

# **Course Introduction**

## **NSTC Course 055**

### **Hypergol Systems: Design, Buildup, and Operation**

#### **BACKGROUND**

This course was developed by personnel at the NASA JSC White Sands Test Facility in conjunction with the NASA Safety Training Center (NSTC). The NSTC was established in May 1991 by the NASA Headquarters Safety Directorate to provide up-to-date, high-quality, NASA specific safety training on location at NASA centers, or simultaneously to multiple centers over the Video Teleconferencing System (ViTS). Our desire is to establish and maintain a strong, long-lasting relationship with all NASA centers in order to fulfill your safety training needs on a cost-effective basis. Our ultimate goal is to provide a positive contribution to safe operations at NASA.

#### **COURSE DESCRIPTION**

NSTC Course 055 is a 2-day course discussing the safe usage of hypergols (hydrazine fuels and nitrogen tetroxide). During the course we will identify the hazards associated with hypergols including toxicity, reactivity, fire, and explosion. Management of risk is discussed in terms of the primary engineering controls – design, buildup, and operation; and secondary controls – personal protective equipment and detectors/monitors. The emphasis is on the design and buildup of compatible systems and the safe operation of these systems by technicians and engineers.

#### **COURSE GOALS AND OBJECTIVES**

The NSTC's goals in teaching this course are:

- ◆ To increase safety awareness;
- ◆ To provide useful information and references;
- ◆ To enable attendees to identify and evaluate typical hazards of hypergols and hypergol systems.

#### **INTENDED AUDIENCE**

Those who would benefit from this course include engineers, technicians, plant managers, and operators involved in hypergol system design, buildup, operation, and maintenance. This course would also be appropriate for safety and health professionals involved in monitoring and evaluating the operation of hypergol systems.

#### **INSTRUCTIONAL TECHNIQUE**

The instructional technique used will be primarily lecture and in-class videos. We do encourage in-class discussion to develop student understanding of the concepts, practices,

and techniques discussed. We encourage students to participate during all parts of the class; and if you have a question, a comment, or a personal experience that would contribute to the subject - please speak up. We also encourage you to ask the instructors to discuss issues specific to your use of hypergols so we can tailor the class to your Center's needs.

## COURSE MATERIALS

The course notebook provided with this class is intended not only for your use in following the classroom presentation, but also for future reference. We hope this notebook is not a trophy adorning your bookshelf, but rather a reference tool you go back to again. We encourage you to follow along and review the material during the class so you can ask any questions you may have.

## COURSE EVALUATIONS

Course critiques are very important to us. We are very interested in your impressions of the class materials and presentation, and your suggestions for improvement. The NSTC staff and the course instructors will review each and every critique, and your written comments will be provided to the point-of-contact at your center.

## COMPLETION CERTIFICATES

We will send you an NSTC course completion certificate along with a class roster after the class. NASA Headquarters will sign these course certificates. Please fill out the course attendance roster fully and legibly for each class, as we will use it to track attendance, to prepare course completion certificates; and potentially to contact you in the future with NSTC news. In order to receive credit for course attendance, you must personally attend approximately 2/3 of the course. Course instructors will have the final say on who should receive credit for the course.

## CONTINUING EDUCATION UNITS (CEUs)

This course has been approved for the award of up to 1.2 Continuing Education Units (CEUs) to students. The primary purpose of a CEU is to provide a permanent record of the educational accomplishments of an individual who has completed one or more significant non-credit educational experiences. CEUs can be used to update and maintain professional certifications. In order for this award, we will be taking attendance every day on a roster, which requires your signature and your social security number. Providing your social security number is voluntary, but you cannot receive CEU credit without it. If you do provide your social security number, this information will be controlled in accordance with Privacy Act requirements, and access will be limited to those with a valid need to know. CEUs earned will be indicated on the course completion certificate under the course title. To receive CEU credit, you will have to attend the entire course (individual decisions as to how much can be missed will be the purview of the NSTC instructor and staff).

## CONTACTING THE NSTC

We hope you enjoy this course. If you are interested in any of our other courses, you may contact your center point of contact or the NSTC staff at (281) 244-1284 for additional information. You may also reach us via e-mail at [larry.gregg1@jsc.nasa.gov](mailto:larry.gregg1@jsc.nasa.gov).

## INSTRUCTORS

Bruce Havenor is a Materials Test Tech, Specialist. He started working at the NASA White Sands Test Facility (WSTF) in March 1976. He is a hazardous fluids handler and test conductor (hydrazine fuels and nitrogen tetroxide), a cryogenics fluid handler and test conductor (LN2, LOX, LH2), and has extensive experience with flight hardware and ground support components. He has written many procedures for building and operating test systems.

His test experience includes:

- Materials Test Facility Buildup
- Hypergol Immersion Testing
- Fluorine and N2F4 Permeation Testing
- Faceshield Fuel Splash Testing
- Adiabatic Compression Testing
- Oxidizer Impact Testing
- Hydrazine Thermal Runaway Testing
- Cadmium Battery Testing
- High Pressure Hydraulic Oil Immersion Testing
- JP-4 Pool Fire
- JP-5 Pool Fire
- Vapor-phase MMH Detonation Testing
- Liquid-phase Hydrazine Detonation Testing
- Cryogenic Hydrogen/Oxygen Detonation Testing
- Tractor Rocket Motor Testing
- Space Shuttle Main Engine LOX Bearing Testing
- GOX and LOX Frictional Testing
- Coefficient of Frictional Heating
- Lockheed Environmental Laboratory Buildup (Las Vegas, NV)
- High Pressure Oxygen Test Facility Buildup
- Hydrogen Igniter Test Buildup
- Helium Tube Bank Buildup
- USAF Oxygen Service Carts Refurbishment
- Space Station Manifold Decon
- Composite Overwrap Pressure Vessel Program
- GN2 Proof of Nitrogen Tank Assembly
- Space Station Oxygen Recharge Compressor Assembly (ORCA) Qual Testing
- Manifold 5 Isolation Valve Propellant Exposure Tests

Kurt Rathgeber has a BS in Physics from UCLA and an MBA from New Mexico State University. He started working at the NASA White Sands Test Facility (WSTF) in December 1989. His test experience includes:

- Liquid-phase detonation studies of hydrazine, MMH, and nitromethane
- Vapor-phase detonation studies of hydrazine/diluents, MMH/air, and MON3/hydrogen
- Pulsed detonation engine concept utilizing hydrogen/oxygen and hydrogen/air
- Mechanical impact testing and rotary friction testing of LOX/metal powder mixtures
- Adiabatic compression testing of hydrazine and hydrogen peroxide
- Water hammer surge pressure tests on shuttle APU system components
- Water hammer surge pressure tests on ISS ammonia heat exchanger
- Pyrovalve testing with MMH and MON3

In addition to designing, building, and testing hypergol systems, Kurt has written hazards analysis procedures for the hydrazine fuels and nitrogen tetroxide.

Steve Hornung has a BS in Chemistry from the University of Kansas and a Ph.D. in Physical Chemistry from the University of New Mexico. He started working at the NASA White Sands Test Facility in March, 1989. His test experience includes:

- Development and validation of NTS 6001, Test 15 for hydrazine, methylhydrazine, ammonia, and nitrogen tetroxide
- Minimum ignition energy studies of hydrazine, methylhydrazine, unsymmetrical dimethylhydrazine, and ethanol
- Materials compatibility with hydrazine and hydrogen peroxide by isothermal microcalorimetry
- Development of a UV / vacuum UV space simulation system
- ESCA / Auger surface analysis of Mir solar array materials, Optical Properties Monitor (OPM) and Alpha Magnetic Spectrometer (AMS) flight experiments
- Stability and thermal studies of HAN-TEAN formulations
- Development of aqueous and alternative solvent methods for cleanliness verification
- Testing of polymers for high temperature oxygen fuel cell applications
- Development of ppb level detection systems for hydrazines

In addition to the experience above, Steve has been involved in numerous investigations of materials compatibility and surface chemistry.

David Baker has a BS and MS in Chemistry from Eastern New Mexico University. He started working at the NASA White Sands Test Facility in November 1981 for Lockheed and moved to NASA in July, 1989. His test experience includes:

- Laboratory scale development of molecular sieve system for the removal of iron nitrate in NTO
- Analytical method development for hypergol propellants
- Corrosion studies of selected metals in NTO
- STS-9 Hydrazine Fire Investigation
- Liquid-phase detonation studies of hydrazine, MMH, and nitromethane
- Vapor-phase detonation studies of hydrazine/diluents, MMH/air, hydrogen/air, ammonia/air, and nitrogen fluoride
- APU hot restart testing
- Water hammer surge pressure tests on shuttle APU system components
- OV-105 R1A Thruster Fire Mishap Investigation
- Passivation of  $\text{OF}_2$  and  $\text{N}_2\text{F}_4$  storage containers using fluorine gas,
- Development of Accelerating Rate Calorimetry for Hydrazine/Material Compatibility
- Development and operation of the APU component test bed
- Shuttle hydrazine fuel tank fleetleader project
- Co-author manuals on the fire, explosion, compatibility, and safety of hypergol propellants
- Compton Gamma Ray Observatory (GRO) Reboost Failure Investigation
- Managed projects involving the characterization of new experimental propellant such as amine azides and hydrogen peroxide
- WSTF Project Manager and Operation Director for the nontoxic dual-thrust RCS engine testing
- WSTF Project Manager and Operation Director for the International Space Station Propulsion Module Hot Fire Testing
- Failure Investigation of Stennis Space Center 5000 gal Hydrogen Peroxide Propellant Supply System

John Jaramillo has a BS in Advanced Technology Education from New Mexico State University. He started working at the NASA White Sands Test Facility in January 1991. His test experience includes:

- Military and shuttle specification analysis of oxidizers and hydrazine fuels
- N<sub>2</sub>O<sub>4</sub> molecular sieve project for the removal of iron and water in off-spec oxidizer
- Personal protective equipment permeation testing
- Analytical development for the detection of derivative fuels by NPD/GC
- Sonochemistry investigation involving the destruction of hydrazine fuels via ultrasonic sound waves
- Hot surface ignition investigation involving hydrazine fuels
- HAZMAT Team Certified
- Production of hypergolic reaction videos
- Minimum ignition energy studies of hydrazine, methylhydrazine, unsymmetrical dimethylhydrazine, and ethanol
- Design Engineer and Project Lead for the construction of hypergolic laboratories that safely handle hypergolic fluids

In addition to the experience above, John has written several site documents regarding the analysis and safe handling of hypergolic fluids.

## COURSE SYLLABUS

1. Course Overview
  - Instructors
  - Admin Information
  - Course Goals
  - Course Evaluations
  - Disclaimer
2. Introduction/Background
  - Why Are We Here?
  - NASA's Safety Initiative
  - NASA's Safety Policy
  - Why This Course?
  - Problem
  - Solution
  - Course Outline
3. Accidents
  - Examples
  - What Have You Seen in Your Career? (discussion)
  - "Chemistry 1-Oh-No!"
4. Toxicity Hazard
  - Environmental Fates
  - Exposure Limits
  - Symptoms of Exposure
  - First Aid
5. Reactivity Hazard
  - Effect of Fluid on Material
  - Effect of Material on Fluid
  - Factors Affecting Reactivity
  - Common Interactions of NTO
    - Corrosion
    - Flow Decay
    - Softgood Reactivity
  - Common Interactions of Hydrazines
    - Corrosion
    - Catalytic Decomposition
    - Thermal Runaway
    - Softgood Reactivity
6. Fire Hazard
  - Fire Criteria
  - Ignition Sources
  - Fire Fighting
7. Explosion Hazard
  - Thermochemical Processes
  - Deflagration
  - Detonation



8. Hypergol Properties, References & Other Information

9. Design

Siting

Paperwork

Hardware

Material Compatibility

10. Buildup

System Construction Considerations

Paperwork

Mockup

Document Physical System

Disassemble

Clean and Proof

Reassemble

Torque and Tag

Integrity Check System

Leak Check

Flow Check Relief Valves

Paperwork

11. Operation

Before → Pretest

During → Test

After → Post test

12. Personal Protective Equipment (PPE)

PPE Hazard Assessment

Chemical Exposure Protection

Level A

Level B

Level C

Level D

13. Hypergol Detection

Methods of Detection

Examples

Ideal Specifications

14. Course Evaluations

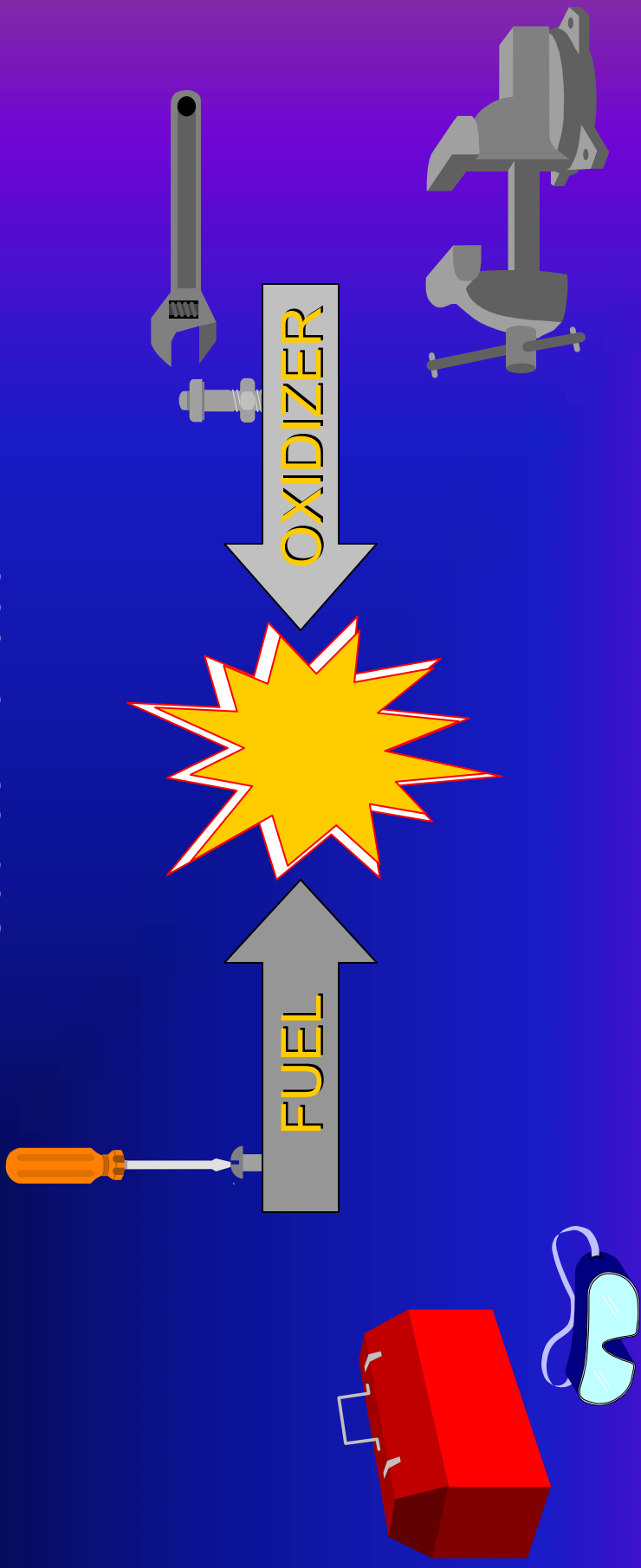
DISCLAIMER

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# Hypergol Systems: Design, Buildup, & Operation

Course No. 055



NASA Safety Training Center

# Safety Note

- ◆ The NASA Safety Initiative states that we ensure safety and health for the following groups, in order of emphasis:
  - The Public
  - Astronauts and Pilots
  - Employees
  - High Value Equipment and Property

# 1.0 Overview

- ◆ Instructors
- ◆ Administrative Information
- ◆ Course Goals
- ◆ Course Evaluations
- ◆ Disclaimer
- ◆ Course Scope

## 1.1 Instructors

- ◆ Bruce Havenor
- ◆ Kurt Rathgeber
- ◆ Steve Hornung
- ◆ John Jaramillo
- ◆ Dave Baker

## 1.2 Administrative Information

- ◆ Attendee Introductions
- ◆ Attendance sheet
  - Social Security Number
  - Privacy Act Statement
  - CEUs available

## 1.2 Administrative Information cont'd

- ◆ Breaks/Bathrooms/Fountains/Vending
- ◆ Emergencies (alarms, sirens, exits, etc.)
- ◆ Environment
- ◆ Questions
- ◆ Course Materials

## 1.3 Course Goals (Instructor)

- ◆ Increase safety awareness
- ◆ Provide useful information and references
- ◆ Enable attendees to identify and evaluate typical hazards of hypergols and hypergol systems



## 1.4 Course Goals (Student)

- ◆ Achieve an understanding of safe practices in design, materials selection, and operation of hypergol systems
- ◆ Become more aware of the safety procedures and features of your own facility/work area
- ◆ Achieve an understanding of how to respond to emergency situations involving hypergols

## 1.5 Course Evaluations

- ◆ The NSTC is strongly committed to providing high-quality training
- ◆ Strong emphasis placed on course evaluations to aid developers in improving course content and delivery
- ◆ ... so please tell us what you think

## 1.6 Disclaimer

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## 2.0 Introduction

Why are we here?

What are the reasons for this training?

If I am through with learning, I am through. - John Wooden

# Terminology



- ◆ Hypergolic
  - The term is used to describe the fuels and oxidizers that ignite spontaneously upon contact with each other without any external initiating energy.
- ◆ Hypergols
  - A general reference to combinations of fuels and oxidizers that are hypergolic.

# Aside



- ◆ Many fuels and oxidizers are hypergolic
  - Hydrazine fuels
  - Nitrogen tetroxide and MONs
  - Chlorine trifluoride and pentafluoride
  - Inhibited red fuming nitric acid (IRFNA)
  - Hydrogen peroxide
  - Others (see the *Hypergolic Combinations* handout in course book)

## 2.1 Scope of This Course

- ◆ The Hydrazine Fuels
  - $N_2H_4$
  - Monomethylhydrazine (MMH)
  - Unsymmetrical Dimethylhydrazine (UDMH)
- ◆ Nitrogen Tetroxide and Variants
  - $N_2O_4$
  - MON1, MON3, etc.

## 2.0 Introduction

- ◆ So why, in particular, a course on hypergol safety?



## 2.1 Safety Certification Requirements

- ◆ NPR 8715.3 Safety Certification Requirements
  - “People who perform or control hazardous operations or use or transport hazardous material must possess the necessary knowledge, skill, judgment, and physical ability (if specified in the job classification) to do the job safely, and be certified to do so (Requirement 25113).”

