Effects of Aniline Impurities on Monopropellant Hydrazine Thruster Performance

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The phenomenon of monopropellant hydrazine thruster catalyst bed poisoning with various grades of hydrazine was studied. Tests with 0.45-N and 0.9-N thrusters, employing Shell 405 spontaneous catalyst, showed that pulse shape distortion could be encountered very rapidly under certain types of pulse mode operation. It was determined that the pulse distortion, in this particular instance, was largely due to the small amounts of the miscible impurity, aniline, which is normally left in hydrazine during the dehydration process of the manufacturing cycle. It was also found that washout could be accelerated by this impurity. During low-usage duty-cycle operation as encountered in limit cycling, thruster catalyst temperatures are cool enough to permit chemisorption of aniline, resulting in a masking of the active catalyst sites and subsequent loss in the bed activity. Although it was shown that this particular poisoning is generally a reversible condition, it could pose in-flight spacecraft control problems if not properly considered beforehand. Removal of the major portions of the aniline from the propellant or artificial heating of the catalyst bed to drive off compounds formed from this impurity was found to be effective in preventing this performance degradation.

Introduction

THE development of Shell 405 catalyst has been responsible for the widespread use of monopropellant hydrazine for space propulsion and power systems. Application requirements have progressively pressed for hundreds of thousands of pulses and hours of operation. The capability of hydrazine reactors has been extended orders of magnitude beyond the requirement for which Shell 405 catalyst was orginally developed.[1]

As reactor application requirements have increased, examples of reactor aging and associated performance loss have been observed. Some types of performance loss are of a permanent, irreversible nature (e.g., iron contamination, catalyst voiding), whereas others have been shown to be reversible. Two examples of reversible performance loss are washout and pulse shape distortion.[§]

Washout has been observed during steady-state operation and is manifested by an observed decrease in chamber pressure, thrust, and temperature, along with an increase in the propellant flow rate. This phenomenon appears to be reversible, usually reverting back to normal operation after shutdown and slow cool in a vacuum. Although the mechanism of washout has not been fully explained, design criteria have been offered to minimize its occurrence.[2]

Pulse shape distortion or pulse collapse has been observed during pulse mode operation after several hundred pulses at a low percent duty cycle. On several occasions pulse mode performance has degraded to a point where undecomposed frozen hydrazine has been observed hanging from the nozzle of a thruster.[3] Ammonia, an exhaust product of hydrazine decomposition, has in the past been the postulated cause of this phenomenon. The results presented in this paper will show that both pulse shape distortion and washout can be caused by the aromatic aniline, which is normally present in military grades of hydrazine.

A comparison of the constituents of the various grades of hydrazine studied in this paper is shown in Table 1. The major impurities in the military grades (standard and monopropellant) of hydrazine are aniline (C_6H_7N) and water. Aniline and water are left in hydrazine during the modified Raschig manufacturing process, which reacts ammonia with sodium hypochlorite.[4] Initially the ammonia and hypochlorite react to form chloramine, and then the chloramine reacts with the excess ammonia to form hydrazine, sodium chloride, and water. The salt is removed in a crystalizing evaporator. The resulting water-hydrazine azeotrope (65% N_2H_4) is then fed into a fractionating column along with aniline, a combination that serves to break the azeotrope. The water and aniline are distilled in this column, which eventually yields hydrazine with a 98% or better purity. This 98+% mixture (military grade) has been commonly used for many years both as a monopropellant and as the fuel in bipropellant engine applications. A so-called purified grade of hydrazine was later developed for the NASA Viking Project to reduce landing-site contamination of the Martian surface by carbon from the lander engine exhaust. The aniline and water are removed from the propellant by a zone cooling process used by the Martin Marietta Corporation which takes advantage of the differences in the solubility of these impurities in the solid and liquid states. During the zone cooling process, these impurities tend to remain in the unfrozen liquid, and the resulting solid hydrazine is essentially pure. The yield of the aniline-free hydrazine using this process is approximately 60%.

Of the two major impurities in military grade hydrazine, water, used in large proportion in gas generator application, is not regarded as a poison. In addition, some thruster manufacturers feel that certain amounts of water in hydrazine are desirable. Aniline impurities were studied in 1969 by Rocket Research Corporation.[5] Various percentages of aniline were tested, and it was shown that increases in ignition delay were observed with attendant increases in aniline content (see Fig. 1). During the development of the standard 0.9-N thruster for the NASA Low Cost Systems Office and the Mariner Jupiter Saturn 1977 (MJS77) spacecraft, pulse shape distortion was observed. In an attempt to investigate the phenomenon, the thruster was moved to a high-vacuum facility and the performance degradation disappeared.[6] It

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§See *Glossary of Monopropellant Hydrazine Engine Technology*, JANNAF Monopropellant Working Group, Chemical Propulsion Information Agency, Laurel, Maryland, March 1976, for definition of terms used in this paper.

