A SUMMARY OF NASA AND USAF HYPERGOLIC PROPELLANT RELATED SPILLS AND FIRES

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ABSTRACT

Several unintentional hypergolic fluid related spills, fires, and explosions from the Apollo Program, the Space Shuttle Program, the Titan Program, and a few others have occurred over the past several decades. Spill sites include the following government facilities: Kennedy Space Center (KSC), Johnson Space Center (JSC), White Sands Test Facility (WSTF), Vandenberg Air Force Base (VAFB), Cape Canaveral Air Force Station (CCAFS), Edwards Air Force Base (EAFB), Little Rock AFB, and McConnell AFB. Until now, the only method of capturing the lessons learned from these incidents has been "word of mouth."

The root causes and consequences of the incidents vary drastically; however, certain "themes" can be deduced and utilized for future hypergolic propellant handling. Some of those common "themes" are summarized below:

- Improper configuration control and internal or external human performance shaping factors can lead to being falsely comfortable with a system
- Communication breakdown can escalate an incident to a level where injuries occur and/or hardware is damaged
- Improper propulsion system and ground support system designs can destine a system for failure
- Improper training of technicians, engineers, and safety personnel can put lives in danger
- Improper personal protective equipment (PPE), spill protection, and staging of fire extinguishing equipment can result in unnecessary injuries or hardware damage if an incident occurs
- Improper procedural oversight, development, and adherence to the procedure can be detrimental and quickly lead to an undesirable incident
- Improper materials cleanliness or compatibility and chemical reactivity can result in fires or explosions
- Improper established "back-out" and/or emergency safing procedures can escalate an event

The items listed above are only a short list of the issues that should be recognized prior to handling hypergolic fluids or processing vehicles containing hypergolic propellants.

INTRODUCTION

Hypergolic fluids are toxic liquids that react spontaneously and violently when they contact each other. These fluids are used in many different rocket and aircraft systems for propulsion and hydraulic power including, orbiting satellites, manned spacecraft, military aircraft, and deep space probes. Hypergolic fuels include hydrazine (N_2H_4) and its derivatives including monomethylhydrazine (MMH), unsymmetrical di-methylhydrazine (UDMH), and Aerozine 50 (A-50), which is an equal mixture of N_2H_4 and UDMH. The oxidizer used with these fuels is usually nitrogen tetroxide (N_2O_4), also known as dinitrogen tetroxide or NTO, and various blends of N_2O_4 with nitric oxide (NO).

Several documented, unintentional hypergolic fluid spills and fires related to the Apollo Program, the Space Shuttle Program, and several other programs from approximately 1968 through the spring of 2009 have been studied for the primary purpose of extracting the lessons learned. Spill sites include KSC, JSC, WSTF, CCAFS, EAFB, McConnell AFB, and VAFB.

PROPERTIES OF NITROGEN TETROXIDE (N_2O_4)

Nitrogen tetroxide is a strong oxidizing agent that is used with the hydrazine family of fuels for rocket propulsion in the vacuum of space. It was accepted as the rocket propellant oxidizer of choice in the early 1950's by the U.S.S.R. and the United States. N_2O_4 itself is nonflammable, non-explosive, and does not exothermically decompose; however, when added to a fire it will increase the intensity of combustion and burning rate by providing an additional oxygen source to the air.[22] N_2O_4 is highly corrosive and extremely toxic. N_2O_4 is a liquid in equilibrium with nitrogen dioxide (NO_2) vapor: N_2O_4 (liquid) $\leftrightarrow$ $2NO_2$ (vapor). This equilibrium favors the vapor with increasing temperature and/or decreasing pressure. This is reversible when the conditions are the opposite. N_2O_4 is available in various "grades" ranging from pure N_2O_4 to 25% NO.

When N_2O_4 liquid or NO_2 vapors come in contact with skin, eyes, or the respiratory system, the oxides of nitrogen react with water to produce nitric (HNO_3) and nitrous (HONO) acids that typically destroy tissue. Together, these compounds oxidize the moist and flexible inner tissue of the alveoli sacs within the lungs when inhaled. The alveoli sacs are the location in which the oxygen and carbon dioxide exchange takes place that is necessary for respiration. Adequate exposure will cause these affected areas oxidative stress and cellular death. The pulmonary capillaries are the next to die. When this occurs, the plasma diffuses through the vessel walls in the lungs, resulting in a build-up of fluid (edema). Since the fluid accumulation results from pulmonary vessel failure, the effect and symptoms may not be immediate. However, at high enough concentrations, immediate death from hypoxia could occur as a result of airway spasm, oxygen displacement, or reflex respiratory arrest. Delayed death could occur as a result of significant fluid build-up leading to respiratory failure. In non-mortal exposure cases, tissue may heal with scarring (in the location where the tissue was significantly exposed), leading to bronchiolitis obliterans (destruction of the small airways and air sacs). Survivors may have varying degrees of permanent restrictive lung disease with pulmonary fibrosis.[58]