# Aside

- ◆ Attendance at this course does not constitute certification for handling hypergols.
- ◆ The authority having jurisdiction within your organization stipulates the certification requirements (i.e. training courses, demonstrated proficiency, etc.).

## 2.2 The Problem

- ◆ We are here because these fluids are....

 Toxic

Flammable 

 Corrosive

Explosive 

- Carcinogenic

- UDMH is
- Hydrazine and MMH are suspected
- NTO is not

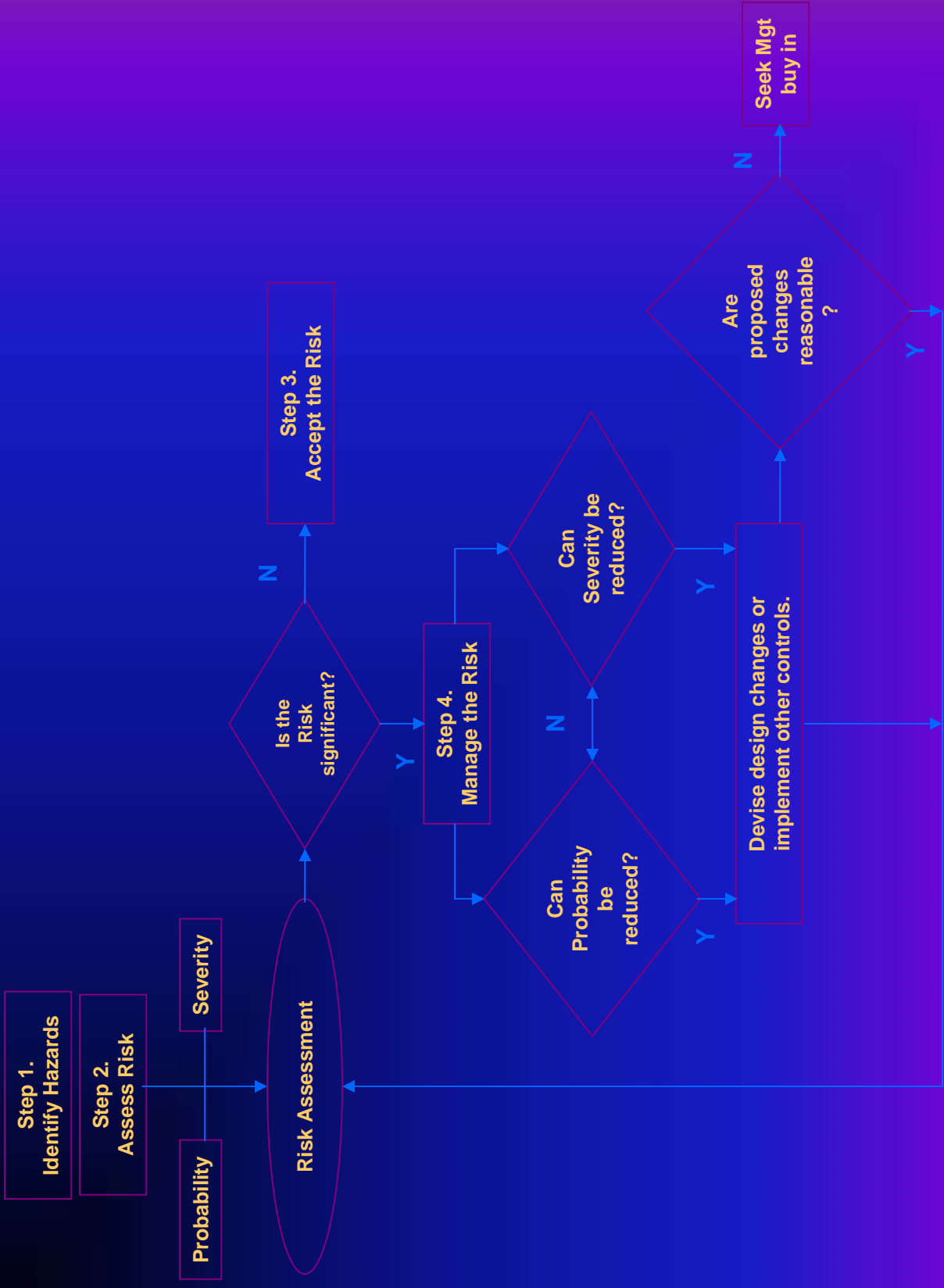
## 2.3 What's the Solution?

1. Identify the hazards
2. Assess the risks
  - probability and severity
3. Accept the risks or . . .
4. Manage the risks by . . .
  - minimizing the probability
  - minimizing the severity

# Terminology



- ◆ Hazard
  - Any condition that could result in
    - injury to people
    - damage to the environment
    - damage to property or equipment, and/or
    - delay or loss of mission or objective
- ◆ Risk
  - A combination of the probability of occurrence and the severity of the consequences of an adverse condition



## Assess Risk

### Probability Ratings

- 0 = Almost impossible
- 1 = Remotely possible
- 2 = Possible
- 3 = Probable
- 4 = Highly probable

### Severity Ratings

- A = Negligible
- B = Marginal
- C = Critical
- D = Disastrous

### Examples:

- Meteor impact
- Car crash
- Paper cut

# Course Outline

- ✓ Introduction
- ◆ Accidents
  - Examples of the “problems”
- ◆ Step 1 - Identify the Hazards
  - Toxicity Hazard
  - Reactivity Hazard
  - Fire Hazard
  - Explosion Hazard
  - Hypergol Properties, References & Other Information
- ◆ Step 4 - Manage the Risks
  - Primary Controls
    - Design
      - Material Compatibility
    - Build Up
    - Operation
  - Secondary Controls
    - PPE
    - Detectors/Monitors
- ◆ Course Evaluations



## 3.0 Accidents

- ◆ One reason we are here for this course - accidents happen. We need to learn from those experiences.

It's what you learn after you know it all that counts.

- John Wooden

- ◆ Your course book has a section on Accidents.

## 3.1 OV-105A Thruster Fire Mishap

- ◆ KSC 1995
- ◆ Removal of thruster from orbiter
- ◆ Isolated, purged, aspirated ... leaked
- ◆ Pressure transducer offset
- ◆ Shift change

## 3.1.1 View of Left Side Thrusters



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## 3.1.2 R1A Thruster with Aspirator

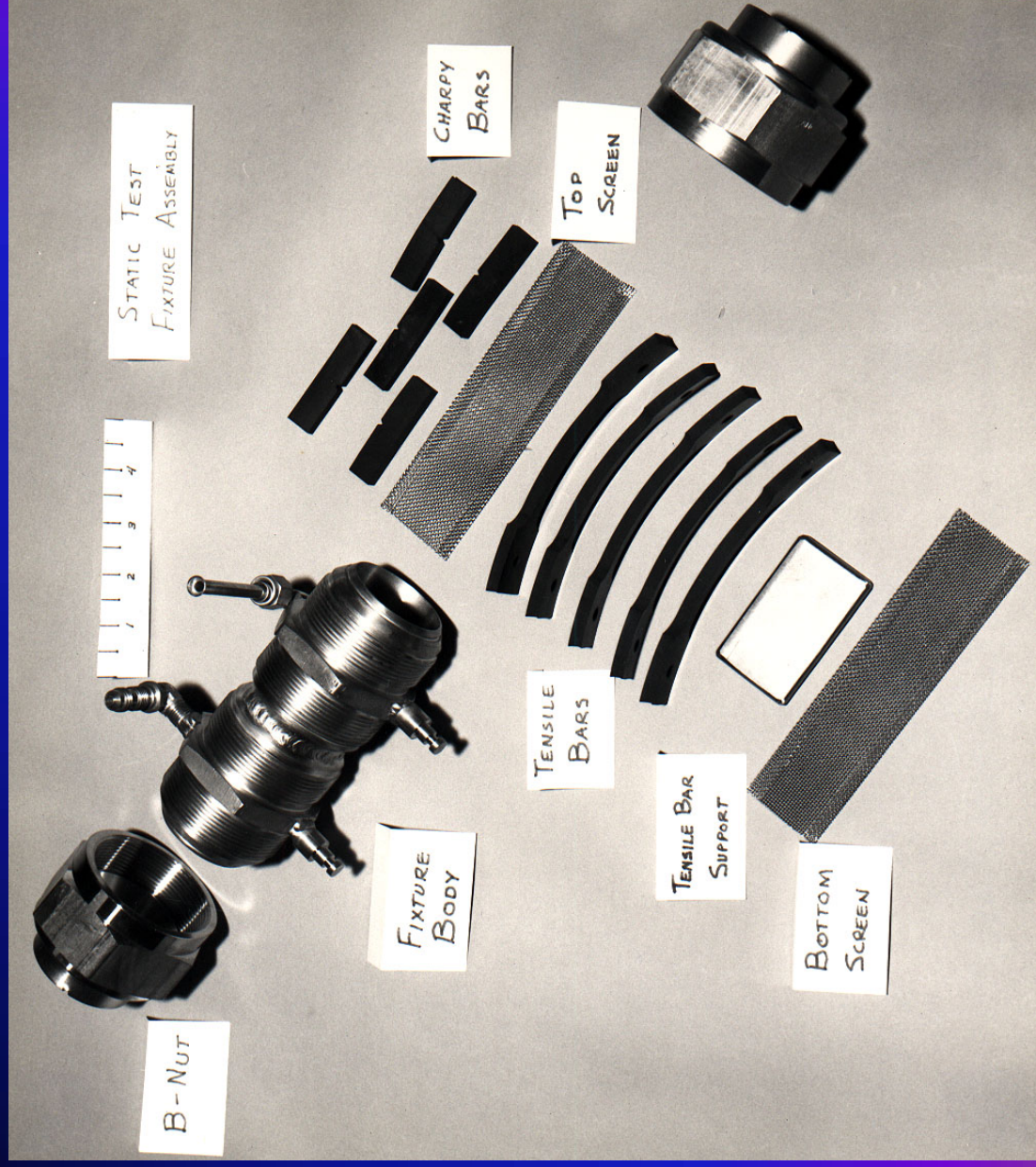


## OV-105 R1A Thruster Fire Mishap

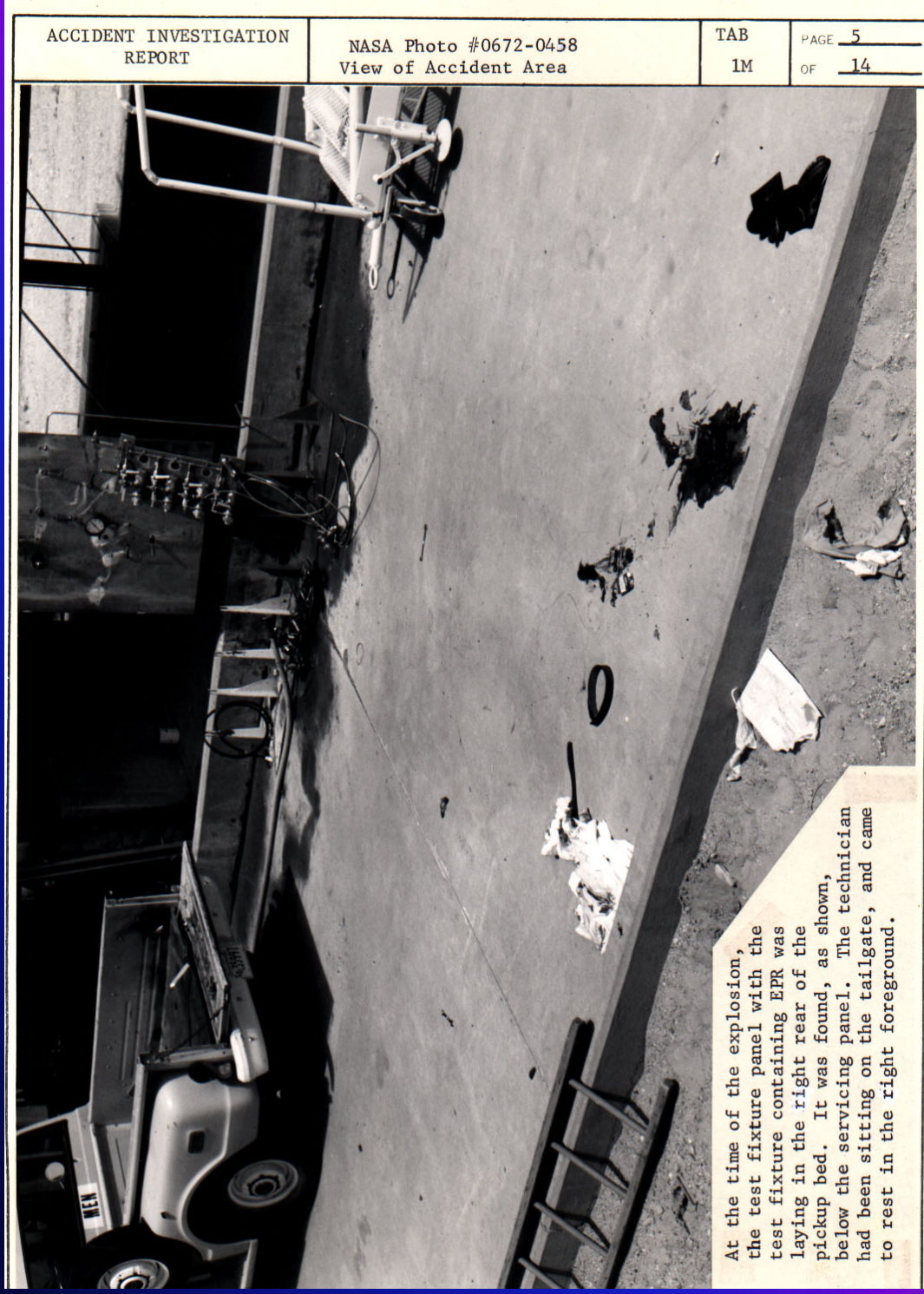
## 3.2 Technician and the B-Nut

- ◆ WSTF 1972
- ◆ Material compatibility test
  - NTO and EPR 50K42
- ◆ Closed test fixture
- ◆ Hands-on operation
- ◆ Test Conductor and one technician

## 3.2.1 Technician and the B-nut



## 3.2.2 Technician and the B-nut



## 3.3 Thermochemical Test Area

- ◆ JSC 1994
- ◆ Altitude test of bi-prop engine
- ◆ Leaking 3-way solenoid valve
  - Half a Teflon o-ring found during investigation
- ◆ Filled liquid vent line to burner
  - First oxidizer release about 0.1 gal.
  - Continued operation despite release
  - Second oxidizer release about 16 gal.





## 3.3.2 Contributing Causes Identified

- ◆ Lack of formal System Safety Process to identify and control hazards
- ◆ Insufficient controls in a system that contained single-point failures
- ◆ Failure of test personnel to recognize anomalous system performance and to take appropriate action
- ◆ Failure to apprise JSC Management of risks inherent to the preparation and conduct of this engine firing test

## 3.4 Accidents

- ◆ What have you seen or experienced?

# Summary

- ◆ OV 105: fire hazard
- ◆ JSC TTA: toxicity hazard
- ◆ WSTF B-nut: reactivity → explosion hazard

Greater awareness about the hazards of hypergols and the associated risks may have prevented these accidents or minimized the adverse effects.

# Course Outline

- ✓ Introduction
- ✓ Accidents
  - ✓ Examples of the “problems”
- ◆ Step 1 - Identify the Hazards
  - Toxicity Hazard
  - Reactivity Hazard
  - Fire Hazard
  - Explosion Hazard
  - Hypergol Properties, References & Other Information
- ◆ Step 4 - Manage the Risks
  - Primary Controls
    - Design
      - Material Compatibility
    - Build Up
    - Operation
  - Secondary Controls
    - PPE
    - Detectors/Monitors
- ◆ Course Evaluations

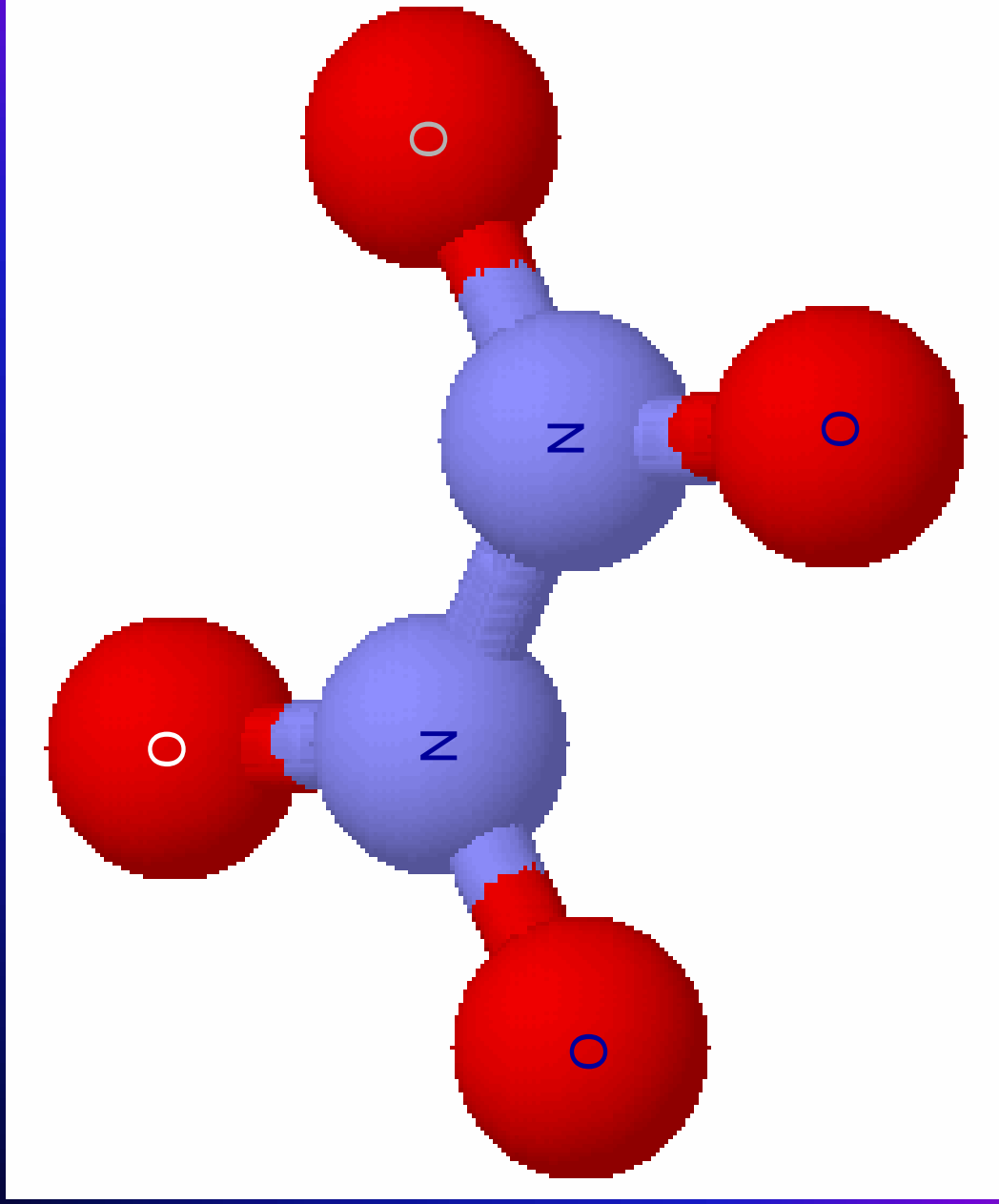
# Notes on Nitrogen Tetroxide

OR

“Chemistry 1-Oh-No!”