Table 1 Comparison of hydrazine grades[a]

Constituents	Standard grade: MIL-P-26536C	Monopropellant grade: Amendment 1 to MIL-P-26536C	Purified grade: Viking STM N020 Martin Marietta	Purified grade: MJS77 Hydrazine specification
Hydrazine (% by weight)	98.0 min	98.5 min	98.0 min	98.5 min
Water (% by weight)	1.5 max	1.0 max	0.5-1.5	0.5 to 1.0
Particulate (mg/l)	10.0 max	1.0 max	10.0 max	1.0 max
Chloride (% by weight)	---	0.0005 max	---	0.0005 max
Aniline (% by weight)	---	0.5 max	0.008 max	0.005 max
Iron (% by weight)	---	0.002 max	---	0.002 max
Nonvolatile residue (% by weight)	---	0.005 max	0.003 max	0.005 max
Carbon Dioxide (% by weight)	---	0.02 max	---	0.005 max
Other volatile carbonaceous material; i.e., UDMH, MMH alcohol (% by weight)	---	0.02 max	---	0.02 max
Ammonia (% by weight)	---	---	0.4 max	0.4 max
Total carbon (% by weight)	---	---	0.012 max	---

[a](---) not controlled.

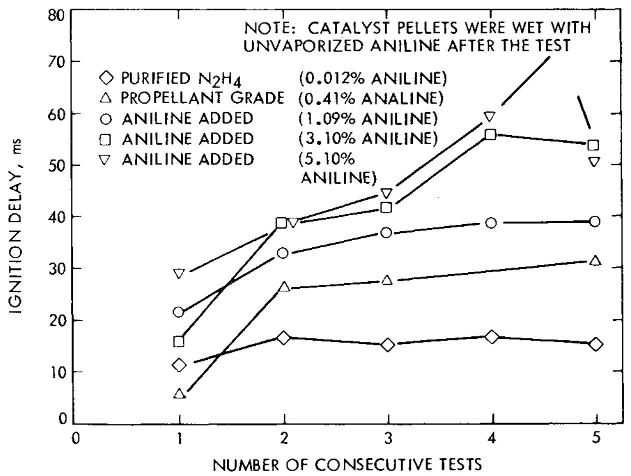

Fig. 1 Effect of aniline in hydrazine on ignition delay (courtesy Rocket Research Corp.).

Table 2 Thruster design characteristics

Design parameters	Hamilton Standard	Rocket Research
Thrust, N (lbf)	0.45 (0.1)	0.90 (0.2)
Injector, type	Cone penetrant	Showerhead
Catalyst, mesh size	25-30	25-30
Bed load, G, kg/m^2-s (lbm/s-$in.^2$)	4.9 (0.007)	5.6 (0.008)
Bed diameter, mm (in.)	6.8 (0.267)	10.1 (0.398)
Bed length, mm (in.)	11.12 (0.440)	15.2 (0.600)
Throat diameter, mm (in.)	0.8 (0.030)	0.6 (0.023)
Expansion ratio	52.4:1	100:1

was initially thought that the improved vacuum environment corrected the problem; however, the poisoning effect later returned. Further investigation revealed that the purified (Viking Lander grade) propellant was used during those tests where the performance appeared to be normal. This discovery set the stage for the investigations discussed in this paper.

Loss of catalyst activity or poisoning is a subject of great importance to the petroleum industry because of the industry's extensive use of catalysts for processing. Since their products are hydrocarbons, the effect of hydrocarbons on catalyst activity has been studied extensively.[7-9] Aromatic poisoning of metallic catalysts has also been studied.[8,10] In the processing of naphtha, the aromatic poisons such as aniline polymerize to polycyclic compounds thought of as catalyst "coke". The reaction paths producing the poisons are reversible. Thus it is not so surprising to observe a similar reversible poisoning phenomenon in catalytic hydrazine thrusters.

Test Hardware

Both 0.45-N and 0.9-N thrusters, each representative of a different design being flown on the three-axis stabilized spacecraft today, were used during the test with the various grades of hydrazine. Both designs employed Shell 405 ABSG spontaneous catalyst. A summary of the pertinent design characteristics of both thrusters is shown in Table 2.

The 0.45-N thruster was the same unit used in some of the performance characterization tests[3] referred to above. The thruster is similar to the one flown on SOLRAD X and was refurbished by the manufacturer[¶] prior to use in this test series. The chamber was wound with heater wire to allow preheating and bed conditioning. Thermocouples were spotwelded on the outer surface of the chamber at the mid-bed and throat stations. A two-piece thermal shield was placed over the heater along the thrust chamber. All tests were conducted with the heat shield in place and with the nozzle exit oriented to exhaust horizontally. The thruster test installation is shown in Fig. 2.

