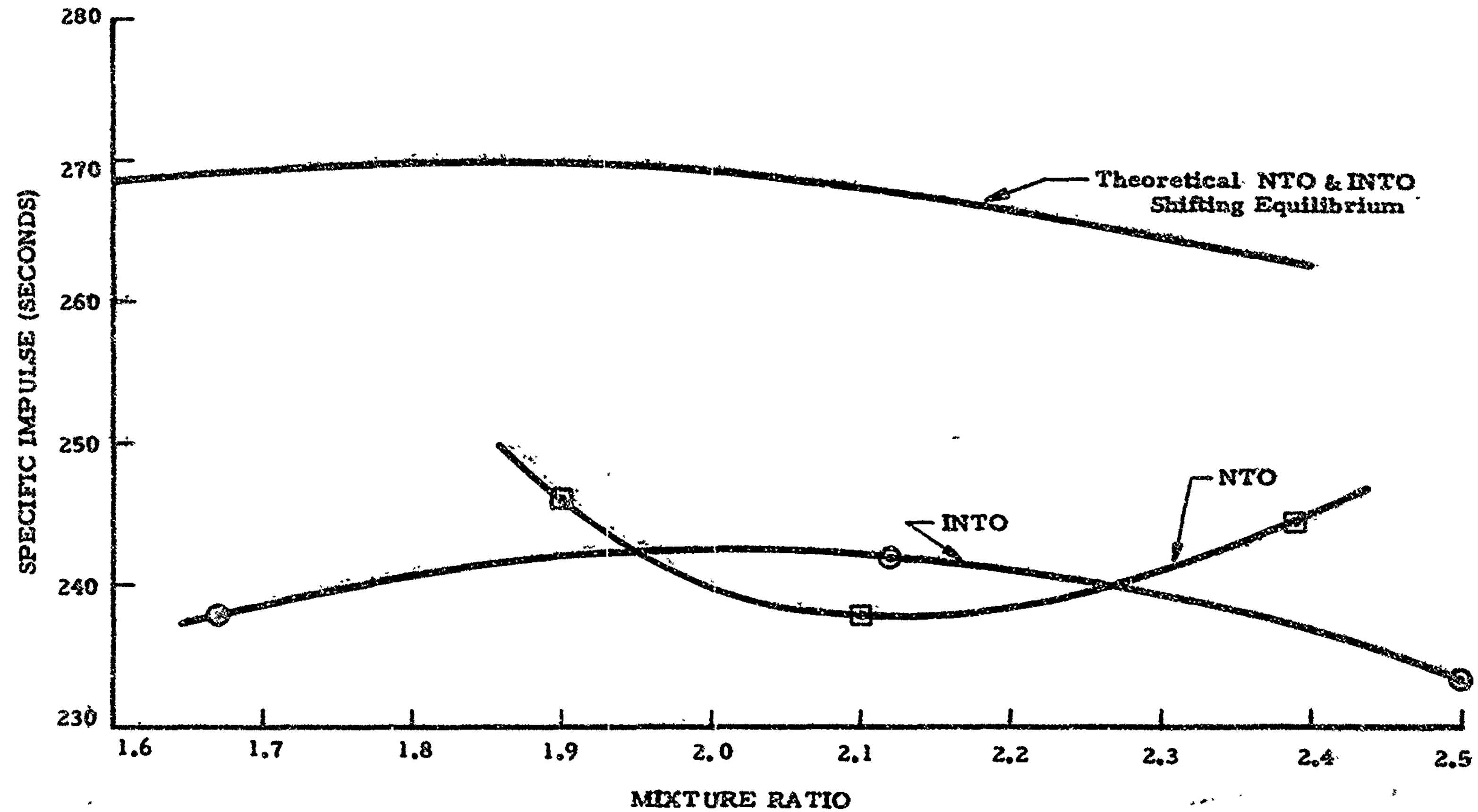

Figure 3. Theoretical and Actual Performance of Neat and Inhibited Nitrogen Tetroxide with Aerozine-50 (P_c = 500 psia and P_e = 13.2 psia)