- ◆ Referred to as **NTO**
- ◆ **NTO** is an equilibrium mixture of  $\text{N}_2\text{O}_4$  and **nitrogen dioxide ( $\text{NO}_2$ )**
  - Dissociation of  $\text{N}_2\text{O}_4$  into  $\text{NO}_2$  varies with temperature
  - Boils at room temperature
  - The reddish-brown color comes from the amount of  **$\text{NO}_2$**  present

# Chemistry of Nitrogen Tetroxide ( $N_2O_4$ )



# Notes on MON

- ◆ Mixed oxides of nitrogen (MON X) specifies a mixture of propellant grade NTO and X percent by weight nitric oxide (NO)
- Added as an oxygen scavenger / corrosion inhibitor



- NO content makes the fluid appear green
- The vapor is still reddish-brown



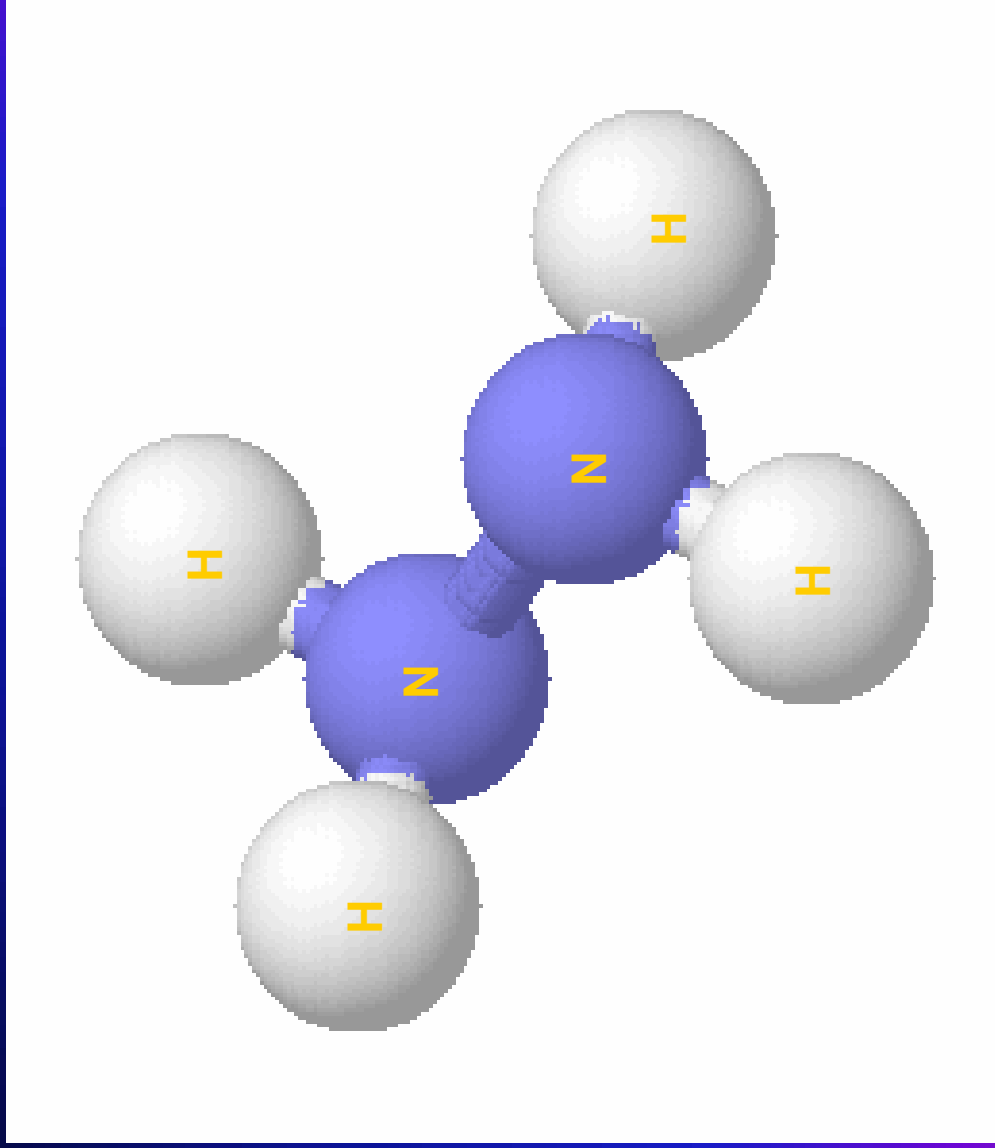
# Physical and Chemical Properties of MON X

GRADE	NTO	MON-1	MON-3	MON-10	MON-15	MON-25
Molecular Weight (N <sub>2</sub> O <sub>4</sub> )	92.01	92.01	92.01	92.01	92.01	92.01
Relative Vapor Density	1.58	1.58	1.58	1.58	1.58	1.58
Color	Brown	Green	Green	Green	Green	Green
NO, %	0	1	3	10	15	25
N <sub>2</sub> O <sub>4</sub> + NO, %	99.5	99.5	99.5	99.5	99.5	99.5
Boiling, F	70	68	65	49	39	16
Freezing, F	12	9	5	-10	-24	-69
Vapor @77F, psia	17.5	18.5	20.5	30.0	40.5	76.0
Sp. Gravity @ 77F	1.431	1.429	1.423	1.407	1.397	1.380

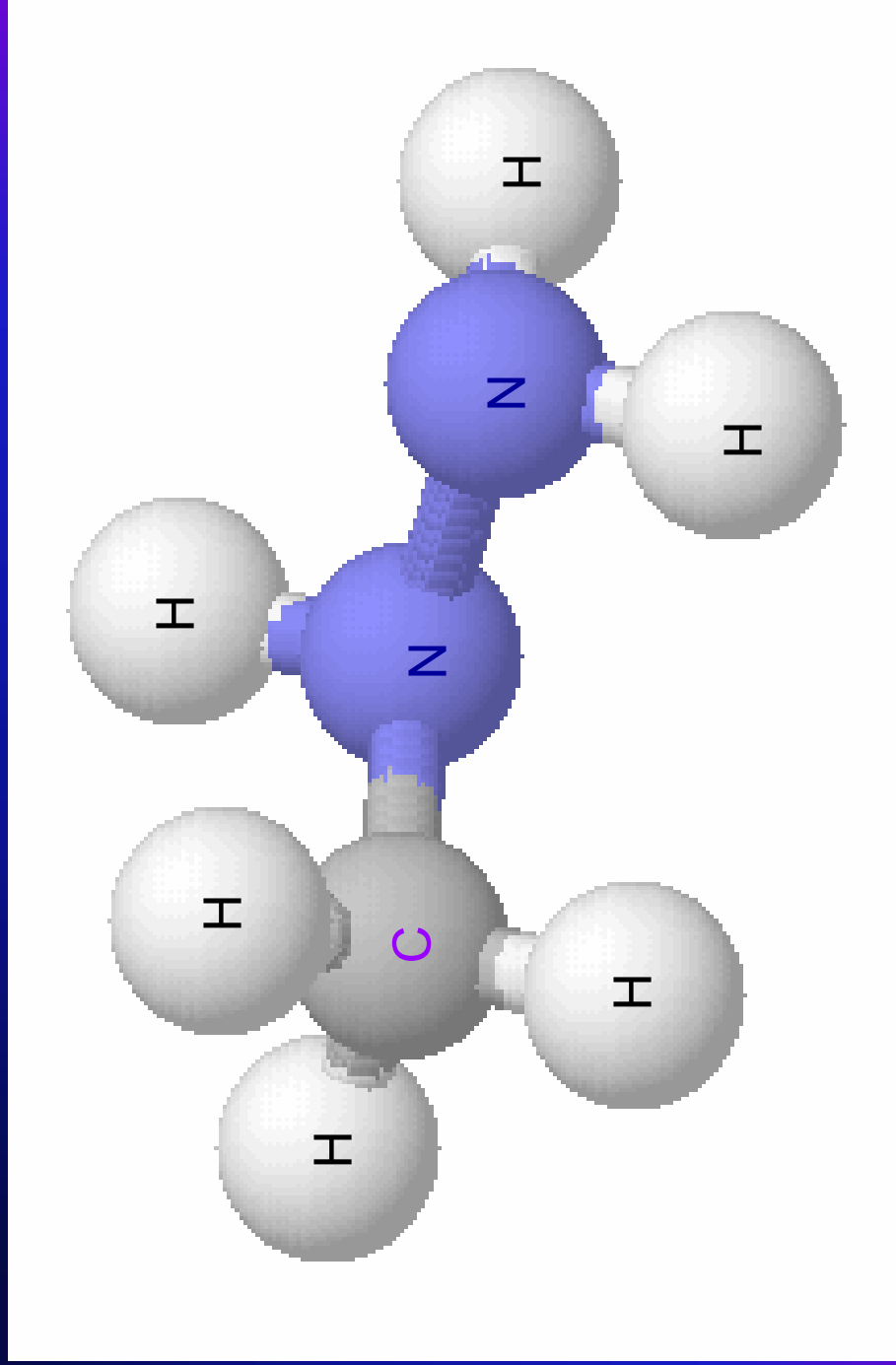
# Hydrazine Fuels Usage

- ◆ Aerospace
  - APUs (shuttle, aircraft, ... )
  - Thrusters (OMS, RCS, satellites, ... )
  - Engines (Titan IV, Delta, ... )
- ◆ Agriculture
- ◆ Boiler systems
- ◆ Pharmaceuticals

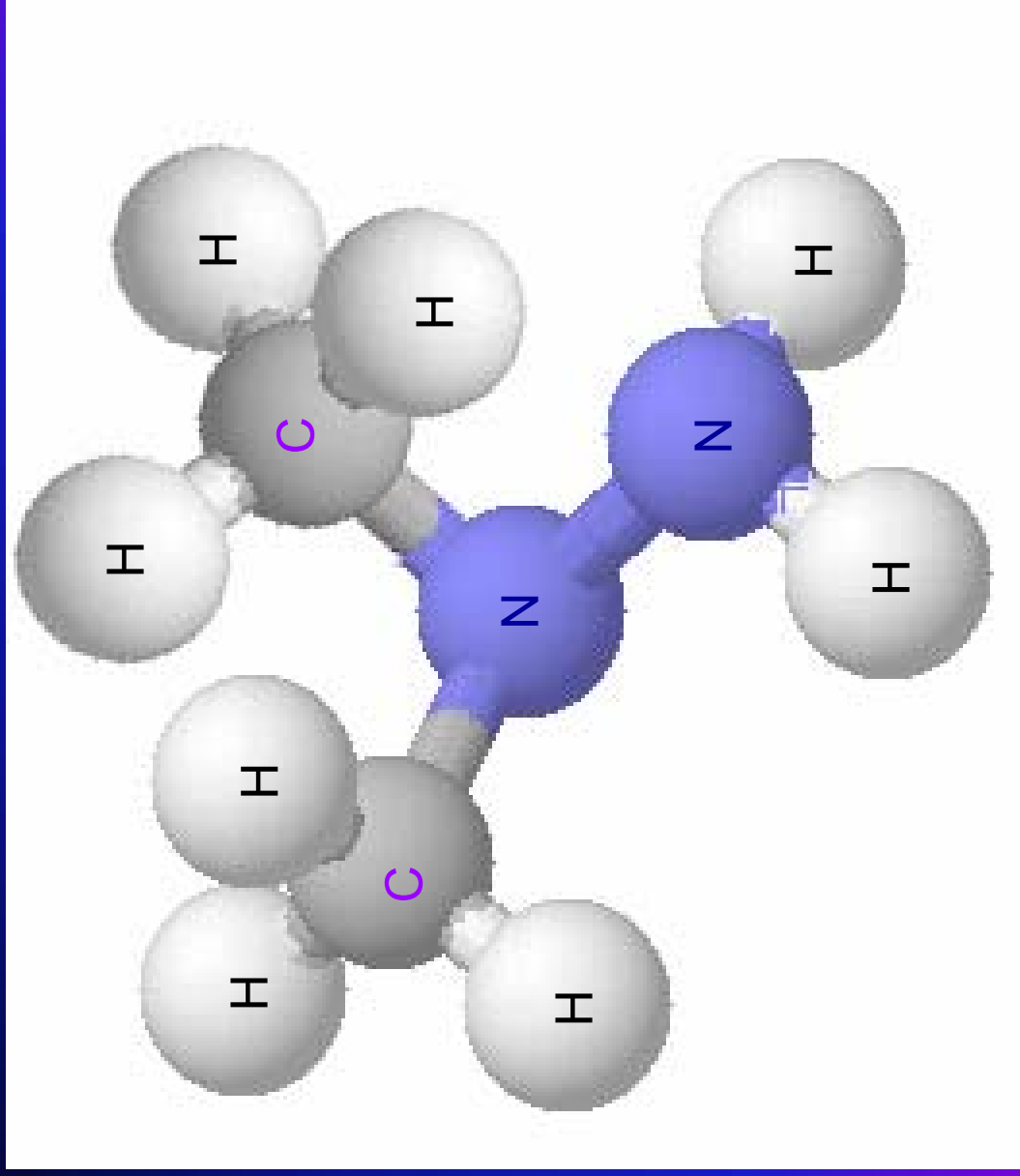
# Chemistry of Hydrazine ( $\text{N}_2\text{H}_4$ )



# Chemistry of MMH ( $\text{N}_2\text{H}_3(\text{CH}_3)$ )



# Chemistry of UDMH ( $\text{N}_2\text{H}_2(\text{CH}_3)_2$ )



# Summary

- ◆ Nitrogen Tetroxide
  - Non-polar
  - Not soluble in water
  - Reacts with water to form nitric and nitrous acids
- ◆ Hydrazine and MMH
  - Polar
  - Soluble in water

# Reminder



- ◆ A **hazard** is defined as any event that creates a condition that could result in injury to people, damage to the environment, damage to property or equipment, and/or delay or loss of mission or objective.

# Step 1 - Identifying the Hazards

- ☠ Toxicity
- ◆ Reactivity
- ◆ Fire
- ◆ Explosion

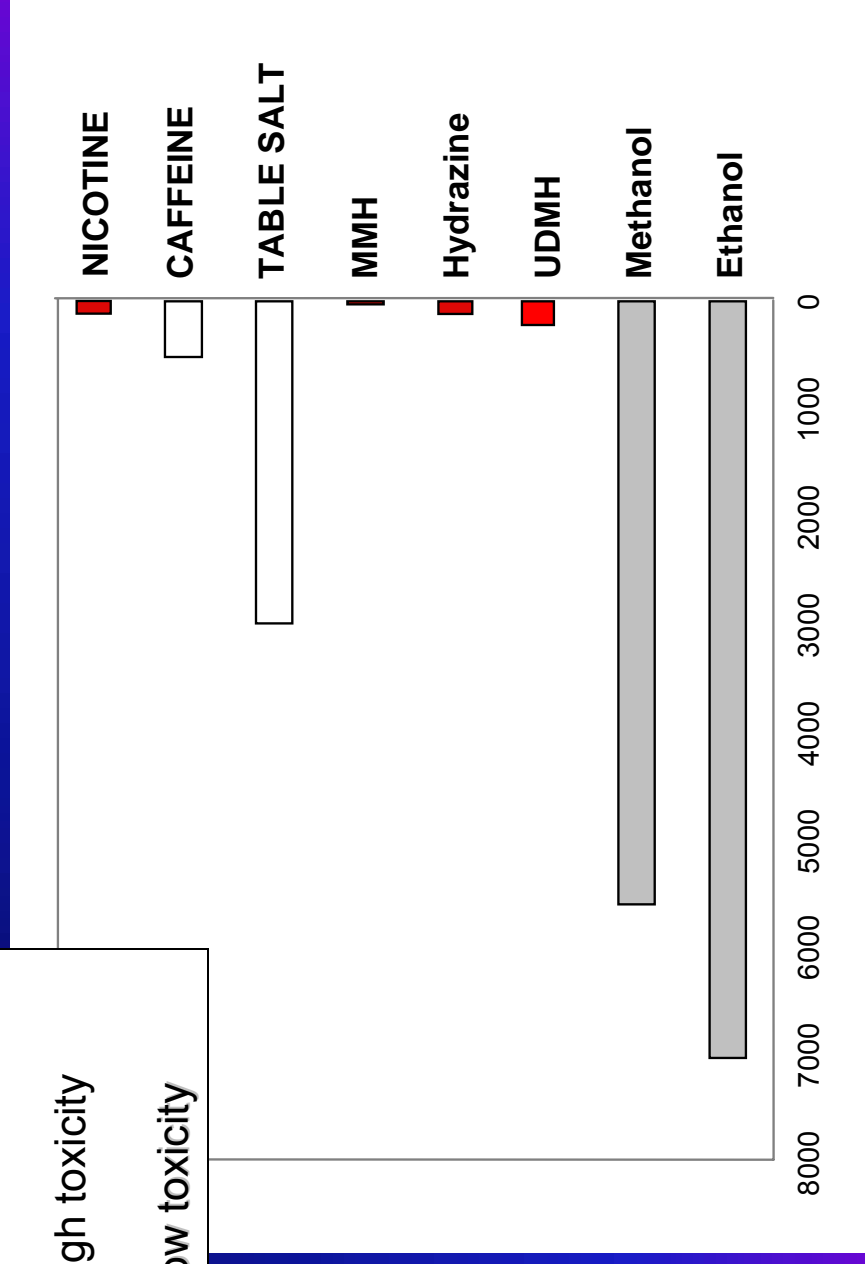


## 4.0 Toxicity Hazard

- ◆ Toxicity can be defined as “ ... the ability of a chemical to cause injury once it reaches a susceptible site in or on the body” (Sax 1984)
- ◆ All of the **hydrazine** fuels and **NTO** and its variants are toxic to humans and harmful to the environment
- ◆ The health hazards associated with **MON** are the same as those for **NTO** (CPIA 1984)