N_2O_4 (NO_2) vapors are approximately three times heavier than air and liquid N_2O_4 evaporates about five times faster than water at room temperature.[22] The vapors of MON-3 are normally reddish-brown in color, which is caused by rapid vaporization of NO_2. Liquid N_2O_4 and its vapors will explode on contact with hydrazine fuels, amines, and alcohol. Ignition may also occur when N_2O_4 comes into contact with wood, paper, hydrocarbon fuels, and some adhesives. A mixture of N_2O_4 and halogenated solvents: carbon tetrachloride, TCE, perchloroethylene, etc., may produce a violent explosion.[22] MON-3 N_2O_4 has the following properties:[22, 29, 61, 66]

- Molecular Weight — 92.016
- Relative Vapor Density — 1.58
- N_2O_4 + NO, % — 99.5
- Boiling Point (14.7 psia), ^{o}F — 70.1
- Freezing Point, ^{o}F — 11.8
- Vapor Pressure (70 ^{o}F), psia — 14.57 {Vp [psi] = 10 ^ (5.247 – 2654 / (T [R]) + 0.00175 * (T [R]))}
- Specific Gravity (77 ^{o}F) — 1.423
- Ignition Capability — Not flammable
- Odor — Bleach-like
- Odor Threshold, ppm — 1 to 3
- Exposure limit, ppm — 1.0 (exposure limit for NASA hardware processing)
- Density (77 ^{o}F & 14.7 psia), lbm/gal — 11.96 {Density [lbm/ft^3] = 95.499 – 0.07804 * (T [^{o}F]) + 0.00072 * (P [psig])}

PROPERTIES OF HYDRAZINE (N_2H_4)

Currently, monopropellant grade hydrazine (N_2H_4) is the fuel used in the Auxiliary Power Units (APU) on the Space Shuttle orbiters and the Hydraulic Power Units (HPU) on the Space Shuttle Solid Rocket Boosters (SRBs). N_2H_4 is also used on many spacecraft for monopropellant rocket propulsion (on the order of single digits to hundreds of pounds of thrust per rocket engine). To produce thrust, monopropellant rockets utilize a metal-based agent to catalytically decompose the N_2H_4 into ammonia, nitrogen, and hydrogen. Liquid hydrazine contains about 98.5% pure N_2H_4 with the remaining 1.5% being primarily water. Aerozine 50 (along with N_2O_4) was used for the first and second stages of the Titan II Intercontinental Ballistic Missile (ICBM) and Titan space launch vehicles including the 23G (a variant of the Titan II used for launching medium-sized spacecraft), IIIB, IIIC, and IV. The Titan II, IIIB, IIIC, and IV rockets used the largest quantities of hypergolic propellants per launch in the history of the United States rocket fleet (for the first stage approximately 13,000 gallons of N_2O_4 and 11,000 gallons of A-50 was used along with 3,100 gallons of N_2O_4 and 1,700 gallons of A-50 for the second stage).

The Occupational Safety and Health Administration (OSHA) classifies N_2H_4 and its derivatives as a possible carcinogen.[66] N_2H_4 and its derivatives are extremely toxic, highly flammable, and highly corrosive. "Hydrazines and their vapors explode on contact with strong oxidizers, such as N_2O_4, hydrogen peroxide, fluorine, and halogen fluorides. Additionally, they react on contact with metallic oxides, such as iron, copper, lead, manganese, and molybdenum to produce fire or explosion."[29]

Hydrazine fires produce little to no smoke or colorful flames. N_2H_4 has a tendency to react exothermically with or without an oxidizer present (the reaction increases the temperature thus increasing the reaction rate; this is also known as a thermal runaway reaction). Another way to describe a hydrazine thermal runaway reaction is "...the rate of heat generation by the reaction exceeds the rate of heat removal from the system."[8] This process is directly related to the auto-ignition temperature, which decreases as pressure increases. The exothermic reaction can end in an explosion if one or more of the following conditions are met within the system containing the hydrazine: the reacting system is confined to a rigid volume; the reacting system is adiabatic or nearly adiabatic; the reaction rate increases with temperature; or if the hydrazine is subjected to rapid over-pressurization through "water hammer".[21]