The 0.9-N thruster was a prototype configuration[**] of the design slated to be used on the MJS77 spacecraft and included

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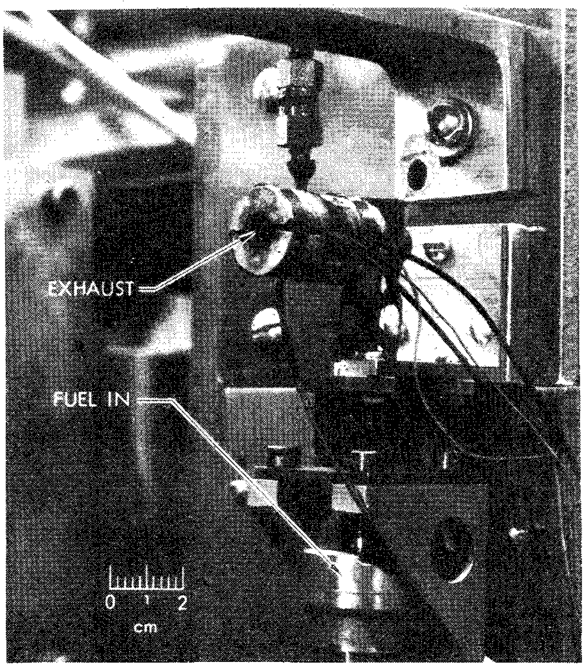

Fig. 2 0.45-N thruster installation.

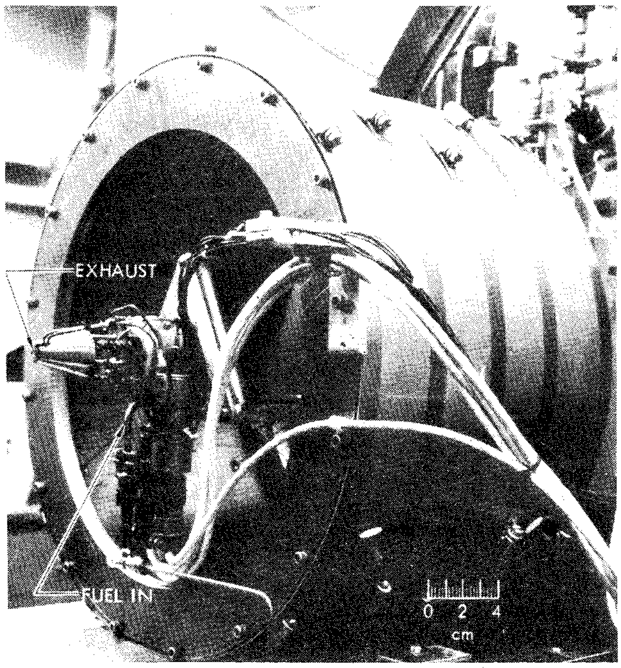

Fig. 3 0.9-N thruster installation.

flight-like thermal shields and heaters. The thruster was mounted on the thrust stand with the nozzle exit directed to fire horizontally as shown in Fig. 3.

The thruster reactor bed conditioning, conducted in a vacuum cell environment, included preheating to the desired temperature before each run. The heaters were cycled by means of a temperature controller for trim heating to maintain the specified bed temperature during the non-thrusting mode of a limit cycle pulse run.

Test Facility

The vacuum test facility includes a double-walled cylindrical steel vacuum chamber 1.22 m in diam by 2.44 m long, coupled with two sets of booster and second-stage pumps in a series-parallel arrangement having sufficient pumping capacity to maintain adequate vacuum with both or either set operating separately. All controls are remote, and the system is equipped with multiple interlock safety devices that are automatically triggered in the event of excessive temperature, loss of power, loss of coolant, overpressure, or loss of vacuum.

The propellant system is mounted on the entry door of the vacuum chamber. The door, resting on a rail carriage for mobility, supports the 3-liter run tank and the thrust stand. The propellant system uses gaseous nitrogen as the pressurant.

The data-acquisition system consisted of an integrated data acquisition and control unit (IDAC), which included pressure integrators capable of "real-time" data display and digital data recording. A generalized data reduction computer program (COMPROP) processed the IDAC tape and served as the source of final performance data. Analog instruments, used as backup, included a high-response multiple-speed oscillograph and strip-chart recorders.