# Oral LD<sub>50</sub> (mg/kg) - Rats

- Moderate toxicity
- High toxicity
- Low toxicity



## 4.1.1 Environmental Hazard -

### Hydrazines

- ◆ Hydrazine fuels released in the environment are considered pollutants
- ◆ May contaminate air, water, and/or soil
- ◆ Toxic to plant and animal life
- ◆ MMH and UDMH decompose to known carcinogens (NDMAs)

## 4.1.2 Environmental Hazard - NTO/MON

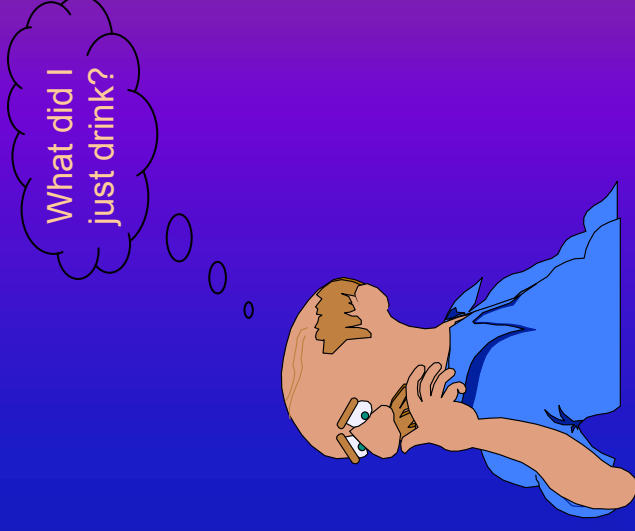
- ◆ Spilled NTO can lead to vapor concentrations of NTO, NO<sub>2</sub>, or nitric oxide (NO) in air that exceed safe limits
  - NO<sub>x</sub> compounds cause the reddish brown haze in smog
  - NO<sub>2</sub> forms nitric and nitrous acids (HNO<sub>3</sub> and HNO<sub>2</sub>) upon contact with water in the air, in the soil, or in you
- ◆ Nitric acid mists may form causing soil and water pollution

## 4.2 Toxicity Hazard

- ◆ To evaluate human toxicity must assess the following:
  - Routes of entry into the body
  - Duration of exposure
  - Concentration of exposure

## 4.2.1 Routes of Entry into the Body

- ◆ **Inhalation**
  - lungs
  - mucous membranes
- ◆ **Ingestion**
  - gastrointestinal tract
  - mucous membranes
- ◆ **Absorption**
  - skin
  - eyes



# NTO Skin Contact from Glove Permeation



## 4.2.2 Duration of Exposure

- ◆ We all know high level exposures to fuels and oxidizers are bad (acute exposure)
- ◆ Be aware long-term low level exposure is also bad (chronic exposure)



## 4.2.3 Exposure Limits

	N2H4	MMH	UDMH	N2O4
OSHA PEL				
TWA	1.0 PPM	-	0.5 PPM	-
CEILING	-	0.2 PPM	-	5 PPM
STEL	-	-	-	-
NIOSH REL				
TWA	-	-	-	-
CEILING (120 min TWA)	0.03 PPM	0.04 PPM	0.06 PPM	1 PPM
IDLH	50 PPM	20 PPM	15 PPM	20 PPM
ACGIH TLV				
TWA	0.01 PPM	0.01 PPM	0.01 PPM	3 PPM
CEILING	-	-	-	-
STEL	-	-	-	5 PPM
Odor Threshold	2 – 3 PPM	1 – 3 PPM	4 – 8 PPM	1 – 3 PPM for most, as low as 0.11 PPM for some

NIOSH - National Institute for Occupational Safety and Health  
 ACGIH - American Conference of Governmental Industrial Hygienists  
 PEL - Permissible Exposure Limit  
 TWA - Time Weighted Average  
 STEL - Short Term Exposure Limit  
 REL - Recommended Exposure Limit  
 IDLH - Immediately Dangerous to Life and Health  
 TLV - Threshold Limit Value  
 PPM - Parts Per Million

See the [Properties & Other table](#) in course book

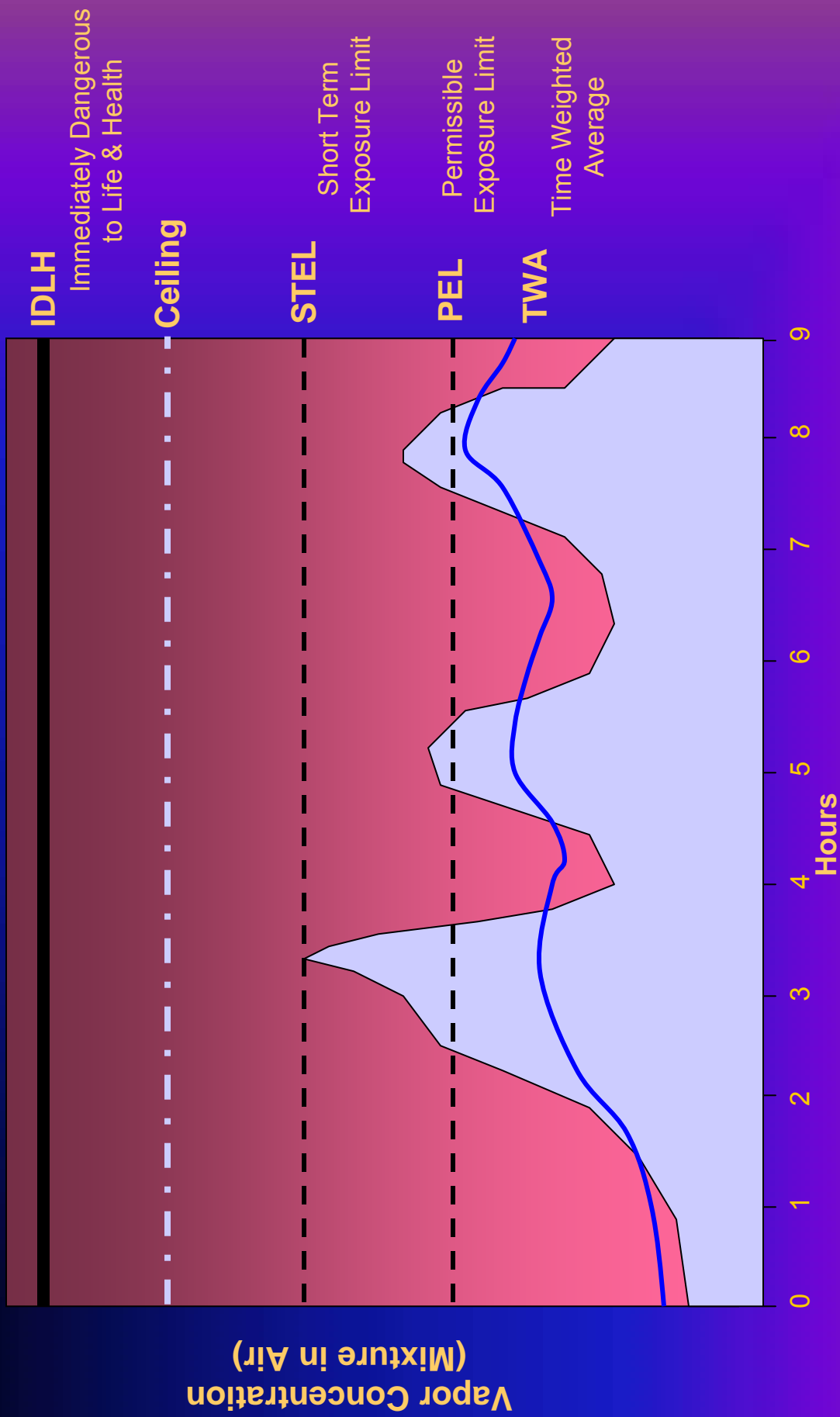
## 4.2.3 Exposure Limits

- ◆ OSHA PEL
  - Force of law
- ◆ NASA adheres to more stringent guideline
  - **Fuels:** ACGIH TLV-TWA
  - **Oxidizer:** NIOSH REL
- ◆ See the *Properties & Other* table in course book.

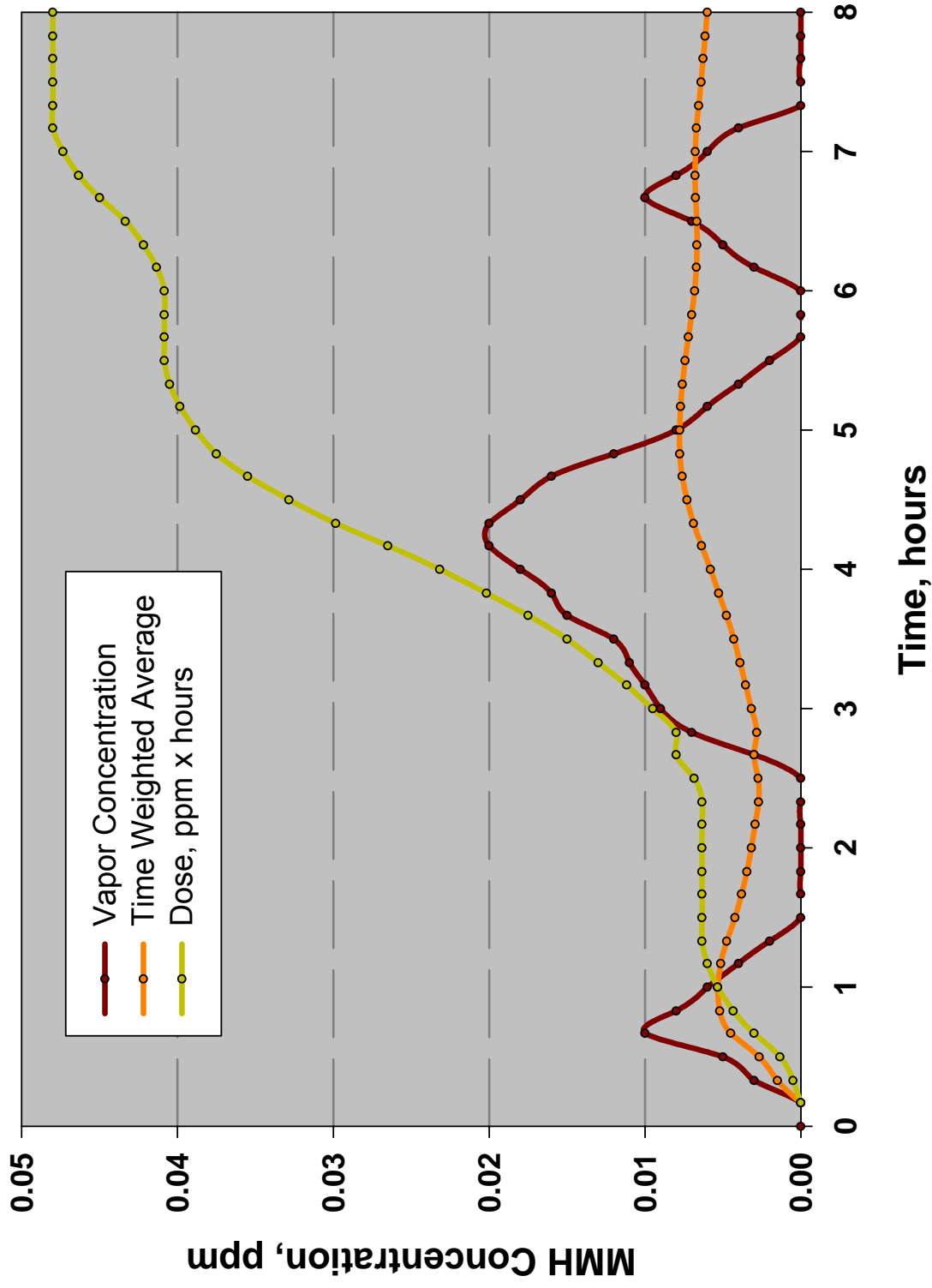
# Visible Concentrations of NO<sub>2</sub>



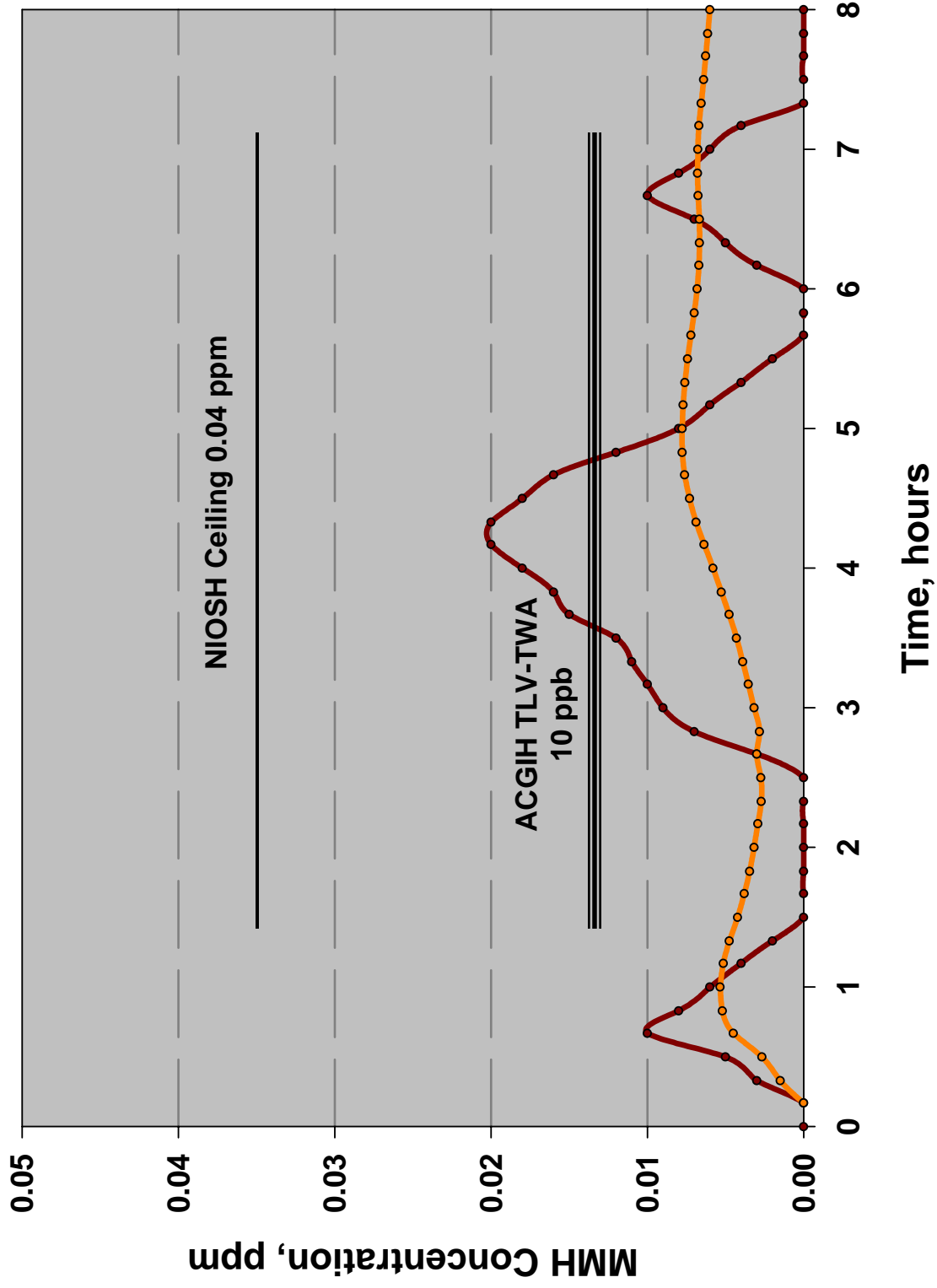
# 4.2.4 What Do the Acronyms Mean?



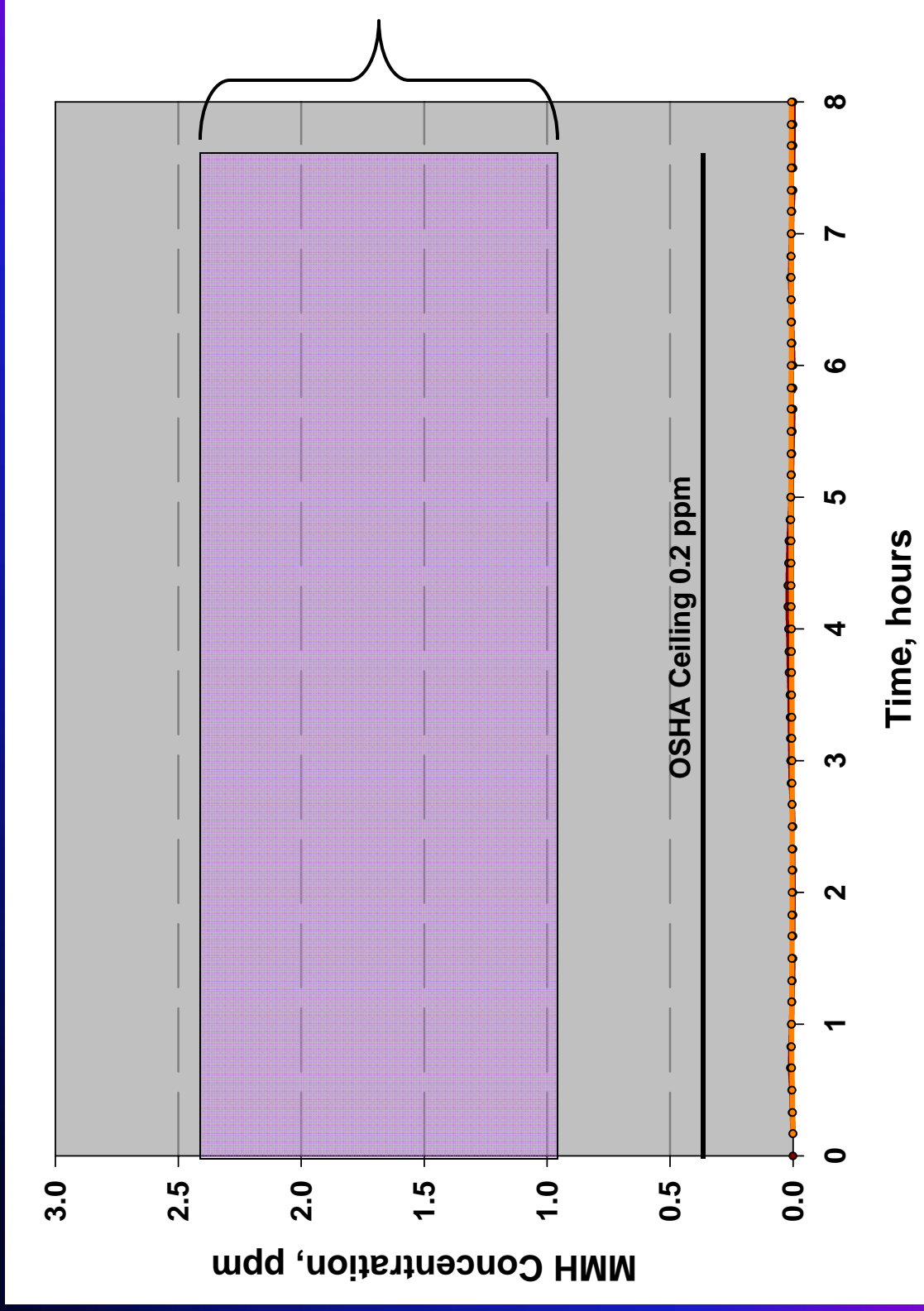
## 4.2.4.1 MMH - Time Weighted Average



## 4.2.4.2 MMH - Time Weighted Average & Limits



## 4.2.4.3 MMH OSHA Limit & Odor Threshold



## 4.2.5 General Symptoms of Hypergol Exposure

- ◆ Throat and nose irritation
- ◆ Eye irritation, burning
- ◆ Breathing difficulties, bronchitis
- ◆ Skin burns
- ◆ Dizziness
- ◆ Nausea and vomiting
- ◆ Headache
- ◆ Fever and chills
- ◆ Tremors, convulsions
- ◆ Abdominal pain



## 4.2.5 General Conditions Arising From Exposure - Hydrazine Fuels

- ◆ Corneal damage
- ◆ Methemoglobinemia
- ◆ Cyanosis
- ◆ Dermatitis
- ◆ Pulmonary edema
- ◆ Kidney damage
- ◆ Liver damage
- ◆ Hemolysis
- ◆ Central nervous system depression
- ◆ Hematuria
- ◆ Heinz bodies in red blood cells
- ◆ Reproductive effects in lab animals

## 4.2.5 General Conditions Arising From Exposure - NTO

- ◆ Dyspnea
- ◆ Corneal damage
- ◆ Methemoglobinemia
- ◆ Cyanosis
- ◆ Tachycardia
- ◆ Arterial dilation
- ☠ Pulmonary edema

## 4.2.6 First Aid



- ◆ **Inhalation**
  - Remove victim to fresh air
    - Rescuers in proper PPE
  - If not breathing, perform artificial respiration
  - Seek medical attention
  - Report all exposures to supervision

## 4.2.6 First Aid



- ◆ **Hydrazine** Ingestion
  - Have victim drink large amounts of water
    - Do not use milk as a diluent
  - Induce vomiting with finger down throat
    - Do not use ipecac to induce vomiting
  - Seek medical attention
  - Report all exposures to supervision

## 4.2.6 First Aid



- ◆ **NTO Ingestion**
  - Have victim drink large amounts of water.
    - Use milk if available.
  - **DO NOT** induce vomiting.
  - Seek medical attention.
  - Report all exposures to supervision.