The vapor densities of all hydrazines are greater than air. Hydrazine evaporates at approximately the same rate as water at room temperature. N_2H_4 liquid at room temperature and pressure is clear and oily. N_2H_4 and MMH are hygroscopic (they readily absorbs water); therefore, water is widely used as a diluting agent. A liquid mixture of 58% water and 42% hydrazine or MMH by weight prevents ignition in an open air environment. A vapor mixture of 65% water and 35% hydrazine or MMH is considered nonflammable in air.[20] The following are properties of N_2H_4:[20, 61, 66]

- Molecular Weight — 32.04516
- Boiling Point (14.7 psia), °F — 237.6
- Freezing Point, °F — 34.75
- Vapor Pressure (77 °F), psia — 0.96
- Ignition Capability — 4.7 to 100% by volume in air
- Auto-ignites, °F — 437 in air, 984 in GN_2, (increases with decreasing pressure)
- Ratio of Specific Heat (gas) — 1.19
- Odor — Ammonia; fishy
- Odor Threshold, ppm — 2 to 3
- Exposure Limit, ppm — 0.01 (exposure limit for NASA hardware processing)
- Density (77 °F & 14.7 psia), lb_m/gal — 8.38

PROPERTIES OF MONOMETHYLHYDRAZINE (MMH)

Monomethylhydrazine is the fuel used in the OMS/RCS on the Space Shuttle orbiters. Monomethyl-hydrazine, $N_2H_3(CH_3)$, is similar to hydrazine, N_2H_4, with the exception that it contains a methyl group in its molecule in place of one hydrogen atom. Most rocket grade MMH contains 98% pure $N_2H_3(CH_3)$ with the remaining 2% being primarily water. MMH is not used for monopropellant rocket propulsion because the carbon formed in its decomposition contaminates the catalyst. It is extremely toxic, highly flammable, and highly corrosive. MMH has greater compatibility with metals as compared to N_2O_4.

MMH may have a slight yellow-orange tinted flame. MMH can also react exothermically with or without an oxidizer present, but the reaction rate has been found to be much slower than N_2H_4.[8] MMH vapor has also been found to be much less sensitive to detonation as compared to N_2H_4.[8] As a result of the molecular differences in comparison to N_2H_4, MMH has slightly different properties as shown below:[21, 29, 66]

• Molecular Weight	46.075
• Boiling Point (14.7 psia), °F	189.5
• Freezing Point, °F	-62.5
• Vapor Pressure (77 °F), psia	3.23
• Ignition Capability	2.5 to 98% by volume in air
• Auto-ignites in air, °F	286 to 386 (increases with decreasing pressure)
• Ratio of Specific Heat (gas)	1.13
• Odor	Amine; fishy
• Odor Threshold, ppm	1 to 3
• Exposure Limit, ppm	0.01 (exposure limit for NASA hardware processing)
• Density (77 °F & 14.7 psia), lb_m/gal	7.27 {Density [lbm/ft^3] = 56.926 – 0.03231 * (T [°F]) + 0.000252 * (P [psig])}

RESULTS AND DISCUSSION

A total of 45 hypergolic related incidents were studied for the purpose of compiling common lessons learned. Table 1 and Figure 1 summarize the fuel and oxidizer incidents. As shown in Table 1, the ratio of fuel to oxidizer incidents is approximately one-to-one. Also, the severity (personnel injury or the extent of the hardware damage) was approximately the same when comparing fuel and oxidizer incidents. One key difference between a fuel and an oxidizer incident was that a fuel incident has the potential to become very dangerous quite abruptly as compared to an oxidizer incident as a result of the potential for fire or explosion. The graphs in Figure 1 illustrate that many of the incidents were directly related to some sort of human error along with the occurrence of the event usually taking place during some sort of transfer of commodity or opening of a system.

Table 1: Hypergol Spill and Fire Summary

	Oxidizer Incidents:		**Fuel Incidents:**
23	Total (Liquid and Vapor)	24	Total
7	Vapor Only	8	Led to a Fire
3	Led to a Fire	2	Led to an Explosion
3	Led to an Explosion	7	Led to Injuries (minor to death)
8	Led to Injuries (minor to death)	12	Led to Hardware Damage
12	Led to Hardware Damage		
	10 Oxidizer/Fuel No Hardware Damage or Injuries		
Root Causes:			
7	Procedure Adherence/Control (engineer or technician did not follow procedure or protocols were ignored)		
11	Improper Personnel Training (engineers or technicians were untrained or too inexperienced)		
17	Human Error (technician and/or engineers making a real-time error)		
24	Improper GSE/Vehicle Design (improper materials, unknown low points, incompatibilities, etc.)		
11	Improper Configuration Management (system configuration and upkeep errors that led to an incident)		
Incident Occurred During:			
18	During Commodity Movement		
15	During a removal and replacement (R&R) Procedure		
41	During a Nominal Hypergol Operation		
13	During Opened Hypergol System		
3	In a Static Hypergol System		