Test Results

Results of tests on two different 0.9-N thrusters and one 0.45-N thruster using various grades of hydrazine with different aniline contents are summarized in Table 3. The nondimensional pressure ratio, p_f/p_0, defined as the ratio of the final peak chamber pressure p_f to the initial peak chamber pressure p_0 in the test run, can be used as a measure of the extent of thruster poisoning. That is, the smaller the pressure ratio the greater the reduction in the pulse peak pressure and the more acute the catalyst bed poisoning.

Conversely, a larger pressure ratio approaching unity would indicate that very little poisoning had set in, and a value of unity would represent the nonpoisoning case. Pressure ratios greater than one are observed when a poisoned thruster is undergoing rejuvenation. Since the number of pulses in any one test series was relatively small compared to the demonstrated life capabilities of these small thrusters, it is felt that a decrease in this pressure ratio represents any reversible poisoning effects that might be occurring and is not to be associated with the irreversible aging effects normally attributed to catalyst loss. It should be pointed out that each test run was begun with a nonpoisoned thruster by subjecting it to a steady-state firing, except for runs 2092-2098, which were performed consecutively without any attempts to rejuvenate the thruster between tests. Whereas the nondimensional pressure ratio provides an indication of thruster state-of-health, the chamber pressure integral, which is the measure of impulse bit, must also be considered, since this is an important parameter from a control system standpoint. It should also be noted that although the pulse can become distorted as a result of poisoning, it does not necessarily indicate that a degradation in pulse performance, i.e., impulse bit, has occurred. In fact, runs 2092-2098 show that the impulse bit remained relatively constant even though the pulse height was distorted by as much as 50%.

The initial tests, runs 1910 and 1914, were performed on a 0.9-N thruster (S/N B001) with the military grade of hydrazine in an attempt to duplicate the pulse collapse phenomenon noted in the earlier test program. The pulse shape distortion encountered during run 1910 is shown in Fig. 4. This figure graphically portrays the catalyst poisoning encountered within a small number of pulses, and it is evident that the pulse centroid is drastically affected. The change in the peak pulse height is shown in Fig. 5 as a function of pulse number. Although the resultant peak pulse height and final pressure ratios for these runs were relatively low, indicating that severe poisoning had set in, the pressure integral or impulse bit shown in Fig. 6 did not significantly drop off until the peak pressure had decreased to approximately 75% of the original pressure. Note that the pressure for these runs was integrated out to 1 sec from the valve actuation signal. There

Table 3 Test summary

Run No.	Thruster	Duty cycle, seconds/seconds (ON/OFF)	Bed temp, K	Inlet pressure, kN/m^2	Propellant[a]	No. pulses	Press ratio[b] (P_f/P_0)
1910	0.9 N S/N B-001	0.040/100.0	394	2537	Mil-P-26536C	1,672	0.03
1914	↓	0.040/100.0	394	2537	Mil-P-26536C	680	0.28
1922	↓	0.040/100.0	394	2558	STM-N020	9,817	0.97
1924	↓	0.040/100.0	394	2572	STM-N020 w/aniline	3,450	0.05
2091	0.9 N S/N B-010	0.010/21.0	477	2896	Mil-P-26536C	15,386	0.40
2092	↓	0.010/15.0	477	2513	↓	11,109	0.86
2093	↓	0.020/28.0	477	2413	↓	20,394	1.05
2094	↓	0.040/48.0	477	2413	↓	10,721	1.84
2095	↓	0.040/36.0	477	1034	↓	14,307	0.64
2096	↓	0.010/11.0	477	1034	↓	13,559	0.67
2097	↓	0.010/9.0	477	483	↓	10,085	0.66
2098	↓	0.020/20.0	477	1034	Mil-P-26536C	22,040	0.79
2133	0.45 N S/N 001	224	422	510-1476	Mil-P-26536C	1	
2135	↓	240	422	531-1358	STM-N020	1	
2137	↓	0.040/120.0	392	1172	STM-N020	2,385	0.86
2140	↓	0.040/120.0	384	1193	Mil-P-26536C	131	0.22

[a] Propellant assay for the propellants used for all the tests is shown in Table 4. [b] Ratio of final peak pressure to initial peak pressure in the run.

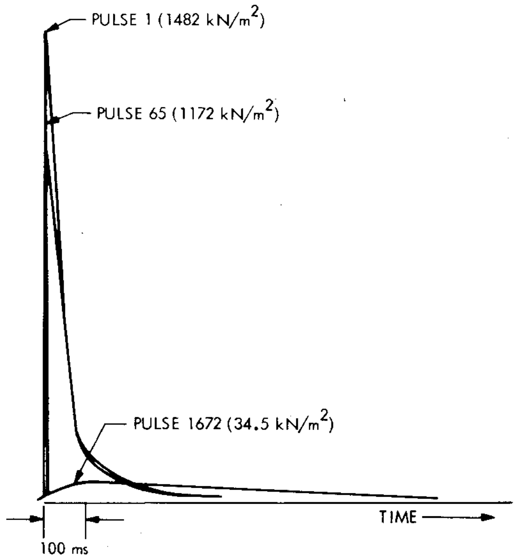

Fig. 4 Pulse shape distortion (Run 1910).