## 4.2.6 First Aid



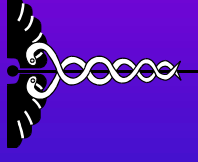
- ◆ Skin Splash
  - Move the victim from the contaminated area
    - Rescuers in proper PPE
  - Remove victim's contaminated clothing and treat as hazardous waste
  - Flush affected area(s) with water for 15-20 mins.
  - Seek medical attention
  - Report all exposures to supervision

## 4.2.6 First Aid



- ◆ **Eye Splash**
  - Move the victim from the contaminated area
    - Rescuers in proper PPE
  - Flush eyes with large amounts of water for 15-20 mins.
    - Occasionally lift upper and lower eyelids
  - Seek medical attention
  - Report all exposures to supervision

## 4.3 Medical Attention



- ◆ Back, K. C., V. L. Carter, and A. A. Thomas. “*Occupational Hazards of Missile Operations with Special Regard to the Hydrazine Propellants.*” Aviation, Space, and Environmental Medicine, April 1978, pp. 591-598.
- ◆ Hall, A. H. and B. H. Rumack (editors). TOMES® Information System. Micromedex, Inc. Englewood, CO (1996). URL: <http://www.tomescps.com>. Contact information can be obtained at (800) 525-9083.
- ◆ Occupational Health Services, Inc. Hazardline. New York, New York: Occupational Health Services, Inc., 1987.
- ◆ Arch Chemicals, Inc. Emergency Line (800) 654-6911.
  - MDs and toxicologists available 24/7
- ◆ Mississippi Chemical N<sub>2</sub>O<sub>4</sub> MSDS



# Course Outline

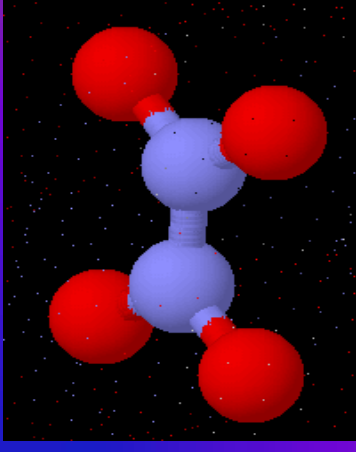
- ✓ Introduction
- ✓ Accidents
  - ✓ Examples of the “problems”
- ◆ Step 1 - Identify the Hazards
  - ✓ Toxicity Hazard
  - Reactivity Hazard
  - Fire Hazard
  - Explosion Hazard
  - Hypergol Properties, References & Other Information
- ◆ Step 4 - Manage the Risks
  - Primary Controls
    - Design
      - Material Compatibility
    - Build Up
    - Operation
  - Secondary Controls
    - PPE
    - Detectors/Monitors
- ◆ Course Evaluations

# Step 1 - Identifying the Hazards

-  Toxicity
-  Reactivity
- ◆ Fire
- ◆ Explosion

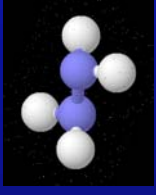
# Physical Properties of NTO

- ◆ Boiling Point 70.1 °F (21.2 °C)
- ◆ Melting Point 11.8 °F (-11.2 °C)
- ◆ Liquid Density 1.43 g/cm<sup>3</sup>
- ◆ Vapor Pressure 17.4 psia



# Physical Properties of Hydrazines

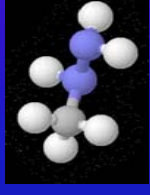
Hydrazine



- ◆ Boiling Point 237 °F (113 °C)
- ◆ Melting Point 34.7 °F (1.5 °C)
- ◆ Liquid Density 1.004 g/cm<sup>3</sup>
- ◆ Vapor Pressure 0.96 psia

(Sea level & 77 °F)

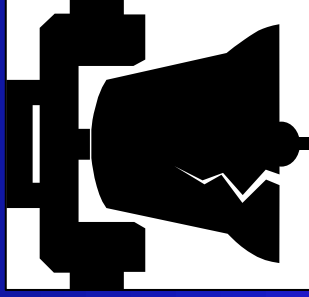
MMH



- ◆ Boiling Point 189 °F (87.2 °C)
- ◆ Melting Point -62.3 °F (-52 °C)
- ◆ Liquid Density 0.87 g/cm<sup>3</sup>
- ◆ Vapor Pressure 3.23 psia

# What are the Hazards?

- ◆ Both react with many metallic and non-metallic materials



Loss of function

**Heat**

**Pressure**



## 5.0 Material Reactivity Hazard

- ◆ The **hydrazines** are strong reducing agents
  - Household example: silver cleaner
- ◆ **NTO** and **MON** are strong oxidizing agents
  - Household examples: bleach, hydrogen peroxide (3%)
- ◆ Both react with many metallic and non-metallic materials

## 5.1 The Hazard Arises Two Ways

- ◆ Material degradation
  - The effect of the fluid on the material
- ◆ Fluid composition change
  - The effect of the material on the fluid

## 5.1 Fluid Properties Possibly Affected by Fluid/Material Interactions

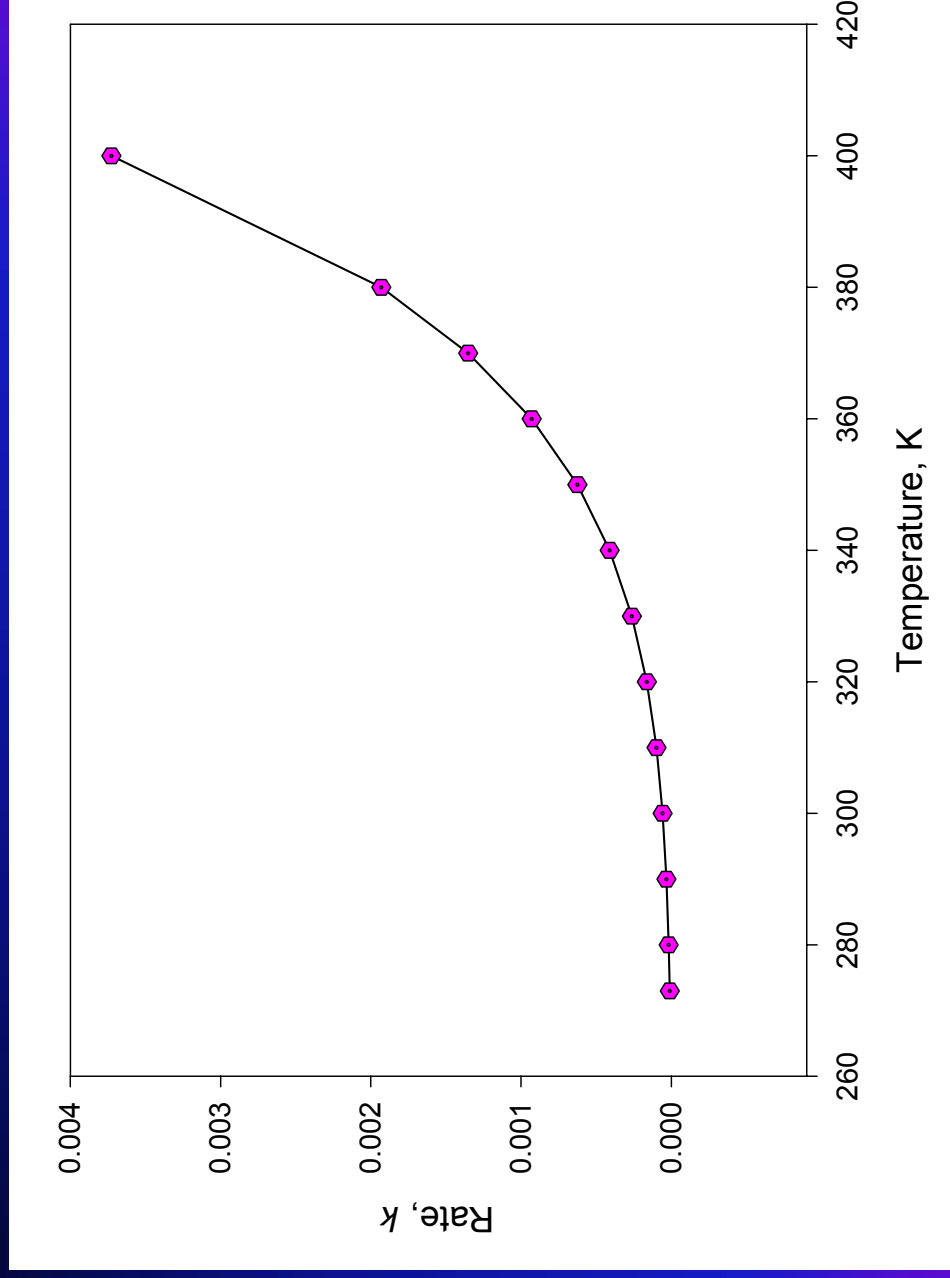
- ◆ Purity or Assay
  - Surface Catalyzed Hydrazine decomposition
- ◆ Non-volatile Residue (NVR) / Particulate Formation
  - Metals
    - Dissolved metals - Iron nitrate or flow decay material
    - Particulate
  - Softgoods
    - Dissolved species
    - Particulate



## 5.2 Factors Affecting Reactivity

- ◆ Duration of exposure
- ◆ Surface area contacted
- ◆ Phase(s) of fluid present
- ◆ Temperature
- ◆ Surface condition
  - oxide layer, coatings, contaminants, surface finish

## 5.2.1 Effect of Temperature on a Reaction Rate



## 5.3 Material Properties Possibly Affected by Fluid/Material Interactions

- ◆ Softgoods
  - Tensile, Compressive Strength
  - Hardness
  - Mass (weight)
  - Visual Appearance
  - Solubility
  - Embrittlement
  - Tackiness
  - Permeability
  - Instability / Impact Sensitivity
- ◆ Metals / Alloys
  - Corrosion
    - Generalized
    - Pitting or Localized
    - Stress Corrosion Cracking

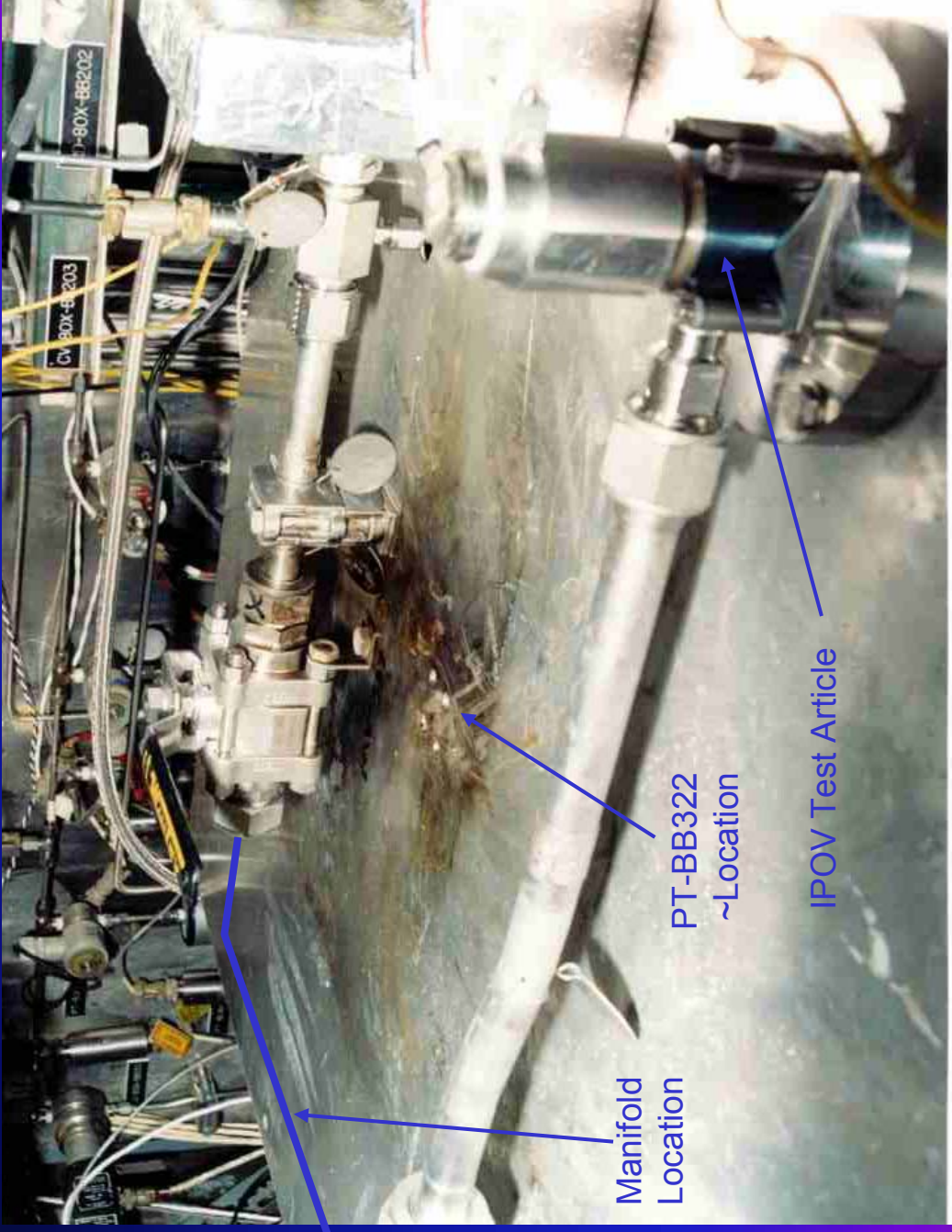
### 5.3.1 Nitration / Instability

- ◆ WSTF Chemistry Lab 2002
  - Oxidizer fume hood
- ◆ Demonstration of improper / Incompatible PPE
  - Effect of MON3 on Latex glove
  - Show material degradation after exposure
- ◆ Don't try this at home.
- ◆ Further testing showed nitration of latex

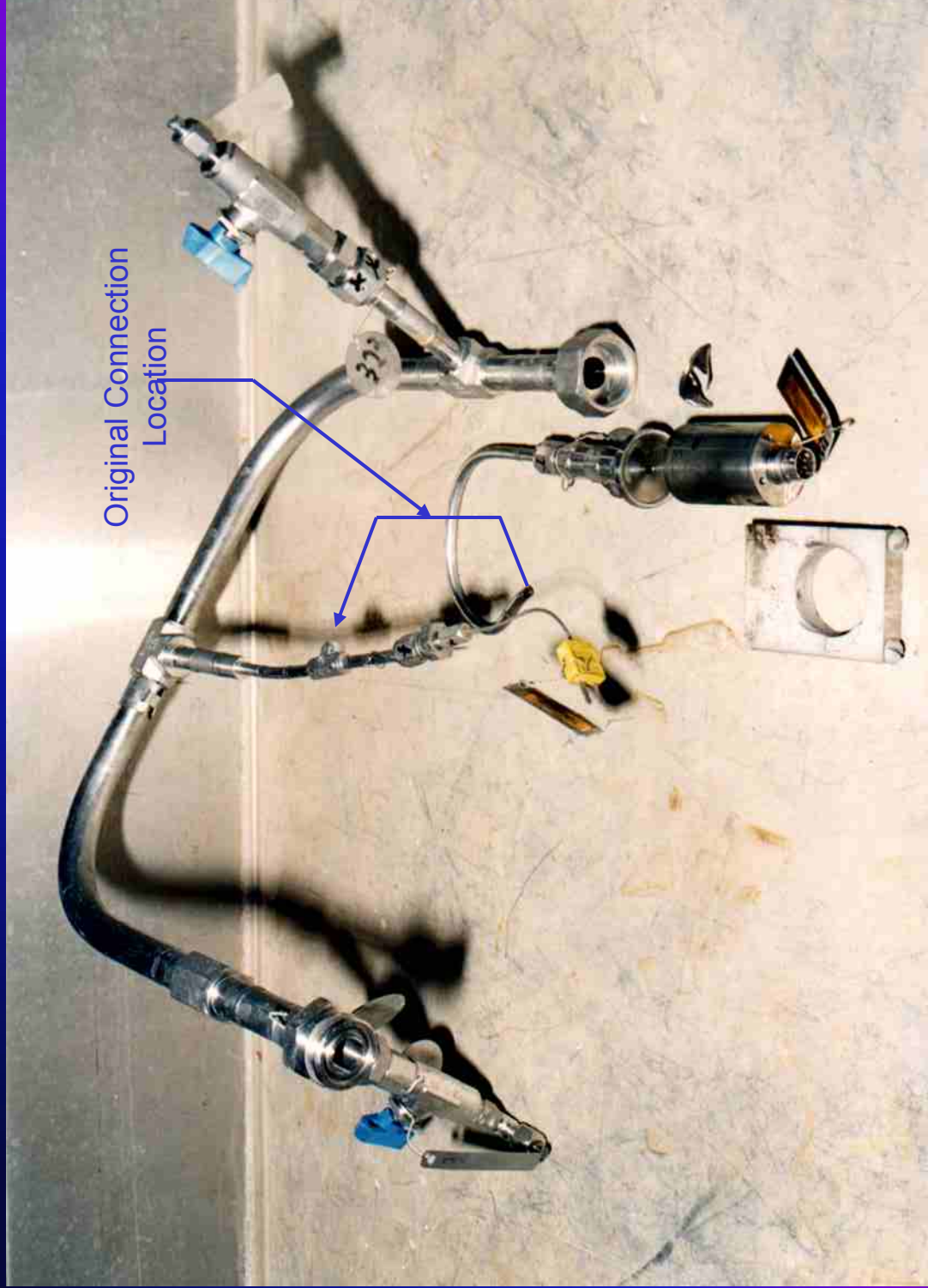
## 5.3.2 Druck Pressure Transducer Failure