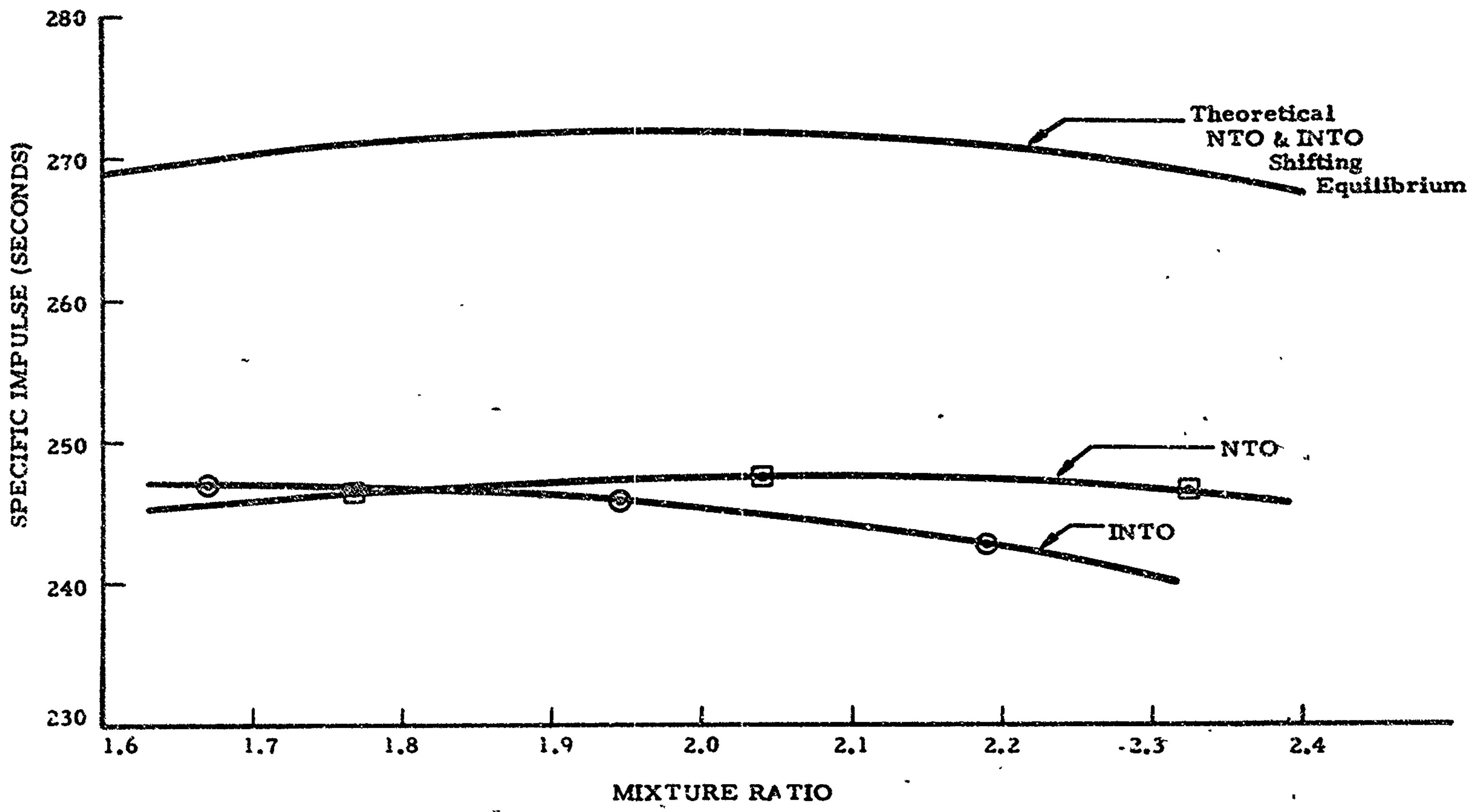

Figure 4. Theoretical and Actual Performance of Neat and Inhibited Nitrogen Tetroxide with MHF-5. (P_c = 500 psia P_e = 13.2 psia)