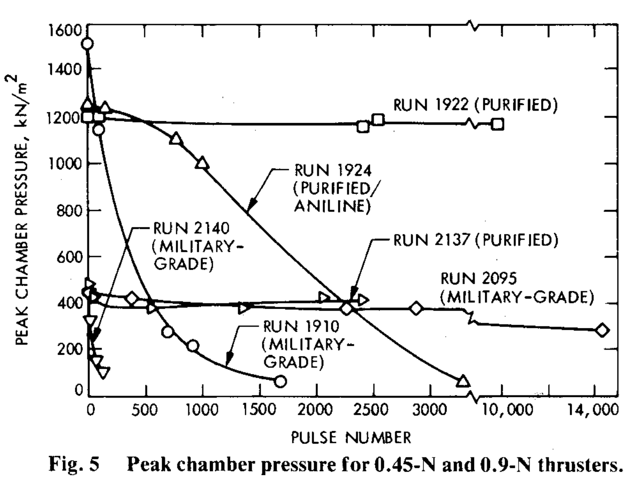

Fig. 5 Peak chamber pressure for 0.45-N and 0.9-N thrusters.

may be impulse in the tail beyond this point, not measurable for the tests plotted in Fig. 6 due to the lack of a low-range pressure transducer. It has been found that for very short pulse widths, i.e., 10 msec, the impulse in the tail taken out to 6 sec can contain as much as 50% of the total impulse. As the pulse width is increased to 40 msec, the duty cycle used for a large portion of these particular runs, the tail contains only about 10% of the impulse for the undistorted pulse shape. Hence, one should be cautioned in arbitrarily applying this correction to the data, since it could change the results significantly, especially if more impulse is contained in the tail of an acutely poisoned thruster. The tests performed on the 0.45-N thruster, under the same conditions (see Fig. 5, run 2140), gave similar results; i.e., the peak pressure had degraded by as much as 70% within 130 pulses. The impulse bit indicator, the pressure integral, was not calculated for this test series, but similar results could be expected.

Test runs 1922 on the 0.9-N thruster and 2137 on the 0.45-N thruster were made with the purified Viking lander grade hydrazine under similar operating conditions. The results shown in Figs. 5-6 indicate that the peak pressure and impulse bit were relatively constant throughout the 9800 and 2400 respective cumulative pulses. To confirm the aniline-associated poisoning phenomenon, the purified hydrazine used in the previous test, 1922, was inoculated with 0.7% aniline and put through the 0.9-N thruster at similar operating conditions (see run 1924). Again the results, presented in Figs. 5 and 6, show the same trends of performance loss associated with the military grade hydrazine. Thus the performance loss can be attributed to the aniline impurity. Recent tests by Rockwell International on a TRW thruster substantiate these results and confirm the conclusion that these effects do not seem to be peculiar to any one thruster design.[11]

To investigate the effects of higher bed temperatures on the aniline poisoning, a series of tests at various limit cycles (runs 2091 through 2098) was performed with the other 0.9-N thruster (S/N B010) using military grade hydrazine. These tests were made with the catalyst bed temperature at 477 K in place of the 394 K used previously. The results of run 2095, which is representative of this series of tests, are presented in

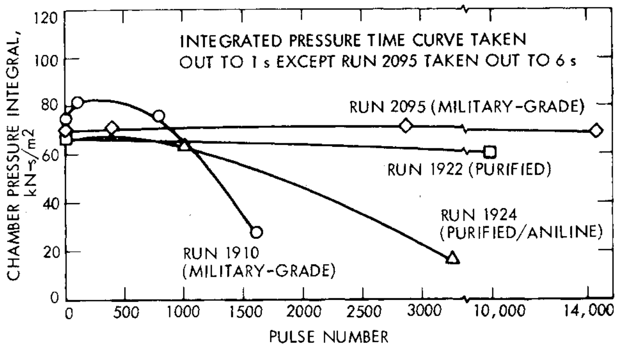

Fig. 6 Chamber pressure integral performance of the 0.9-N thruster.