- ◆ Improved Pilot Operated Valve (IPOV) life cycle test with **MON3**
  - Nominal Inlet Pressure: 276 psia
  - Valve opened & closed in 80 ms cycles
  - ~ 36,000 cycles were completed (80,000 planned)
- ◆ System inlet pressure transducer failed
- ◆ Loud pop heard in HFPA Control Room
- ◆ Oxidizer was released inside test cell then flowed outside
- ◆ Test Cell was secured and shut down
- ◆ Air Handlers were shutdown
- ◆ No injuries

# Test Cell 831 Manifold Location



# Manifold & Pressure Transducer

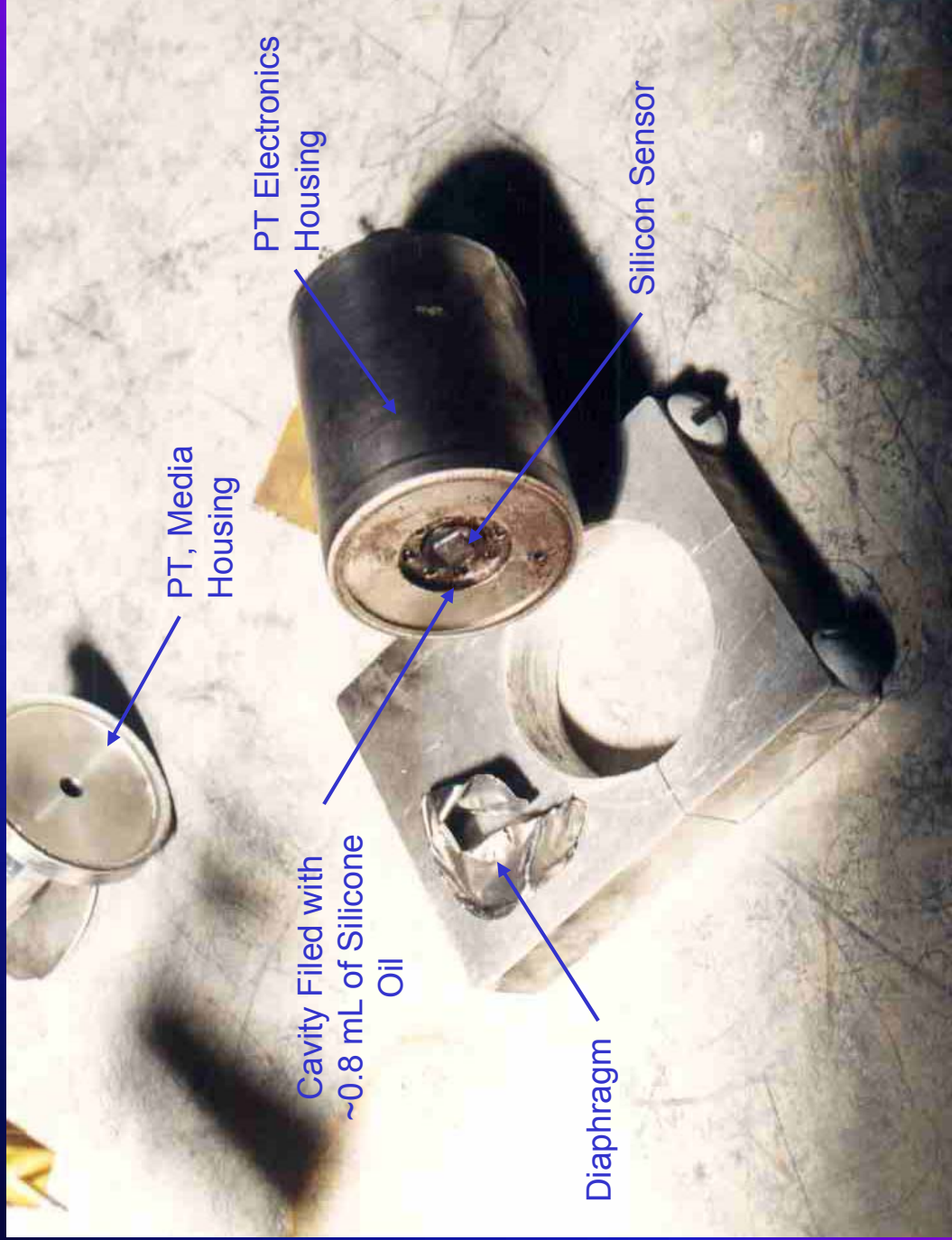


# Pressure Transducer





# Pressure Transducer



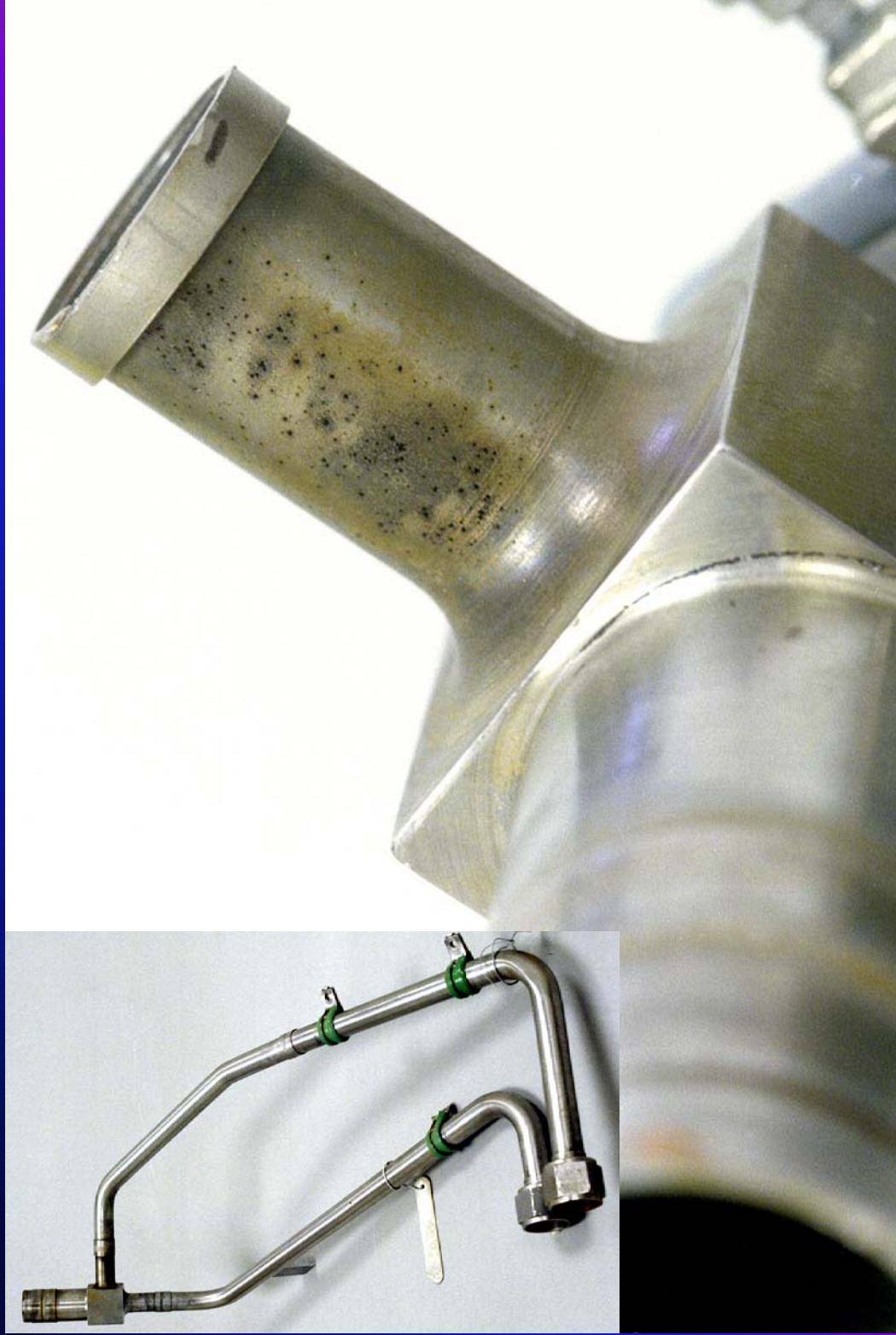
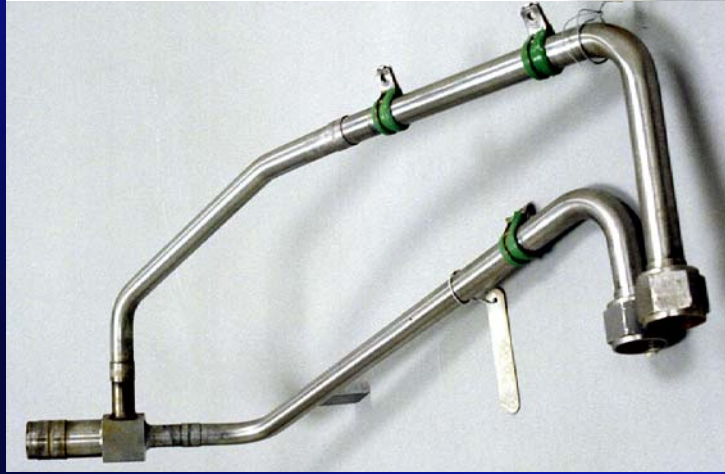
## 5.3.2 Investigation Findings

- ◆ Chem Lab beaker test indicates silicone oil is not compatible with **MON3** but reaction is not vigorous
- ◆ Analysis of beaker test residue identified dinitrophenol, a shock-sensitive compound
- ◆ The beaker test of **MON3** with 242 mg of silicone oil produced ~37 mg of dinitrophenol
- ◆ Diaphragm showed a fatigue failure
- ◆ Valve housing showed one time ductile failure

## 5.3 Material Properties Possibly Affected by Fluid/Material Interactions

- ◆ Softgoods
  - Tensile, Compressive Strength
  - Hardness
  - Mass (weight)
  - Visual Appearance
  - Solubility
  - Embrittlement
  - Tackiness
  - Permeability
  - Instability / Impact Sensitivity
- ◆ Metals / Alloys
  - Corrosion
    - Generalized
    - Pitting or Localized
    - Stress Corrosion Cracking

# Corrosion in NTO System



5/9/2006

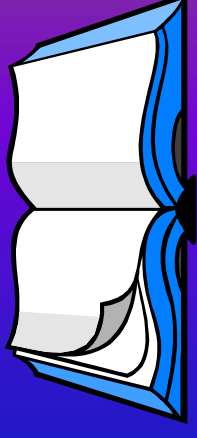
NASA Safety Training Center

91

## 5.4 Contamination of NTO

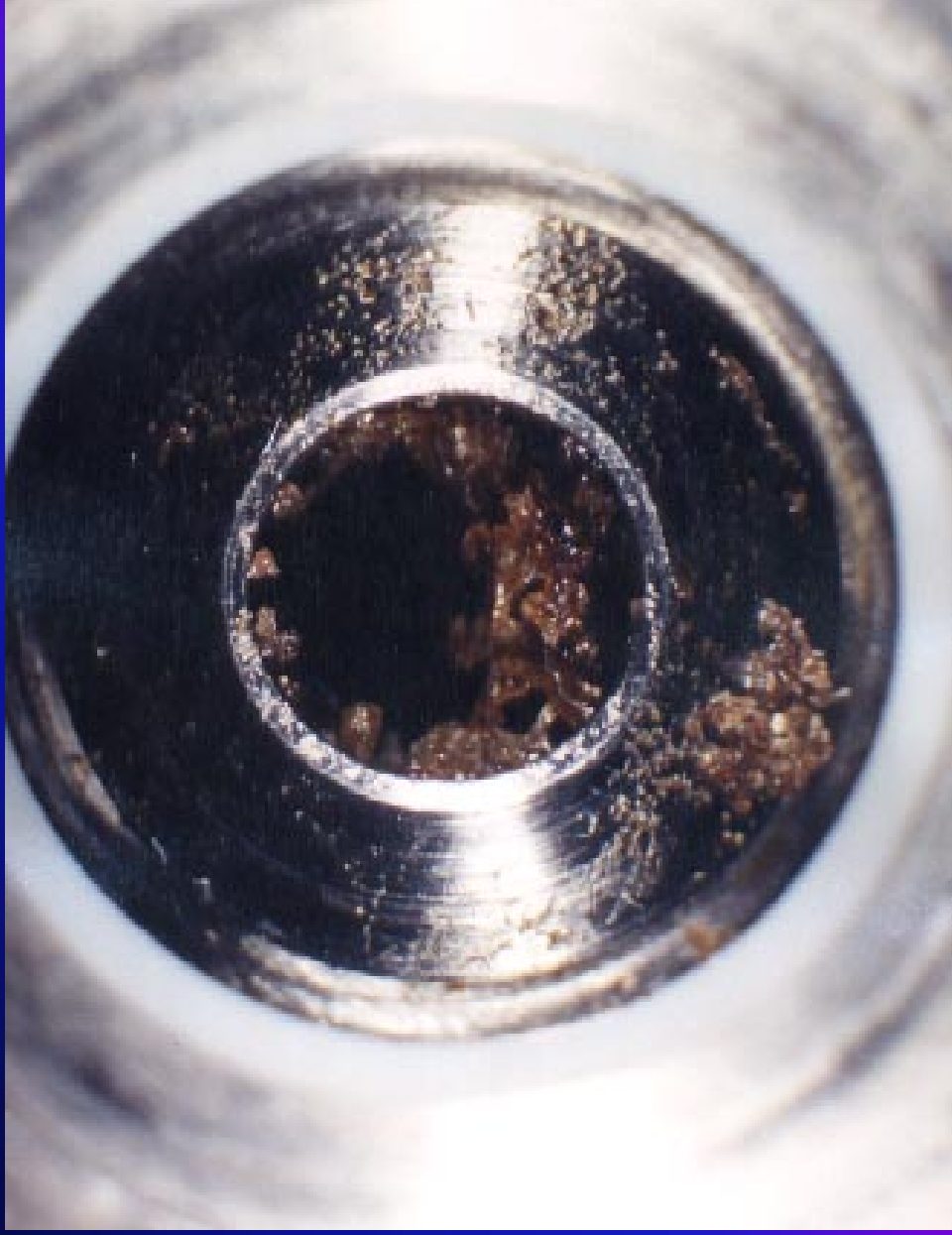
- ◆ **NTO** always contains trace water
  - Causes formation of nitric ( $\text{HNO}_3$ ) and nitrous ( $\text{HNO}_2$ ) acids
  - Increases corrosion rate
  - Anhydrous **NTO** would present few compatibility problems to metals
- ◆ System impurities
  - Cleaning solvents, lubricants, softgood materials
- ◆ Unpassivated systems are subject to flow decay

# Terminology



- ◆ Flow Decay
  - Nitric acid ( $\text{HNO}_3$ ), which is always present in some level in **NTO**, dissolves iron out of stainless steels and other iron containing materials. The iron can be deposited in other parts of a system as an insoluble iron nitrate. This is known as flow decay, because it tends to form in orifices and filters decreasing the flow through them.