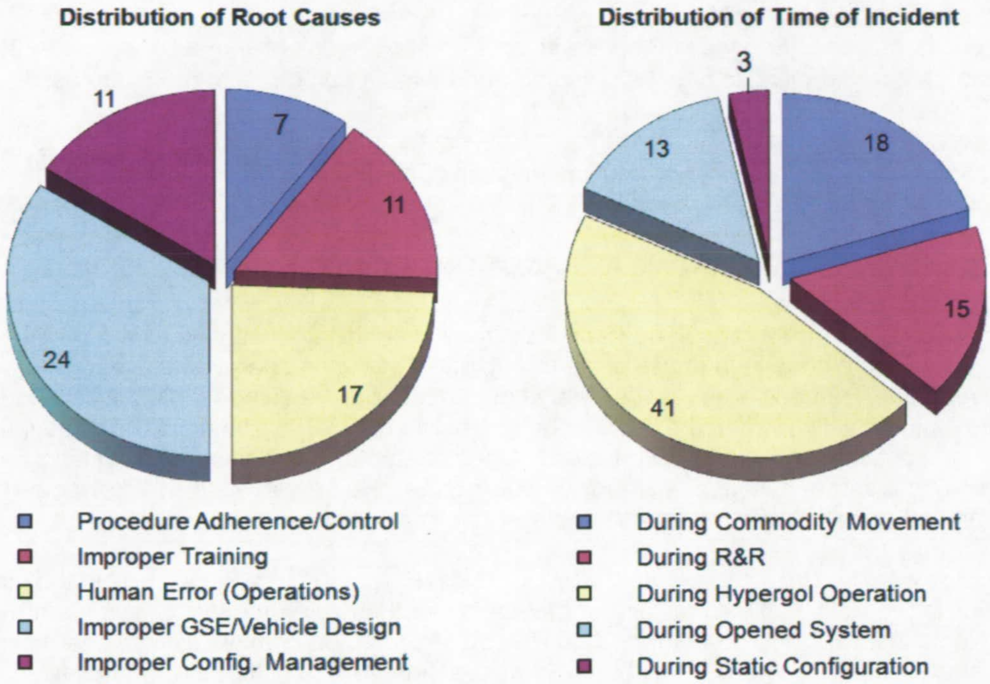

Figure 1: Distributions for Root Cause and Time of Incidents

Some common lessons learned deduced from the various root causes of the studied incidents are shown in the following list. If these items were properly addressed prior to the incidents, prevention may have been possible (in hindsight) or the impact or consequence of the incident could have been reduced.

- Improper configuration control and internal or external human performance shaping factors can lead to being falsely comfortable with a system
    - Vent systems are often neglected and treated as non-hazardous even though they can capture and contain hypergolic liquids (especially in low points)
    - Aging support hardware should be routinely inspected to reduce the risk of a failure during critical operations
- Communication breakdown can escalate an incident to a level where injuries occur or hardware is damaged
- Improper propulsion system and ground support system designs can destine a system for failure
    - Low points in ground support equipment (GSE) should be designed out
- Improper training of technicians, engineers, and safety personnel can put lives in danger
    - Inadequate knowledge of electrostatic discharge while working fuel operations can lead to a fire or explosion
    - Knowledge of transducer offsets is very important for system oversight
    - Unknown incompatibilities (from lack of training or research) with propellants can cause surprising failures
    - If an incident does occur, the system should immediately be placed into a stable configuration; following this, the procedure should be stopped to assess the problem and its possible ramifications
    - A heightened amount of situational awareness of technicians and engineers working operations can reduce the risk of an incident and decrease the possibility of injuries or damage if an incident does occur
- Improper PPE, spill protection, and staging of fire extinguishing equipment can result in unnecessary injuries or hardware damage if an incident occurs

- Improper procedural oversight, development, and adherence to the procedure can be detrimental and quickly lead to an incident
    - Improper emergency procedures can increase the risk of injuries or hardware damage
- Improper local cleanliness or housekeeping (for example iron oxide or rust) can result in fires or explosions
- A thorough hypergol system evacuation should be completed (wherever a vacuum is tolerable by the system) prior to the removal or disconnection of any hypergolic propellant fittings
    - A pulse purge has proven to be inadequate for the removal of residual propellants

SUMMARY AND CONCLUSIONS

Some type of human error can be traced to nearly every incident studied as a root cause, whether it be an error in the design phase or an error prior to or during operational use of hardware containing hypergols. Humans are most definitely not perfect and even when the most knowledgeable personnel are intimately involved in the design phase (vehicle or GSE) or during an operation, mistakes can be made and critical items can be overlooked. One can deduce, however, that most incidents happen during some sort of dynamic operation. Hypergols tend to be very stable in a static configuration (as long as the compatibility characteristics have been well addressed).