Figs. 5 and 6. They indicate that some poisoning appears to be occurring even at the higher temperature. Table 5 summarizes in detail the results of this particular test series. During run 2094, the pulse height increased, indicating a self-rejuvenation of the thruster. This test and the data in Table 5 suggest that some aniline poisoning had occurred during low inlet pressure and short pulse width runs. During run 2097, an inadvertent increase in thruster temperature to nearly 533 K (pulse 8320) caused a rejuvenation. However, as indicated in Table 5, by the end of run 2097, the thruster had returned to a degraded condition. These results indicate that even at 477 K bed temperature, some pulse distortion can occur, particularly for very low inlet pressures and short *on* times. The pressure integral, taken out to 6 sec for these runs, remained relatively constant, as shown in Table 5.

Prior to investigating pulse distortion with the 0.45-N thruster, a "seven level" test series was performed to establish a performance baseline. The test consisted of a steady-state run in which the inlet pressure was periodically increased during a 240-sec period. Run 2133 was performed with a military grade propellant, and run 2135 was performed with a purified propellant. Performance results are shown in Tables 6 and 7 and Fig. 7. As can be seen, a definite decrease in the specific impulse is evident during run 2133 made with aniline-contaminated propellant and was not observed in run 2135 with the purified propellant. These results then suggest that

Table 4 Hydrazine assay [a]

Constituent	Mil grade	Purified	Purified/ aniline added
Aniline, %	0.54	<0.002	0.74
H_2O, %	0.85	0.91	0.71
NH_3, %	0.13	0.05	<0.05
Total carbon, %	---	0.0025	0.0025
CO_2, ppm	48	---	36
NVR, %	0.001	0.001	0.001
Particulate, mg/l	0.7	---	---
Cl, ppm	<1	---	---
F_2, ppm	<0.5	---	---
Fe, ppm	1.3	0.23	0.44
Cr, ppm	<0.1	<0.04	<0.04
Mn, ppm	0.06	<0.01	0.02
Ni, ppm	0.21	<0.05	0.07

[a] (---) not measured.

this anomaly, which is characteristic of washout, is associated with the aniline. This particular poisoning phenomenon was not evident during similar performance tests conducted in 1972 with military grade hydrazine prior to the refurbishment mentioned earlier.[3]

Postulated Poisoning Mechanism

Washout

Washout of a monopropellant hydrazine thruster is postulated to be a direct result of poisoning caused by aniline contained in hydrazine. The postulated mechanism for steady-state washout is as follows:

1) As shown in Fig. 8a, during steady-state operation, hydrazine entering a reactor will pass through the injector as a liquid, vaporize in a zone of the catalyst bed around the injector, and set up a decomposition zone near the injector.

Table 5 477 K test performance data with military-grade hydrazine and 0.9-N thruster

Test No.	Duty cycle, seconds/seconds (ON/OFF)	Pulse number	Peak chamber pressure, kN/m^2	Chamber pressure integral,[a] $kN\text{-}s/m^2$	Cumulative pulses
2091	0.010/21.0	30	203	30.2	15,386
		15,360	83	27.7	
2092	0.010/15.0	30	86	26.7	26,495
		11,080	74	24.9	
2093	0.020/28.0	30	150	43.5	46,889
		500	186		
		10,700	157	44.1	
2094	0.040/48.0	30	454	109.1	57,610
		280	915		
		10,700	836	90.8	
2095	0.040/36.0	30	438	69.3	71,917
		14,270	284	69.2	
2096	0.010/11.0	30	69		85,476
		13,535	46	21.8	
2097	0.010/9.0	30	39	16.0	95,561
		8300	16		
		8320	41		
		10,060	26	16.5	
2098	0.020/20.0	30	163	35.2	117,601
		22,020	129	35.1	

[a] Pressure integrated out to 6s.

Table 6 Run 2133 performance with military-grade hydrazine and 0.45-N thruster

Performance	60 s	100 s	140 s	170 s	180 s	190 s	220 s
Inlet pressure, kN/m^2	513.0	724.6	882.5	1008.0	1065.2	1315.5	1467.2
Chamber temperature, K	943	959	961	958	955	959	963
Chamber pressure, kN/m^2	377.1	516.4	562.6	568.8	574.3	655.0	655.7
Thrust, N	0.295	0.406	0.444	0.450	0.454	0.522	0.522
Mass flowrate, $kg/s \times 10^{-3}$	0.1345	0.1825	0.2515	0.3298	0.3668	0.4490	0.5107
Specific impulse, N-s/kg	2166.3	2228.1	1768.1	1364.1	1238.6	1162.1	1022.8

Table 7 Run 2135 performance with purified propellant and 0.45-N thruster

Performance	60 s	90 s	120 s	150 s	180 s	210 s	240 s
Inlet pressure, kN/m^2	535.0	785.3	883.9	1025.3	1095.6	1223.1	1359.0
Chamber temperature, K	961	1003	1015	1035	1046	1056	1066
Chamber pressure, kN/m^2	390.9	573.0	624.0	729.5	761.2	828.1	937.0
Thrust, N	0.302	0.451	0.496	0.584	0.610	0.666	0.756
Mass flowrate, $kg/s \times 10^{-3}$	0.1303	0.1966	0.2144	0.2497	0.2635	0.2921	0.3225
Specific impulse, N-s/kg	2327.3	2296.7	2313.4	2366.9	2316.3	2280.0	2352.6