# Example of Flow Decay Material Iron Nitrate in Valve Throat



## 5.4.1 Avoiding Flow Decay

- ◆ Molecular sieve used successfully
  - Porous zeolite pellets
  - Reduces water content in NTO
  - Also removes iron from NTO
- ◆ Use only passivated materials in storage and delivery systems
- ◆ Avoid water contamination
  - Maintain inert gas pad



## 5.5 Common Interactions of NTO

- ◆ Corrosion
- ◆ Flow Decay
- ◆ Softgood Reactivity

## 5.5.1 Decomposition of NTO

- ◆ Heat will push the  $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$  equilibrium to the right
  - NTO does not decompose exothermically
  - Can not lead to a thermal runaway
- ◆ Unlike the **hydrazine fuels**, NTO will not catalytically decompose
  - NOTE: NTO can be consumed by a reaction with the material

## 5.6 Reactions of Hydrazines

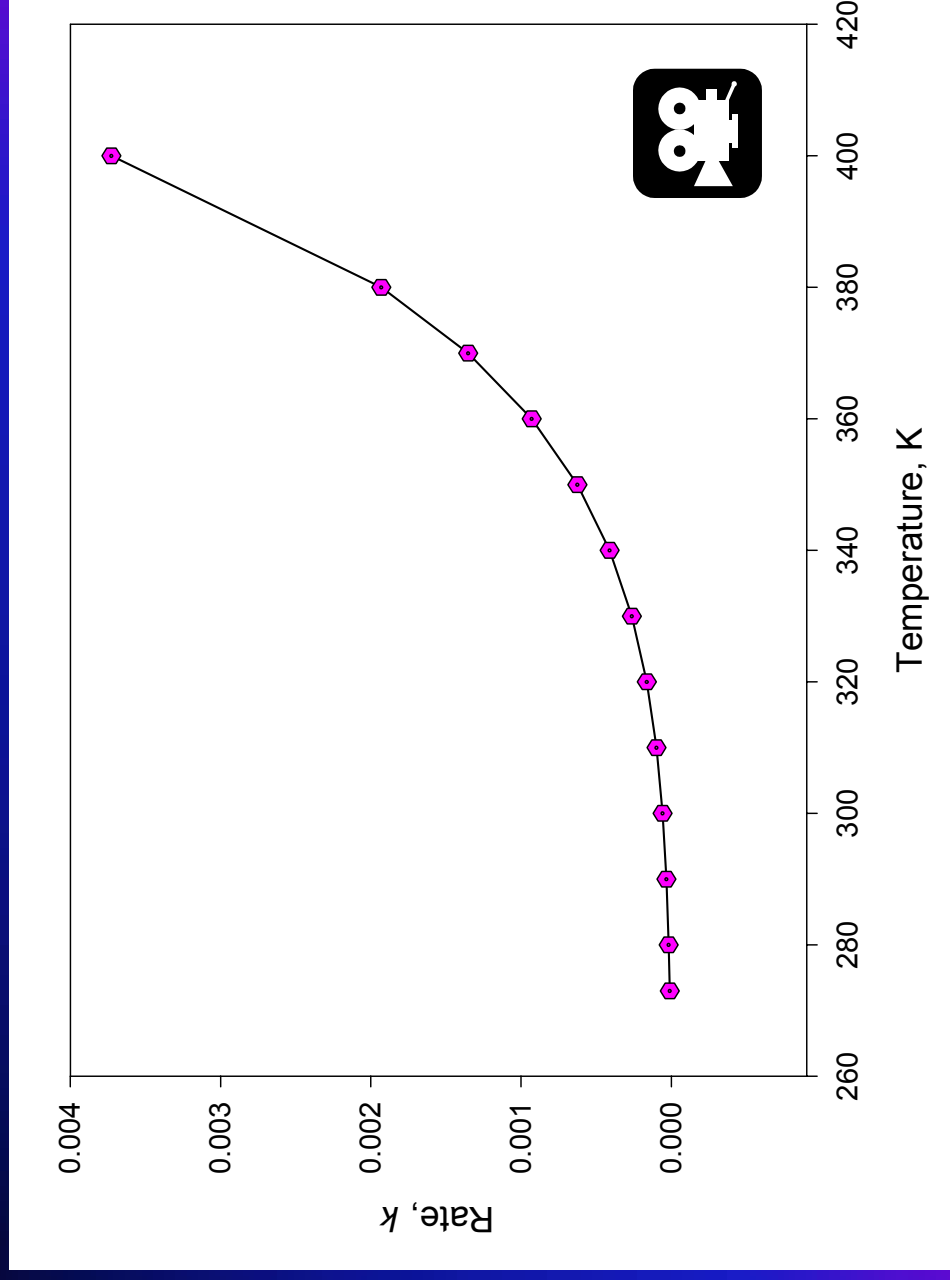
- ◆ Thermal
  - Due to external heat source
- ◆ Catalytic
  - Due to material incompatibility
- ◆ Oxidation
  - Oxidizers
  - Metal oxides
- ◆ Reactions are exothermic

# Terminology



- ◆ Thermal Runaway
  - An exothermic reaction in which the rate of heat generation exceeds the rate of heat transfer to the surroundings. The increased system temperature leads to an increased reaction rate.

## 5.6.1 Effect of Temperature on a Reaction Rate



# Aside

## Decomposition



$$\Delta H = -140 \text{ kJ mole}^{-1} \text{ (298 K)}$$

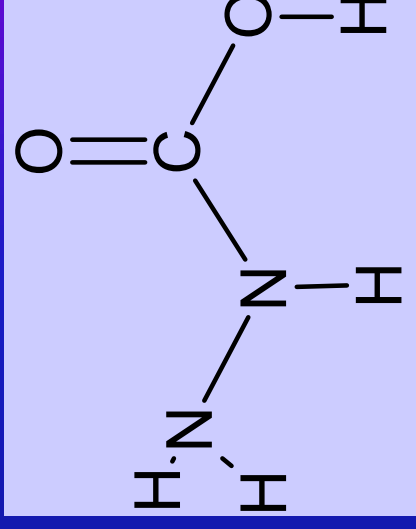
## Oxidation



$$\Delta H = -577 \text{ kJ mole}^{-1} \text{ (298 K)}$$

## 5.7 Contamination of Hydrazines

- ◆ Water
  - Increases corrosion rate
- ◆ CO<sub>2</sub>
  - Forms carbazic acid
  - Increases catalytic decomposition
  - Increases corrosion rate
- ◆ System impurities
  - Cleaning solvents, lubricants, softgood materials
  - Can increase corrosion rate



# Military weather satellite repaired for October liftoff

BY JUSTIN RAY  
SPACEFLIGHT NOW

Posted: June 27, 2002

With its propulsion system replaced after an acid residue ruined its first one during a year-long launch delay, a military weather satellite is ready to begin the campaign for an October liftoff...

.... "The (destructive physical analysis) confirmed the presence of carbazic acid residue (a by-product of hydrazine and air interaction) contamination in each of the thrusters" said Col. Randy Odle, system program director for DMSP.

"Apparently, air was introduced into the thrusters/propulsion system during testing and interacted with residual hydrazine remaining from the hydrazine defueling accomplished after the January '01 launch abort.

"The contamination found in the two thrusters also implicated the remaining two thrusters and the entire propulsion system. As such, we decided to replace the hydrazine-contaminated F-16 propulsion system with one from another DMSP spacecraft." Liftoff is now scheduled for October 6.



A DMSP weather satellite. Photo: Lockheed Martin



# Terminology



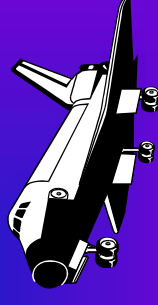
- ◆ **Stress Corrosion Cracking**
  - Stress corrosion cracking is caused by the simultaneous effects of tensile stress and a specific corrosive environment. Stresses may be due to applied loads, residual stresses from the manufacturing process, or a combination of both.

- McDanel, S. J., "An Overview of Fatigue and Other Metallurgical Failure Modes and Analysis at the Kennedy Space Center", Flammability and Sensitivity of Materials in Oxygen-Enriched Atmospheres: Eight Volume, ASTM STP 1319, W. T. Royals, T. C. Chou, and T.A. Steinberg, Eds., American Society for Testing and Materials, 1997.



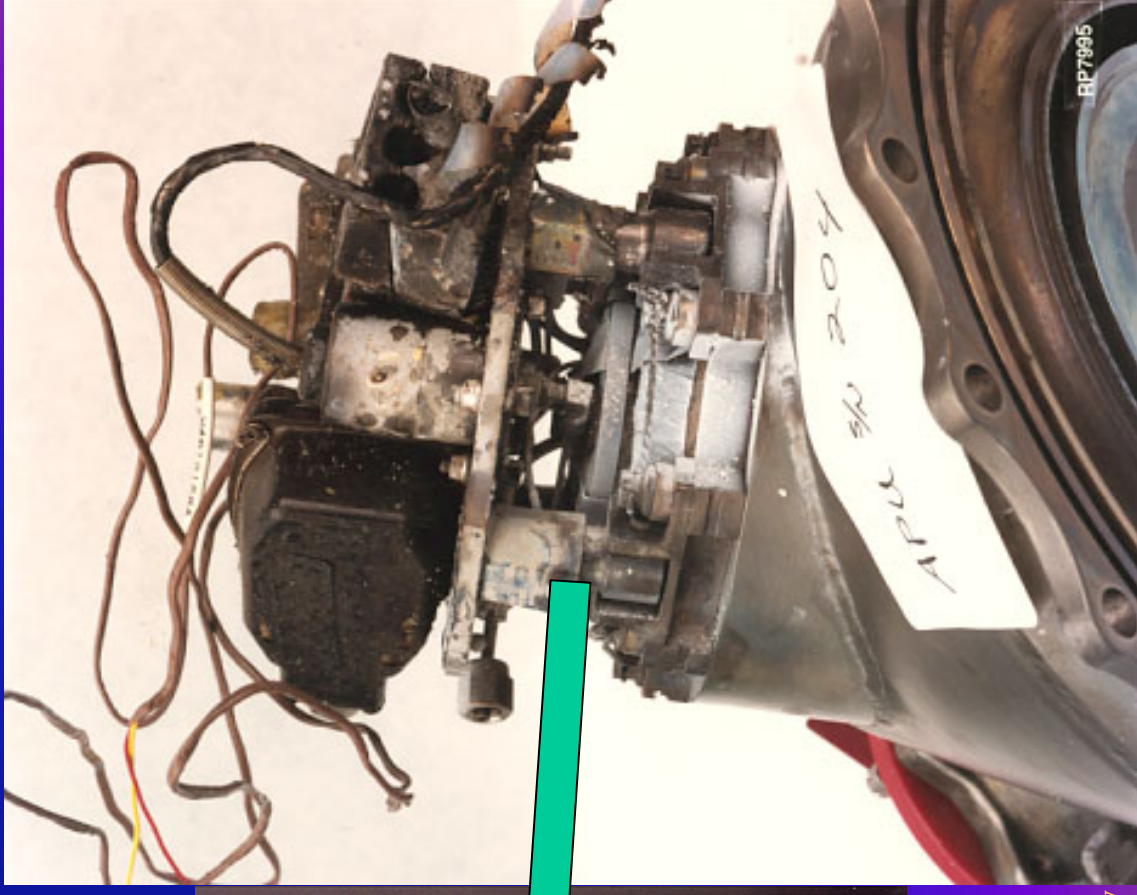
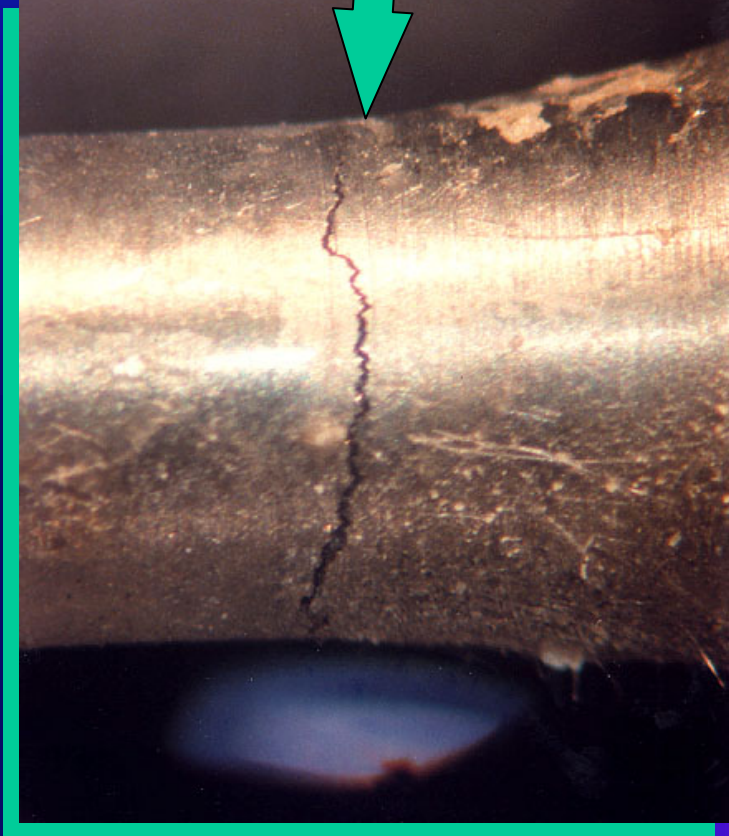
## 5.8 STS 9 APU Fire

- ◆ Hydrazine leakage 17 minutes after APU start for re-entry
- ◆ Hydrazine accumulated between valve mounting plates and gas generator heat shield
- ◆ Hydrazine froze then melted during descent
- ◆ Fire started 4 1/2 minutes prior to landing
- ◆ Decomposition propagated through supply lines
- ◆ APU-1 and APU-2 shutdown 7 & 10 minutes after landing



## 5.8.1 STS 9 APU Fire

Hastelloy B Stress Corrosion Cracking



5/9/2006

NASA Safety

## 5.9 Common Interactions of Hydrazines

- ◆ Corrosion
- ◆ Catalytic Decomposition
- ◆ Thermal Runaway
- ◆ Softgood Reactivity

## 5.10 Overall Hazards from Material / Fluid Reactions

- ◆ Failure / loss of function
  - Fluid, component, or system
- ◆ Loss of fluid containment
  - Personnel exposure
  - Fire
  - Rapid Unscheduled Disassembly Event (RUDE)

# Course Outline

- ✓ Introduction
- ✓ Accidents
  - ✓ Examples of the “problems”
- ◆ Step 1 - Identify the Hazards
  - ✓ Toxicity Hazard
  - ✓ Reactivity Hazard
  - Fire Hazard
  - Explosion Hazard
  - Hypergol Properties, References & Other Information
- ◆ Step 4 - Manage the Risks
  - Primary Controls
    - Design
      - Material Compatibility
    - Build Up
    - Operation
  - Secondary Controls
    - PPE
    - Detectors/Monitors
- ◆ Course Evaluations

# Step 1 - Identifying the Hazards

- ✓ Toxicity
- ✓ Reactivity
-  Fire
- ◆ Explosion

# What is the Hazard?

## HEAT!

- ◆ Not where you want.
- ◆ Not when you want.
- ◆ Not at the rate you want.



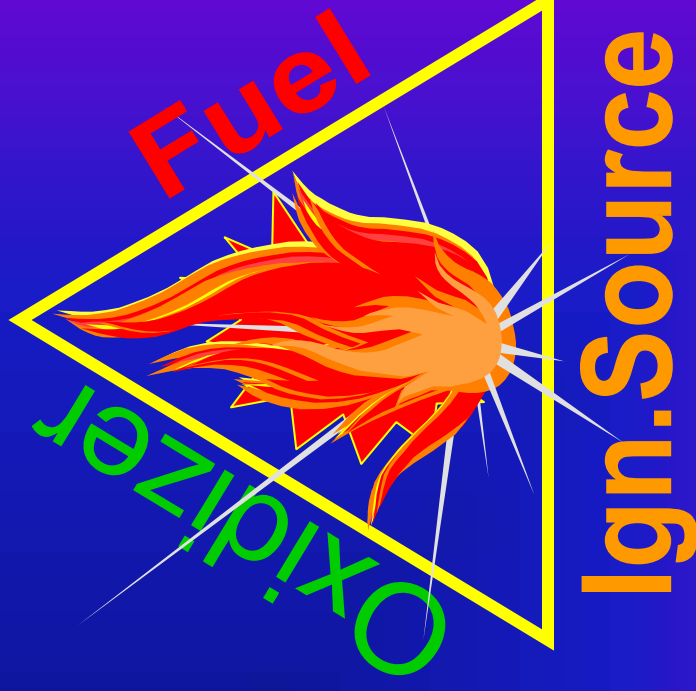
# Terminology



- ◆ **Fire**
  - Sustained burning, as manifested by any or all of the following: light, flame, heat, and smoke (ASTM E 176-90).
- ◆ **Combustion**
  - A chemical process (as an oxidation) accompanied by the evolution of light and heat.

## 6.0 Fire Hazard

- ◆ With hypergols, the familiar fire triangle does not necessarily apply.



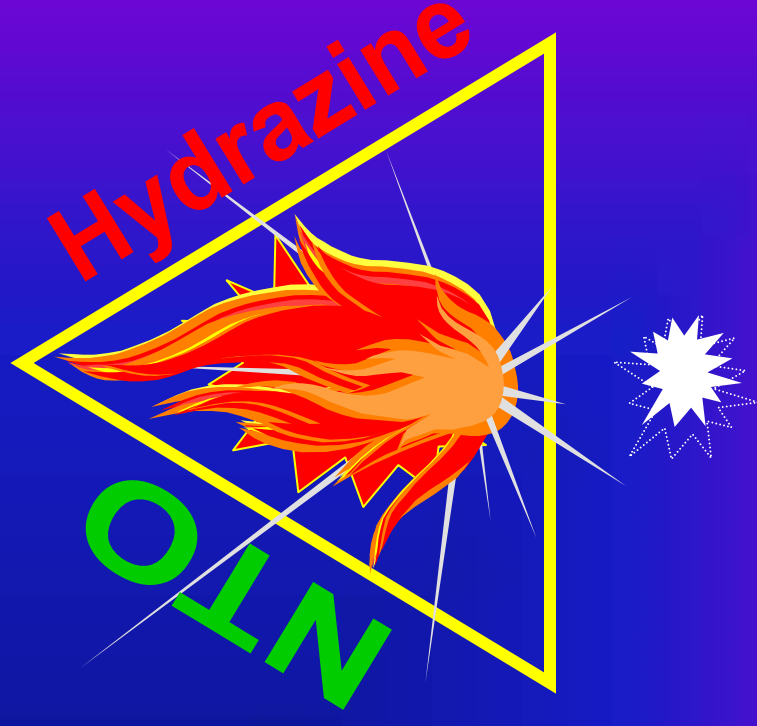
## 6.1 Fire Hazard

- ◆ **Hydrazine** fuels can decompose exothermically without the presence of an oxidizer.