Advance warning (prior to any liquid or vapor release) was available in several of the incidents to the technicians in the vicinity of the spill and/or the engineers that were monitoring from a remote location. The warning indications include off-nominal data (remote or local), off-nominal system characteristics, and/or local changes that occurred without human intervention. Some of these went unnoticed or were ignored during the operation, thus resulting in an incident. There was advance warning in 19 out of 38 total incidents (50% of the time). This percentage does not include spilled fuel as an advance warning of a fire (5 occurrences). Depending on the local environment, there is a reasonable probability that if hydrazine (or one of its derivatives) is spilled, there will be a fire; therefore, the fuel spill itself is an advance warning of a fuel fire. Roughly 42% of the documented fuel fires studied resulted in a fire or explosion. The Titan IV K-9 N_2O_4 spill likely had an advance warning; however, there was no one in the vicinity of the indications to receive the warning, therefore, this was not included in the above percentage along with the OV-101 APU spill in 1977, since it was unable to be determined if there was an advanced warning for this incident.

Hypergolic rocket propellants have proven to be a highly reliable asset in manned and unmanned spaceflight; however, their maintenance on the ground has proven to be relatively difficult. Do the operational risks from possible human errors or hardware failures causing a catastrophic incident outweigh the usefulness of hypergols even though they have been used for the last 50 years of manned and unmanned spaceflight? One would have to say probably not, since hypergols are so widely used in the space industry currently and are being proposed to be used on many vehicles in the future. Therefore, ground operations on hypergol systems have become increasingly scrutinized for possible unknowns, and rightfully so. The data shown in this report are not an example of why we should not be using hypergolic propellants on spacecraft and launch vehicles, but rather what we can and should do to mitigate possible unforeseen ground operation and/or design problems.

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REFERENCES

1. Anderson, John C. "Test Cell 831 Druck Pressure Transducer Failure on March 25, 2003." Johnson Space Center, White Sands Test Facility Laboratories Office. Investigative Report Number WSTF-IR-0185-001-03. May 5, 2003.

2. Applewhite, John B. "Update on L3D Removal Incident." Informal email. May 31, 1995.

3. Apollo (ASTP). Wade, Mark. 1997-2007. Encyclopedia Astronautica. <http://www.astronautix.com/flights/apooastp.htm>.

4. Banke, Jim. "Shuttle's Leaking Line Gets Finishing Touches." Florida Today. August 19, 1988, 1st edition: 4A.

5. Banke, Jim and Ann Mittman. "NASA Explores Shuttle Options." Florida Today. July 19, 1988, 1st edition: 1A+.

6. Baum, B. "Impact Sensitivity of Chem Pump Stator Materials After Oxidizer Exposure." Martin Marietta Corporation Inter-Department Communication 0483/81-32. January 28, 1981.

7. Benson, Charles D. and William Barnaby Faherty. "Moonport: A History of Apollo Launch Facilities and Operations." NASA Special Publication-4204. 1978.

8. Benz, F. J. and M. D. Pedley. "A Comparison of the Explosion Hazards of Hydrazine and Methylhydrazine in Aerospace Environments." CPIA-PUB-455, Volume 1, pp 477-488. 1986.

9. Bowman, H.D. "Oxidizer Leak/OPF High Bay 2, 17 Feb. 84 at 0945." Interdepartmental Communication. 2301-84-021HDB. February 18, 1984.

10. Buzzard, Frank et. Al. "NASA Management Briefing of OV-105 R1A Thruster Fire Mishap." Presentation slides given by NASA Investigation Board. May 18, 1995.

11. Comfort, James L. "ORB Minutes – SLC-40 Oxidizer Farm Pump Incident." Memo for 45 OG/CC, Department of the Air Force, Patrick AFB, FL. August 14, 2003.

12. Cotton, R. K. "Pad A Monomethylhydrazine (MMH) Fuel Farm Mishap." Lockheed Space Operations Company Mishap Investigation Board Investigation Report. January 21, 1986.

13. Craig, Anna F. "Procedure for Connecting, Disconnecting and Maintaining the Cleanliness of Forward Reaction Control Subsystem and Aft Propulsion Subsystem Disconnect Couplings." The Boeing Company Specification. ML0310-0032 Rev. G. February 21, 2002.

14. Crass, Larry, Art Geer, Steve Cronau, and Mark Maccan. "SLC-4E Blast Cage Modifications/Ox Pump F/A Results." Baker Engineering & Risk Consultants. ERB 03-2076R1. December 16, 2003.