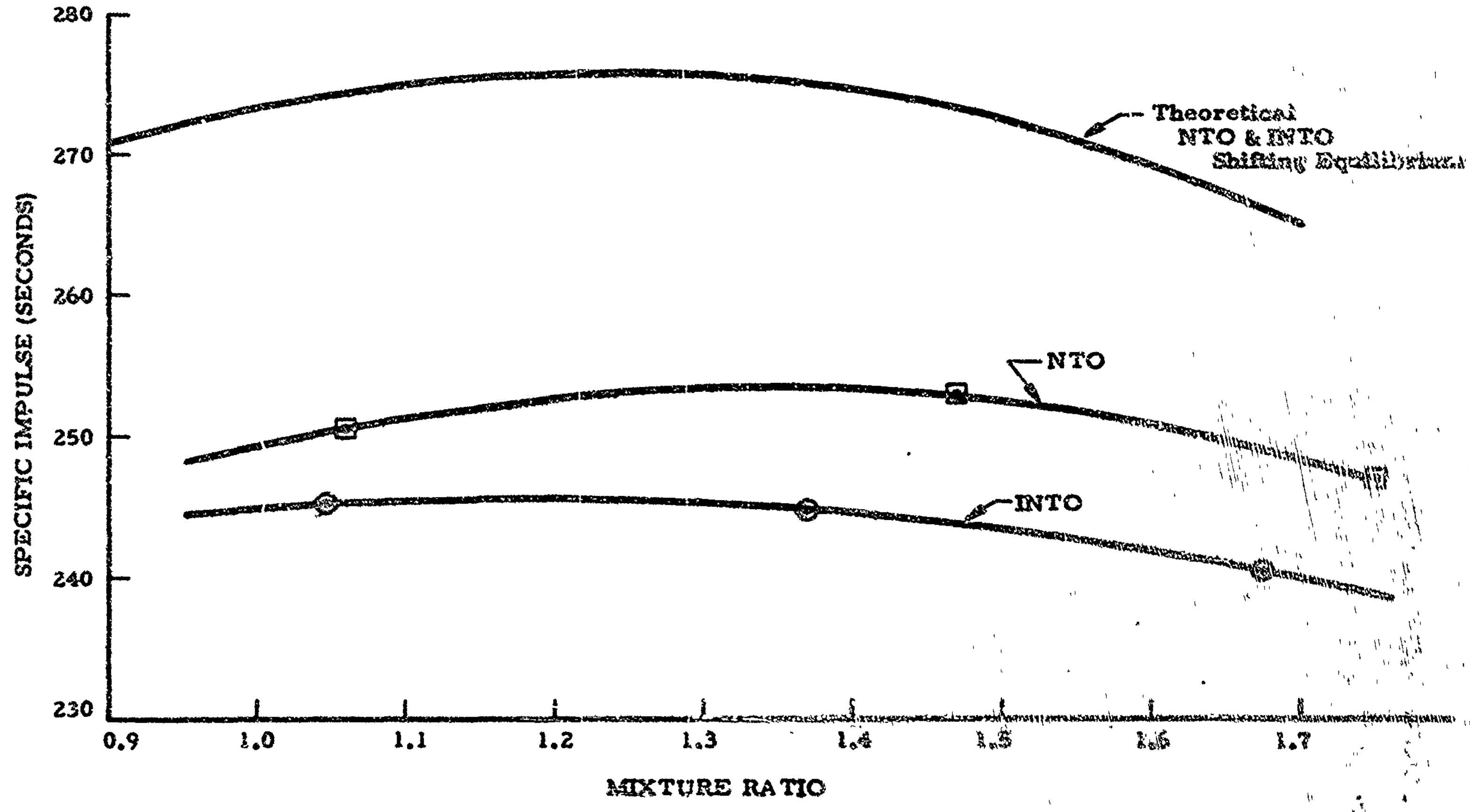

Figure 5. Theoretical and Actual Performance of Neat and Inhibited Nitrogen Tetroxide with Hydrazine. (P_c = 500 psia P_e = 13.2 psia)