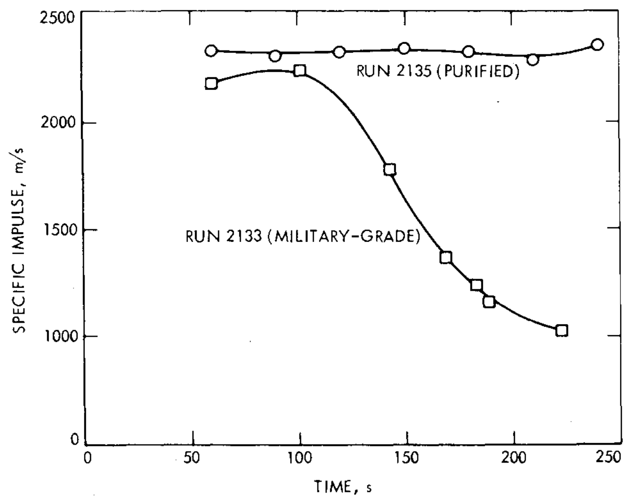

Fig. 7 Pressure step performance of the 0.45-N thruster.

2) The zone of liquid and vaporized unreacted hydrazine between the injector and the decomposition zone continues to exist during a long steady-state burn due to the cooling provided by incoming hydrazine and the latent heat of vaporization (Fig. 8b).

3) Within this cool (360 to 500 K) unreacted hydrazine zone, aniline impurities in the hydrazine form polycyclic compounds (coke) which are strongly chemisorbed to active catalyst sites within this region.

4) As active catalyst sites are covered with coke, the mean distance to an active site for decomposition increases, causing a slow shift in the decomposition zone away from the injector (see Fig. 8b).

5) This process continues until the decomposition zone reaches a point near the nozzle end of the catalyst bed (Fig. 8c) where because of insufficient availability of active sites, a mixture of partially decomposed hydrazine passes through the bed, causing decreased chamber pressure, decreased thruster temperature, and a resultant increase in propellant flow rate and decrease in specific impulse.

This mechanism is reversible since upon engine shutdown the heat stored in the catalyst bed is sufficient to release the chemisorbed coke and restore activity to the catalyst bed during thermal soakback.

Earlier studies of washout have resulted in design criteria for minimizing this phenomenon.[2] Specifically, the bed loading factor G should be less than 350 kg/m^2-sec. This design criterion may be too simple to apply across the board for all sizes of hydrazine thrusters. The postulated poisoning mechanism suggests development of new washout design criteria based on bed loading and propellant purity – a factor neglected in previous investigations of washout.

Pulse Shape Distortion

Degradation of the pulse shape at bed temperatures below 500 K for low-duty cycle operation is also postulated to be a direct result of poisoning caused by aniline. The postulated mechanism for this degradation in performance is as follows:

1) As shown in Fig. 8a, during pulse mode operation a quantity of hydrazine enters the reactor through the injector as a liquid and must seek an active catalyst site to promote decomposition and the associated temperature rise. The average temperature rise registered by the reactor for a typical limit cycle pulse width is generally less than 311 K, with

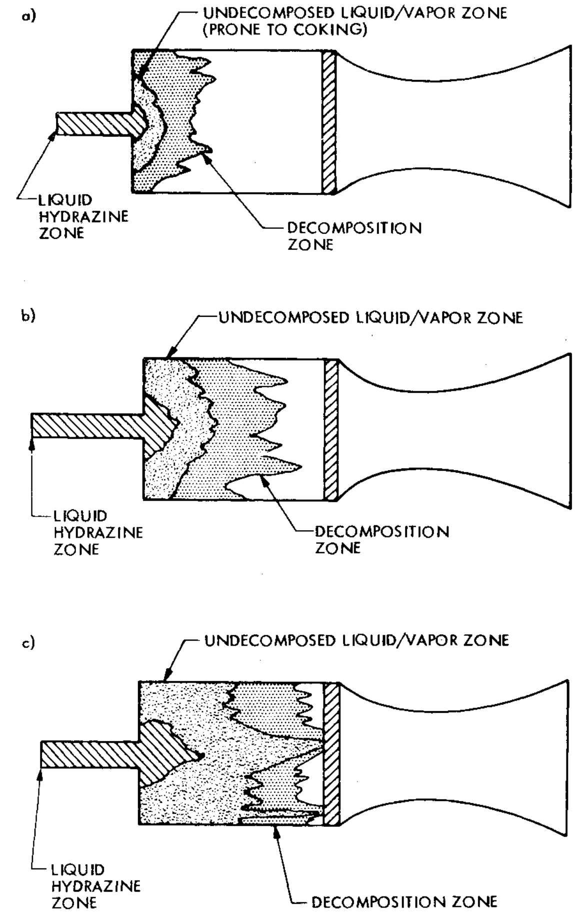

Fig. 8 Poisoning mechanism.

somewhat larger temperature rises confined to very small areas where the decomposition occurs.