15. Delventhal, R. A. and N. M. Faget. "Space Shuttle RCS Oxidizer Leak Repair for STS-26[R]." NASA Johnson Space Center. Document ID 19900009169. May 1, 1989.

16. Demarchi, E. N. "Hydrazine Leak – Ov-101 Aft Fuselage Wiring." Rockwell International Internal Memo 392-620-77-619. October 3, 1977.

17. Dougert, Robert S. "RE: Hypergolic Spill/Fire Report." E-mail to Robert Dougert. May 18, 2009.

18. Draus, Thomas. Branch Chief, Shuttle Hypergolics, Hydraulics, & Auxiliary Power Branch. NASA Kennedy Space Center. Personal interview. July, 21, 2008.

19. Ezell, Edward C. and Linda N. Ezell. "The Partnership: A History of the Apollo-Soyuz Test Project." NASA SP-4209. 1978.

20. "Fire, Explosion, Compatibility, and Safety Hazards of Hypergols – Hydrazine. American Institute of Aeronautics and Astronautics Special Project Report. AIAA SP-084-1999. 1999.

21. "Fire, Explosion, Compatibility, and Safety Hazards of Hypergols – Monomethylhydrazine." American Institute of Aeronautics and Astronautics Special Project Report. AIAA SP-085-1999. 1999.

22. "Fire, Explosion, Compatibility, and Safety Hazards of Nitrogen Tetroxide." American Institute of Aeronautics and Astronautics Special Project Report. AIAA SP-086-2001. 2001.

23. Fisher, James and John J. Glisch. "Leak Could Put Discovery on Shelf." The Orlando Sentinel. July 17, 1988, 1st edition: A-1+.

24. Fisher, James. "Shuttle May Go Back to Hangar for Repair Work." The Orlando Sentinel. July 19, 1988, 1st edition: A-3.

25. Gehman, Harold W. Jr et al. "Columbia Accident Investigation Board Report Volume I." August, 2003.

26. Gehman, Harold W. Jr et al. "Columbia Accident Investigation Board Report Volume II." October, 2003.

27. Glisch, John J. "Shuttle Tank Problem May Not Have Had Thorough Check." The Orlando Sentinel. July 20, 1988, 1st edition: A-1+.

28. Gorham, Richard. "MMH Fire at Test Stand 401." Honeywell Technology Solutions Inc. Memorandum. PD00-096. August, 21, 2000.

29. Hall, George F., Raymond Lake, John H. Storm, and Ross J. Utt. "Fire Protection Research and Development Requirements Analysis for USAF Space Systems and Ground Support Facilities Volume I – Fire Protection Operational Requirements Analysis." Flight Dynamics Directorate Wright Laboratory Air Force Materiel Command, Tyndall Air Force Base, FL. WL-TR-96-3010. April, 1995.

30. Hartsell, Heather. "Top Story – Titan Missile Crisis." The Arkansas Leader. September 27, 2006. <http://www.arkansasleader.com/2006/09/top-story-titan-missile-crisis_27.html>.

31. Heinrich, Manfred M. United Space Alliance Chief Engineer, KSC. Personal Interview. September 17, 2007.

32. Henderson, J. "Fuel Waste Incident Report." WSTF Internal Memo. February 21, 1990.

33. Henson, D. M. "Hypergolic Oxidizer Spill." IERB 0003-98. December 8, 1997.

34. Hill, Gary et. Al. "FCV Vent Port Leakage." Titan IV SRM Program Technical Interchange Meeting. Meeting briefing log number 7260. July 31, 1997.

35. Houston, D. W. "MMH Spillage Investigation." Rockwell International Laboratory Test Report LTR 3406-4579. October, 1981.

36. "Investigation of the WSTF 400-Area Oxidizer Spill Incident." Johnson Space Center, White Sands New Mexico, Las Cruces New Mexico. March 29, 1996.

37. "Investigation Report of the WSTF Peacekeeper Axial Engine Valve Damage." WSTF-MR-00-0004. Lyndon B. Johnson Space Center, White Sands Test Facility, Las Cruces New Mexico. September 15, 2000.

38. Johnson, B. H. "Failure Analysis of a Fluid Mechanics Check Valve from Orbiter Processing Facility (OPF) Toxic Vent System." NASA Engineering Development, Ground Support Office, Materials Analysis Office, Malfunction Analysis Branch. MAB-221-86. September 30, 1986.

39. Kamp, G. J. "N_2O_4 Release at Oxid Farm IPR-6V-1189." Memorandum for the Record. February 10, 1983.

40. Kehler, Robert C. "30 SW Operations Review Board Minutes." Memo for 30 SW/CC, Vandenberg AFB, CA. August 22, 1997.

41. Keinath, Richard. "Flash # 008214 – Hypergolic Maintenance Facility (M7-1212) Oxidizer Spill." Investigation Committee Slides. March 10, 2006.