IV. CONCLUSIONS AND RECOMMENDATIONS

1. FNO_2 in 3 to 5 percent concentrations does not affect the performance of nitrogen tetroxide when combusted with hydrazine, Aerozine-50 or MHF-3.

2. Field preparation of INTO is impractical due to the increased corrosive effects of GF_2 in a nitrogen tetroxide atmosphere. INTO preparation and tank passivation should proceed as separate steps with INTO being added to tankage after passivation.

3. INTO should be filtered between preparation and addition to storage tanks.

4. INTO should be stored in unvented systems and assayed after any vent process because of the high evaporation rate of FNO_2.

5. Although performance is not degraded by the inhibitor, the corrosion problem and physical properties make the use of INTO impractical for future Air Force applications.

REFERENCES

1. AFRPL-TR-66-320, " Inhibited N_2O_4"; Contract No. AF04(611)-10809 Rocketdyne, A Division of North American Aviation, Inc., Canoga Park, California, January 1967.

2. AFRPL-TR-69-4, " Research and Engineering Data on Inhibited N_2O_4"; Contract No. F04611-67-C-0099, Rocketdyne, A Division of North American Rockwell Corporation, Canoga Park, California, January 1969.

3. R.C. Armstrong III; " Experimental Performance Evaluation of Liquid Propellants " ; Paper presented to JANAF/ARPA/NASA Liquid Propellant Test Methods Panel; Astran Div., Spacecraft Inc., January 1964.

APPENDIX

TABULATED TEST DATA

TABLE A-1. AEROZINE-50 TEST DATA

Aerozine - 50 Test Data									
Mixture Ratio	Isp_{corr}	C*	C_f	Run		Mixture Ratio	Isp_{corr}	C*	C_f
				NTO	INTO				
1.90	245.7				441	1.676	243.4	5388	1.369
1.90	245.2					1.674	243.9	5641	1.339
1.90	248.2					1.674	234.9	5485	1.340
1.90	246.8					1.674	235.3	5417	1.335
						1.677	234.4	5455	1.339
2.128	244.9	5456	1.429	423	422	2.187	240.4	5585	1.366
2.101	234.5	5292	1.405			2.015	253.6	5864	1.361
2.099	236.6	5357	1.402			2.101	241.7	5560	1.355
.095	236.1	5269	1.419			2.156	237.3	5331	1.346
2.095	238.1	5193	1.448			2.158	236.6	5408	1.366
2.459	245.6	5632	1.434	432	431	2.578	235.9	5380	1.399
2.387	244.4	5480	1.411			2.570	234.7	5356	1.390
2.379	244.2	5452	1.413			2.532	235.1	5536	1.349
2.370	244.1	5459	1.406			2.429	230.2	5375	1.339
2.366	242.7	5313	1.381			2.417	231.7	5338	1.371