2) As liquid enters the reactor during every pulse, aniline impurities in the hydrazine form polycyclic compounds (coke) that are strongly chemisorbed to active catalyst sites near the injector (unreacted liquid/vapor zone of Fig. 8a). The average temperature rise after each pulse is insufficient to remove the coke formed in areas outside the decomposition zone.

3) As active catalyst sites are covered with coke the mean distance to an active site for decomposition increases, causing a slow shift in the decomposition zone away from the injector (see Fig. 8b).

4) This process continues until the decomposition zone reaches an area near the nozzle end of the reactor (Fig. 8c) when, because of insufficient availability of active sites for decomposition, a mixture of partially decomposed hydrazine passes directly through the catalyst bed, causing severe distortion of the pulse shape.

Earlier studies of this poisoning phenomenon have assumed the cause to be chemisorption of exhaust products.[3] This may not be a valid across-the-board assumption, especially in light of the results described in this paper. However, during the development of a hydrazine plenum system (the catalytic reactor remained in the ammonia-rich decomposition product environment) it was found necessary to heat the reactor to drive off chemisorbed ammonia to promote a smooth start.[12] The mechanism for the observed degradation in this case is probably still valid since the system functioned properly at a temperature lower than that required to drive off aniline coke deposits, but further testing should be conducted to confirm this.

Studies by Kesten and Martenoy[13] have indicated that the longer the ignition delay for hydrazine on Shell 405 catalyst, the more the likelihood of catalyst breakup. The previously described mechanisms both postulate a period of slow growth of poisoned catalyst prior to any observation of performance degradation. During this period of coke growth the reduction in active sites can cause increased ignition delay on a microscopic level. Thus, along with a reversible poisoning of the reactor, an associated irreversible breakup of catalyst may be occurring. The magnitude of this breakup and its effects on thruster performance has not been quantified.

Conclusions and Recommendations

The primary conclusion drawn from these studies is that pulse shape distortion can be minimized, if not eliminated, with the use of aniline-free hydrazine. The mechanisms for both steady-state and pulse-mode performance loss are associated with the formation of a catalyst coke similar to the polycyclic aromatic poisons encountered in the petroleum industry. These poisoning mechanisms are reversible, with high-temperature operation being required to drive off the aniline coke deposits.

Operation at catalyst bed temperatures greater than 500 K with aniline-contaminated propellant can result in a reduction of the observed performance loss. At bed temperatures approaching 500 K there is no conclusive evidence of degradation in the impulse bit, even though some pulse distortion can be encountered. The exact temperature above which no distortion is observed has not been determined because of the difficulty in determining microscopic catalyst temperature from local reactor wall temperatures, and the fact that substantial poisoning must occur on a microscopic level before macroscopic performance loss is observed.

Although a phenomenon characteristic of washout was experienced only once during these studies, it can be concluded that this anomaly is more apt to occur with aniline-contaminated propellant. It is recommended that a more detailed investigation of thruster washout and its relationship to propellant purity should be conducted. A better understanding of this phenomenon would benefit all reactor designs. Additionally, the possible secondary effects of aniline poisoning on catalyst breakup should be investigated more fully. This study should be of interest to all reactor designs, since the mechanism of aniline poisoning and its secondary effect on catalyst may be occurring without the performance loss registered with advanced aniline poisoning. Thus catalyst breakup, an irreversible process, may be accelerated as a result of undetected aniline poisoning.

Purfied hydrazine has been selected for the 4-year MJS77 mission because of spacecraft power constraints and the unknown life risks associated with catalyst poisoning. A purified-grade hydrazine should be considered for any mission that imposes operational conditions on a thruster that can result in aniline-induced poisoning of the catalyst bed. The added costs of purified propellant to a project are relatively small in comparison with the risks associated with the use of high-aniline-content propellant.

The development of a military specification for purified-grade hydrazine is recommended. If such a specification is invoked, the manufacturing process for hydrazine should be reviewed to determine whether the aniline injection step presently used to break the water-hydrazine azeotrope can be replaced by a single-step differential freeze-thaw process to dehydrate hydrazine.

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