42. Kersey, Judith. 'Independent Assessment of the OV-103 OMS/RCS Pod Leak and OMS Pod Processing." KSC IAI 0988-01. NASA Kennedy Space Center, Florida. February 13, 1989.

43. Kolcum, Edward H. "NASA Managers Scramble to Limit Leak's Impact on Discovery Launch." Aviation Week & Space Technology. July 25, 1988: 24-25.

44. Kowalski, Robert R. "Test Cell 844 Manual Valve Failure Mishap Investigation." NASA Propulsion Test Office, Johnson Space Center, White Sands Test Facility. WSTF-MR-05-0005. March 14, 2006.

45. KSC Hazard Report. "Personnel Injury and Flight Hardware Damage Resulting from SRB Hydrazine Leak or Spill." Report Number SPC-K13167-86 Rev. B. September 2, 2002.

46. KSC Hazard Report. "Possible Fuel/Oxidizer Vapor Release During Maintenance/Calibration of Relief Valves on the MMH/N_2O_4 Storage Tank." Report Number SPC-K12186-85 Rev. A. May 22, 2006.

47. KSC Incident Reporting Information System (IRIS) Database. Incident Numbers: 1985-144-00001, 1986-021-00001, 1986-210-00001, 1999-232-00007, 2003-224-00006, 2004-162-00002, 2006-027-00002. 2008.

48. KSC SSP PRACA Database. "During Attempted Removal of Adapter from Throat of Thruster Liquid Spilled from Thruster R4D." PR RP04-9-08-0031 (page 1A). Initiated May 24, 1985.

49. KSC SSP PRACA Database. "Fuel Waste Barrel Inadvertently Filled With Fuel (MMH). Suspect FV-2 Valve Inadvertently Opened By Lifeline for Traffic in Area." PR HMFE-0299. Initiated December 12, 1990.

50. KSC SSP PRACA Database. "FV-1 and FV-2 Valve Handles Extend Into Walk Area and May Be Inadvertently Cycled on the Fuel FCU." PR C72-1631-03-001-0015. Initiated March 4, 1991.

51. KSC SSP PRACA Database. "Liquid MMH Released from Sample Valve at I/F A94209 After Drain and Evacuation Procedure Completed; S/B No Liquid." PR FRC4-19-0470. Initiated March 26, 1997.

52. KSC SSP PRACA Database. "Oxid [N_2O_4] Cross Country Line Pressure is Decreasing, Indicating an External Leak." PR S70-0700-06-002-0019. Initiated November 6, 1997.

53. KSC SSP PRACA Database. "Small Flame Reported When Sample Gear Was Removed from A78626 Sample Valve N_2O_4 Drain When F/H Was Removed Came in Contact With Insulation Which Burned Momentarily." PR PADB-0209. Initiated June 24, 1988.

54. Lance, Renée J. "Approach and Landing Tests Auxiliary Power Unit Subsystem Flight Report." January, 1978.

55. McCoy, R. W. "January Interim Report: LT-152 Fire Investigation." EG & G Florida Interoffice Correspondence 631-5-008. January 15, 1985.

56. MER Problem Report (STS-9) STS-9-V-26. November 26, 2007. MER Problem Tracking Database. July 11, 2008. <http://mer.jsc.nasa.gov/merptd/Public/Home.cfm>.

57. Meyer, R. R. "Incident Report: Aspiration of Oxidizer into the Fuel Aspirator System at Test Stand 401." Lockheed Engineering & Sciences Company Interdepartmental Communication. PTD90-119. March 29, 1990.

58. Myers, Jeffrey, M.D. "RE: Hyper Spills & Accidents Lessons Learned Report – Toxicology of NO_2 Inhalation." E-mail to Jeffrey Myers and Frank Golan. August 7 2008.

59. National Aeronautics and Space Administration. "Project: Apollo 7 Press Kit." Release No: 68-168K. September 27, 1968.

60. Nufer, Brian M. "FRC3 HMF Building M7-1212 West Test Cell FRC3 N2O4 Spill on January 9. 2006." Incident Summary Report. May, 2006.

61. "Occupational Exposure to Hydrazines." NIOSH Criteria for a Recommended Standard. U.S. Department of Health, Education, and Welfare (DHEW), Public Health Service, Center for Disease Control, national Institute for Occupational Safety and Health (NIOSH). DHEW (NIOSH) Publication No. 78-172. June 1978.

62. Olney, J. N. "OV-101 Hydrazine Exposure Investigation." Rockwell International Laboratory Test Report LTR 2291-4466. March, 1978.