TABLE A-2. MHF-3 TEST DATA

MHF-3 Test Data									
Mixture Ratio	Isp_{corr}	C*	C_f	Run		Mixture Ratio	Isp_{corr}	C*	C_f
				NTO	INTO				
1.826	253.9	5693	1.423	511	512	1.673	246.9	5550	1.412
1.768	246.0	5554	1.412			1.669	247.0	5575	1.407
1.754	244.7	5395	1.441			1.677	247.1	5559	1.411
1.749	244.8	5463	1.425			1.679	246.2	5540	1.411
1.743	244.0	5447	1.423			1.678	247.7	5446	1.441
2.088	248.4	5609	1.413	521	522	1.950	242.8	5404	1.4[illegible]2
2.043	245.9	5509	1.420			1.941	244.6	5384	1.438
2.033	246.4	5602	1.399			1.942	247.5	5415	1.446
2.024	248.6	5588	1.413			1.940	246.9	5357	1.456
2.017	248.5	5591	1.409			1.942	247.0	5320	1.465
2.414	246.8	5465	1.431	531	532	2.219	241.8	5160	1.474
2.317	244.8	5422	1.427			2.151	244.4	5287	1.454
2.305	246.1	5356	1.447			2.196	240.0	5180	1.454
2.297	246.6	5509	1.433			2.195	244.0	5195	1.471
2.290	247.8	5371	1.446			2.196	243.5	5181	1.469

TABLE A-3. HYDRAZINE TEST DATA

Hydrazine Test Data

Mixture Ratio	Isp_{corr}	C*	C_f	Run		Mixture Ratio	Isp_{corr}	C*	C_f
	Seconds	ft/sec		NTO	INTO		Seconds	ft/sec	
1.091	241.8	5486	1.401	611	612	1.045	244.4	5431	1.413
1.077	250.9	5732	1.391			1.046	244.0	5432	1.405
1.025	251.8	5797	1.382			1.049	244.8	5643	1.411
1.041	254.3	5835	1.387			1.050	244.5	5642	1.409
1.069	254.1	5754	1.404			1.051	244.9	5592	1.421
1.478	249.7	5289	1.492	621	622	1.360	243.6	5435	1.376
1.475	248.9	5396	1.455			1.371	242.0	5489	1.383
1.470	252.2	5353	1.480			1.372	244.1	5578	1.391
1.462	254.6	5332	1.493			1.372	246.5	5586	1.399
1.447	258.5	5294	1.519			1.375	247.5	5674	1.409
1.762	246.9	5611	1.404	631	632	1.652	240.7	5552	1.376
1.754	246.5	5673	1.387			1.676	238.9	5485	1.383
1.744	247.8	5722	1.381			1.679	240.3	5480	1.391
1.740	246.8	5608	1.399			1.681	241.1	5470	1.399
1.740	246.9	5558	1.409			1.684	241.3	5428	1.409

TABLE A-4. INSTRUMENTATION SPECIFICATION SHEET

							INTO CELL 34		3/13/68
PT-1	Pres.	Fuel Line	S. G.		0-2000		D.SC	20	
PT-2	"	Fuel Tank	S. G.		0-2000		D.SC	21	
PT-3	"	Ox Tank	S. G.		0-2000		D.SC	22	
PT-4	"	Ox Line	S. G.		0-2000		D.SC		
PP-1	"	Purge Line	S. G.		0-500		SC		
PC-1	"	Chamber	S. G.		0-750		D.SC	23	
PC-2	"	Chamb[illegible]r	S. G.		0-750		D.	24	
PT-1	"	Fuel In	S. G.		0-1500		D.	25	
PT-2	Pres.	Ox In	S. G.		0-1500		D.	26	
TL-1	Temp	Fuel Line	I/C T. C.		30-150°F		D.	28	
TL-2	"	Fuel Line	I/C T. C.		30-150°F		D.	29	
TL-3	"	NTO Line	I/C T. C.		30-150°F		D.	30	
TL-4	"	NTO Line	I/C T. C.		30-150°F		D.	31	
TL-5	"	INTO Line	I/C T. C.		30-150°F		D.	32	
TL-6	Temp	INTO Line	I/C T. C.		30-150°F		D.	33	
F-1	Thrust	Engine	S. G.		0-1500 lbs		D.SC		

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13. ABSTRACT

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Two 50-gallon batches of INTO were field-prepared. Severe tank corrosion and iron fluoride precipitation occurred, resulting in clogged feed lines and flowmeters.

Although performance is not degraded by the inhibitor, the corrosion problem and physical properties make the use of INTO impractical for future Air Force applications.

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