63. Perez, Conrad. "RE: Apollo 7 Spill." E-mail to Conrad Perez. June 24, 2008.

64. Porter, Alan R. "RE: 2005 N2H4 Spill Questions." E-mail to Alan Porter and Kurt Rathgeber. May 29, 2008.

65. RCS Thruster Heater Power During Ferry Flight Stopovers. Kline, James G. June 2, 1994. NASA Lessons Learned Website. Lesson Learned Entry 0059. August 1, 2007. <http://nen.nasa.gov/portal/site/llis>.

66. Rathgeber, Kurt A., Bruce Havenor, and Steven D. Hornung Ph.D. "Hypergol Systems: Design, Buildup, and Operation." NSTC Course 055. January 6, 2006.

67. Reynaud, Raymond. "Lessons Learned – Quick Disconnect (QD) Oxidizer Exposure Incident." QARSO-WSTF Informal Memo. November 20, 1992.

68. Rodgers, James L., Maj., USAF. "Titan Oxidizer Leak ORB." Memorandum for Record for the Department of the Air Force, 45th Space Wing (AFSPC), Patrick AFB, Florida. September 16, 1994.

69. Sargent, Douglas E. "MMH Spill Mishap Report (January 21, 1986)." Lockheed Space Operations Company Internal Letter. July 3, 1986.

70. Schindzielorz, Howard. "Titan IV-A FCV Vent Port Leakage TIM." Memorandum for Record for the Department of the Air Force, 45th Space Wing (AFSPC), Patrick AFB, Florida. July 31, 1997.

71. Skaja, Jeffrey T. "RE: Titan IV N_2O_4 Spill on CCAFS." E-mail to Jeffrey Skaja. September 4, 2008.

72. Smitelli, Joseph III. "HMF Oxidizer Exposure." Standing Accident Investigation Board Team Report IPB-04-025-D. June 5, 2004.

73. Stefanovic, Mike et. Al. "OPF Bay 2 Fuel Spill." Mini-Investigation Report. February 17, 1997.

74. Sullivan, J. L. "HMF FRCS #4 Fuel Spill." Formal Accident Investigation Board Report. KSC Mishap Report Number USK-97-020. March 26, 1997.

75. Titan-II.com. Currie, George. September 9, 2007. July, 11, 2008. <www.Titan-II.com>.

76. Titan II Missile Explosion. 2008. The Encyclopedia of Arkansas History and Culture. The Central Arkansas Library System. July 11, 2008. <http://www.encyclopediaofarkansas.net/>.

77. Torpey, Tom. "Situational Awareness" course notes. NASA Safety Training Center Course Number 034. January 18, 2006.

78. Tribe, J. "Apollo Hypergolic Systems-Command and Service Modules." December 2007.

79. Tribe, J. "Incident/Error Review Board Item 70 – Inadvertent Flow of MMH to Atmosphere Resulting in Ignition/Fire on June 29, 1982." Rockwell International Internal Letter. L0-JT-82-044. October 29, 1982.

80. Tribe, J. "Incident 029-83, MMH Spill During FRCS Ferry Plug Removal." Rockwell International Internal Letter. L0-JT-82-043. May 2, 1983.

81. Utsman, T. E. "Monomethylhydrazine (MMH) Spill/Fire, June 29, 1982." NASA Internal Memo. VO/Director of Shuttle Operations. Undated.

82. Walker, J. J. "Evaluation of Materials for N_2O_4 and Aerozine 50 Compatibility for Chemical Pumps." Martin Marietta Corporation Mechanical Engineering Materials Engineering MeME 81/273R. September, 1981.

83. Washburn, J. F. "Final Report of the Fire Involving Hypergolic Fuel (MMH) Tanker LT-152." KSC-E-863. August, 1984.

84. Weber, D. A. "Reported Fire During OV-105 L3D Thruster Changeout." Lockheed Martin Space Operations Interdepartmental Communication. June, 12, 1995.

85. What You Should Know about Refrigerants When Purchasing or Repairing a Residential A/C System or Heat Pump. August 25, 2008. Ozone Layer Depletion – Regulatory Programs. U.S. Environmental Protection Agency. August 26, 2008. <http://www.epa.gov/Ozone/title6/phaseout/22phaseout.html>

86. Wilder, J. "Release of Oxidizer Vapor During Flight Cap Installation on MD338." Rockwell International Internal Letter. L0-JW-81-010. July 14, 1981.

87. Wilder, J. "Incident Report LC-39A." Rockwell International Internal Letter. L0-JW-81-011. July 15, 1981.

88. Williams, Wiley E. "LC-39A STS-2 Oxidizer Leak." Mishap Investigation Committee Final Report. October 9, 1981.