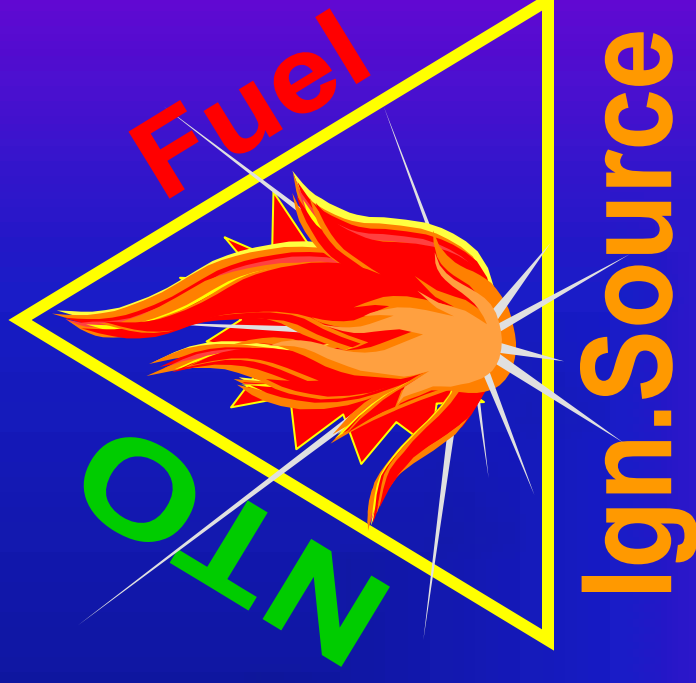
## 6.2 Fire Hazard

- ◆ As previously discussed, **hydrazine** fuels are hypergolic with **NTO** and other oxidizers and do not require an external ignition source



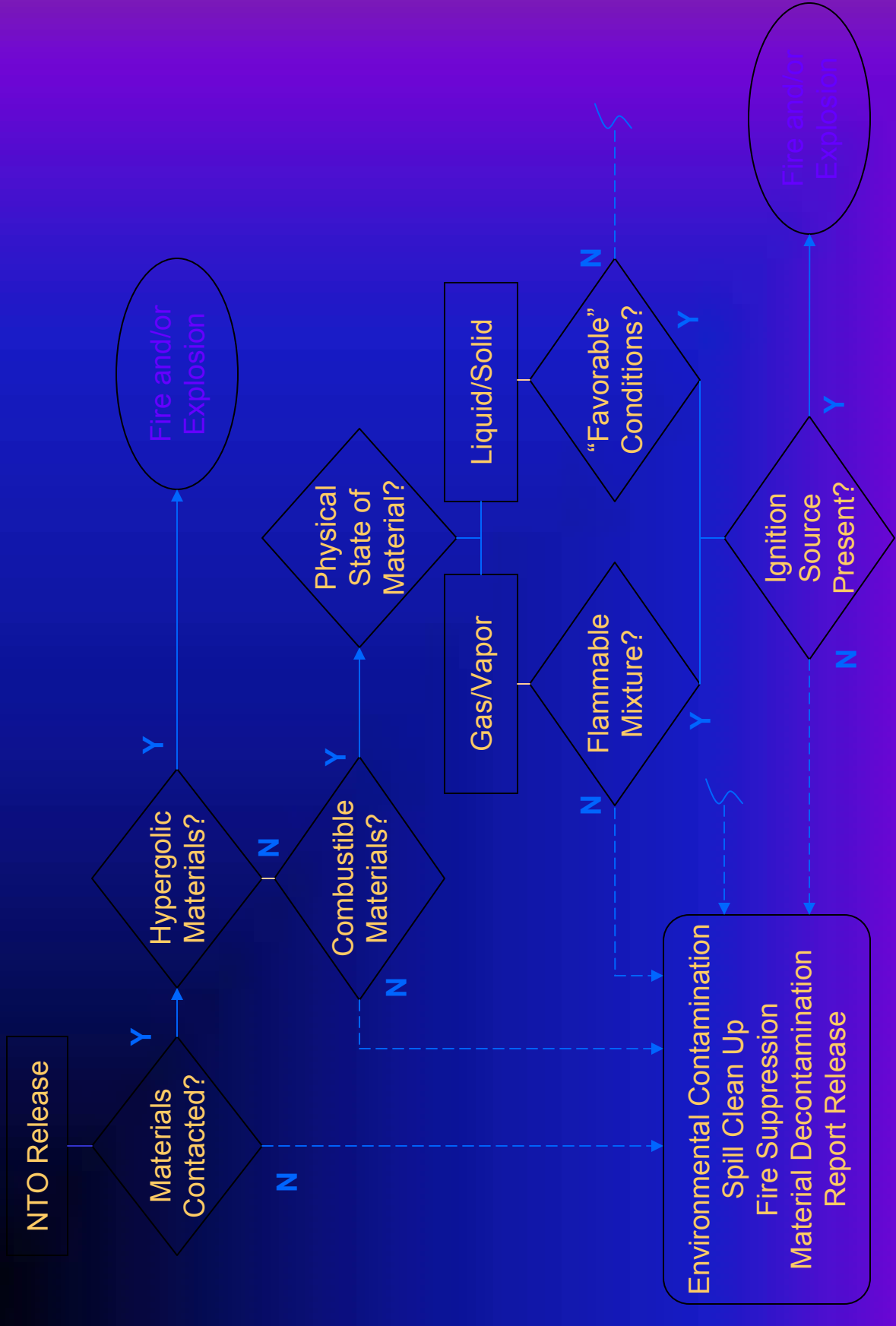
## 6.3 Fire Hazard

- ◆ **NTO** is an oxidizer, so any material it contacts is a potential fuel.



## 6.4 Fire Hazard

- ◆ **NTO** is chemically stable, nonflammable, and nondetonable
- ◆ **NTO** does not exothermically decompose
- ◆ The potential for fire or explosion arises only when **NTO** mixes with combustibles

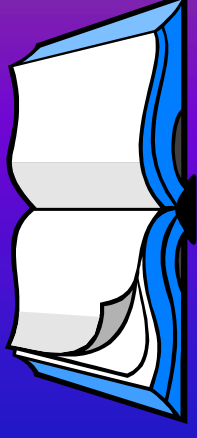


## 6.5 Fire Hazard

- ◆ **Hydrazine** fuels burn in the vapor phase around the liquid, as well as in mist, droplet, and spray forms
- ◆ Must meet the criteria for a fire depending on the form of the fuel



# Terminology



- ◆ **Flash Point**
  - The lowest temperature at which the liquid gives off enough vapor to form an ignitable mixture at or near the surface (Sax 1984)
- ◆ **Fire Point**
  - The lowest temperature at which fire continuously burns, in still air, over a liquid surface upon exposure to an ignition source (Scott, Burns, Lewis 1949)

## 6.5.1 Flash Points

- **HZ:** 124 °F (51 °C)
- **MMH:** 70 °F (21 °C)
- **UDMH:** 5 °F (-15 °C)
- **NTO:** Nonflammable
- **MONX:** Nonflammable

# Terminology

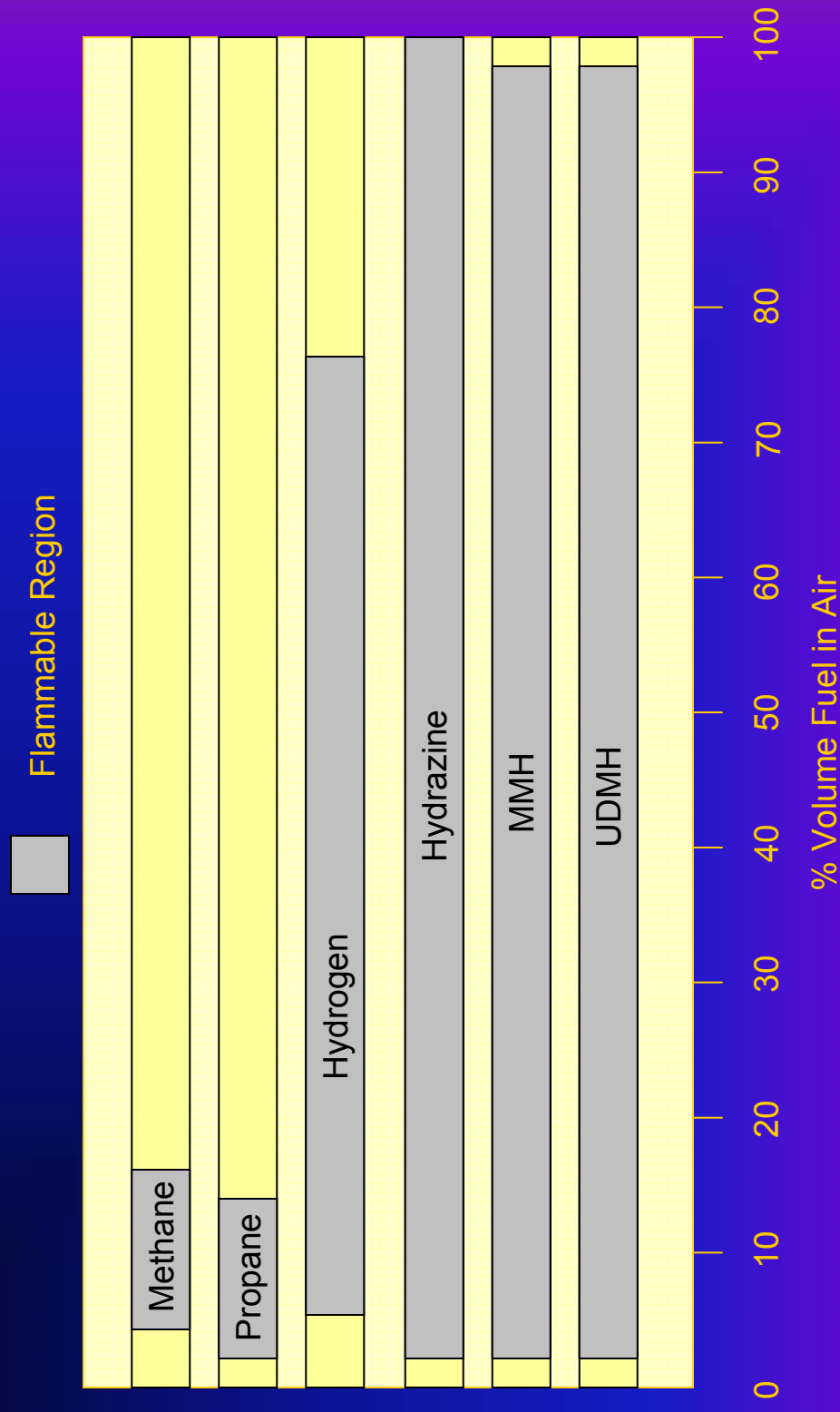


- ◆ Vapor Pressure
  - The pressure of the vapor in equilibrium with the liquid phase
    - Is a function of temperature
  - The boiling point is the temperature at which the vapor pressure equals ambient pressure

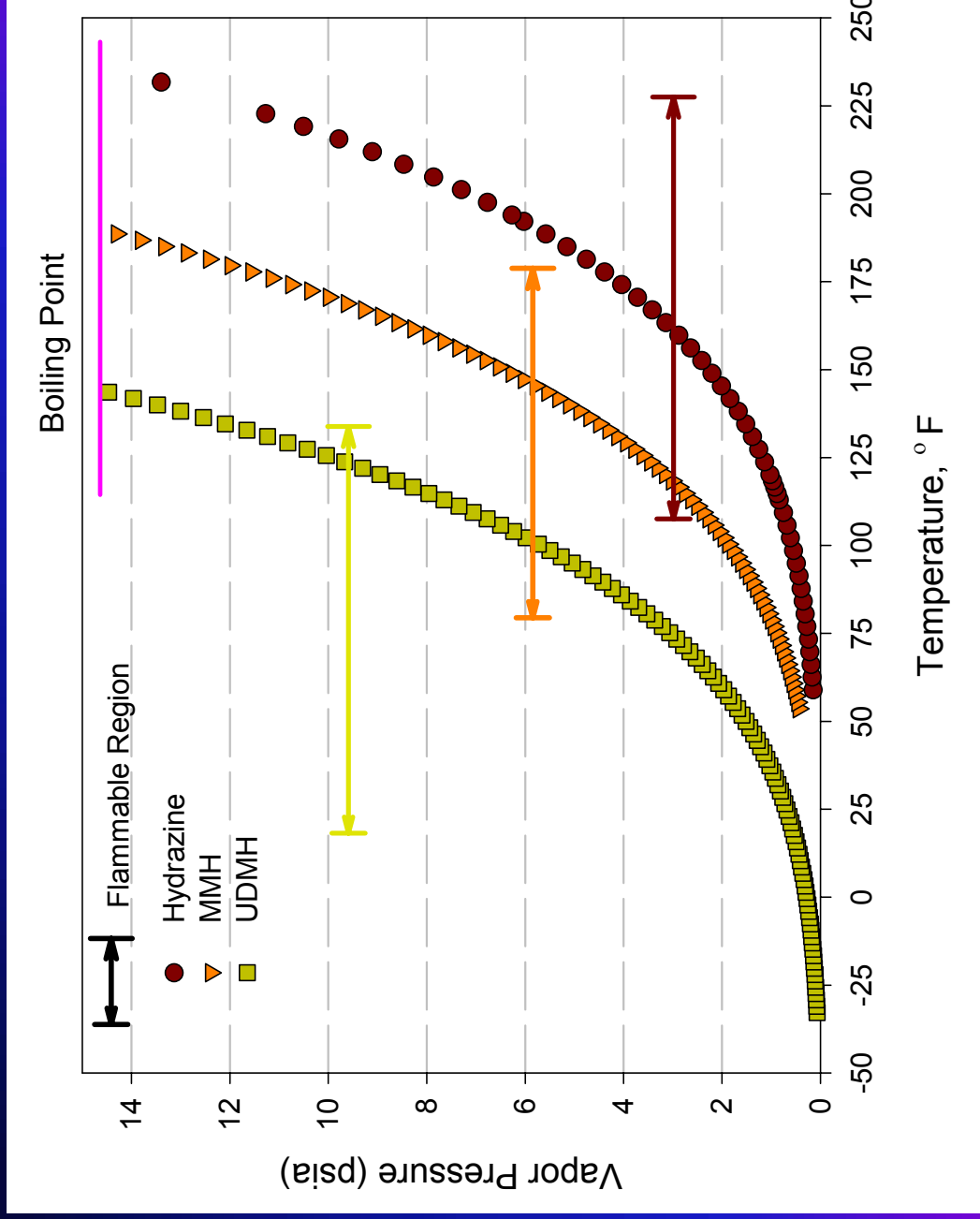
## 6.5.1 Fire Criteria - Vapor

- ◆ Ignition source of sufficient energy
- ◆ Mixture is within flammable limits
  - **HZ:** 4.7-100% by vol. in air
  - **MMH:** 2.5 - 98% by vol. in air
  - **UDMH:** 2 - 95% by vol. in air
  - **NTO:** Nonflammable
  - **MONX:** Nonflammable

# 6.5.1.1 Flammability Limits in Air



# Vapor Pressure and Flammable Regions



## 6.5.2 Fire Criteria - Liquid

- ◆ Ignition source of sufficient energy
- ◆ Liquid is at or above its fire point
  - **HZ:** 124 °F (51 °C)
  - **MMH:** 70 °F (21 °C)
  - **UDMH:** 5 °F (-15 °C)
  - **NTO:** Nonflammable
  - **MONX:** Nonflammable

# Terminology



- ◆ Stoichiometry
  - The proportion of substances exactly right for a specific chemical reaction with no excess of any reactant or product.
- ◆ Stoichiometric Combustion
  - The burning of fuel and oxidizer in the exact proportions required for complete reaction to give a set of products.



# Hydrazine Stoichiometry

- ◆ Hydrazine / Oxygen



- 50%  $\text{N}_2\text{H}_4$  by mass

- 50%  $\text{N}_2\text{H}_4$  by volume

- ◆ Hydrazine / Air



- 18.9%  $\text{N}_2\text{H}_4$  by mass

- 17.4%  $\text{N}_2\text{H}_4$  by volume

# MMH Stoichiometry

- ◆ **MMH / Oxygen**



- 36.6% MMH by mass

- 28.6% MMH by volume

- ◆ **MMH / Air**



- 11.8%  $\text{N}_2\text{H}_4$  by mass

- 7.8%  $\text{N}_2\text{H}_4$  by volume

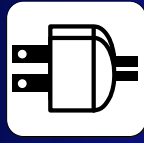
## 6.6 Fire Hazard

- ◆ One of the main criteria for a fire is an ignition source of sufficient energy
- ◆ What are possible ignition sources?

## 6.6.1 Ignition Sources

- ◆ **Material**
  - Catalysis
  - Oxidation

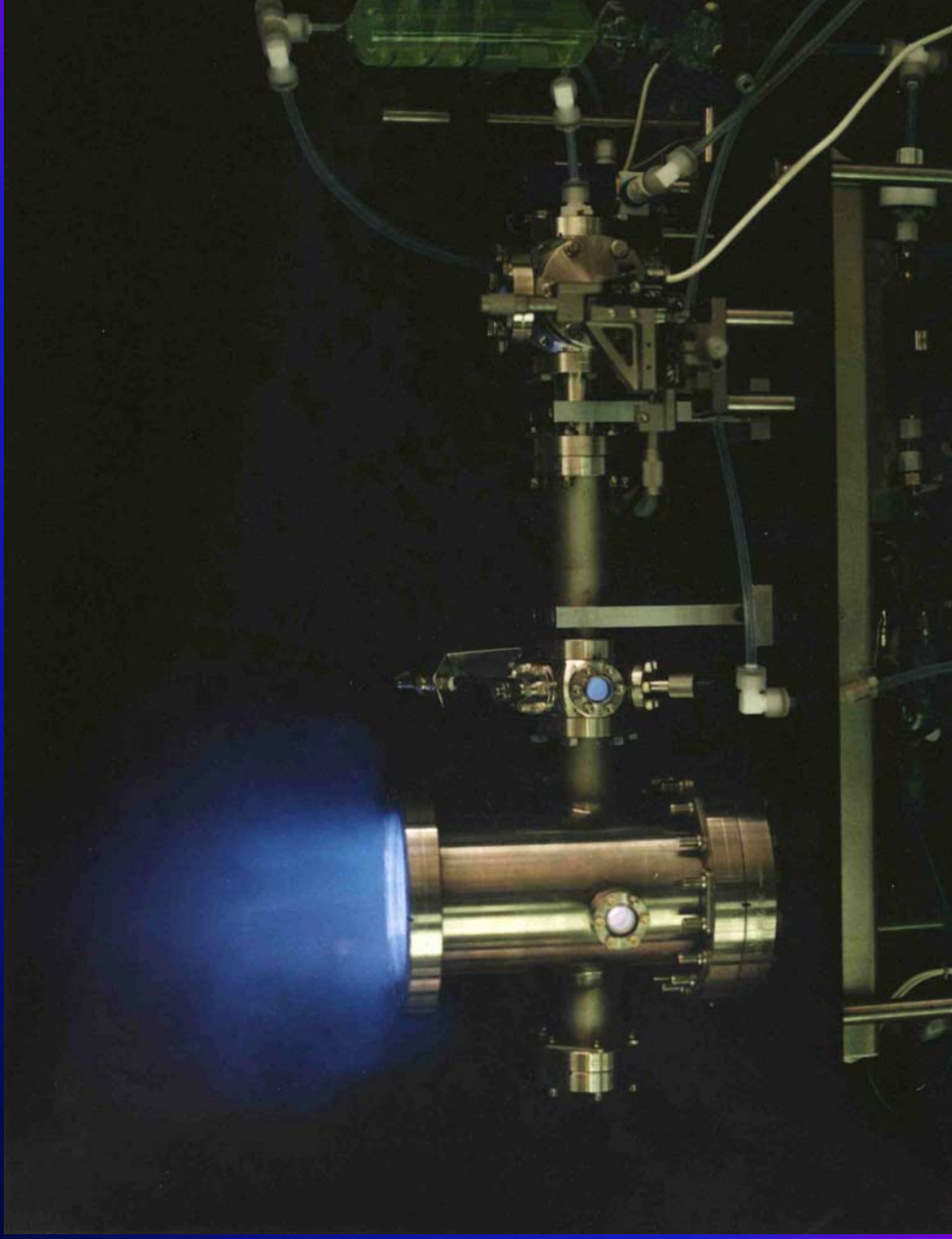
## 6.6.2 Ignition Sources



### Electrical

- Static discharge
- Electrical short circuits, arcs, and sparks
- Lightning

# Minimum Ignition Energy System



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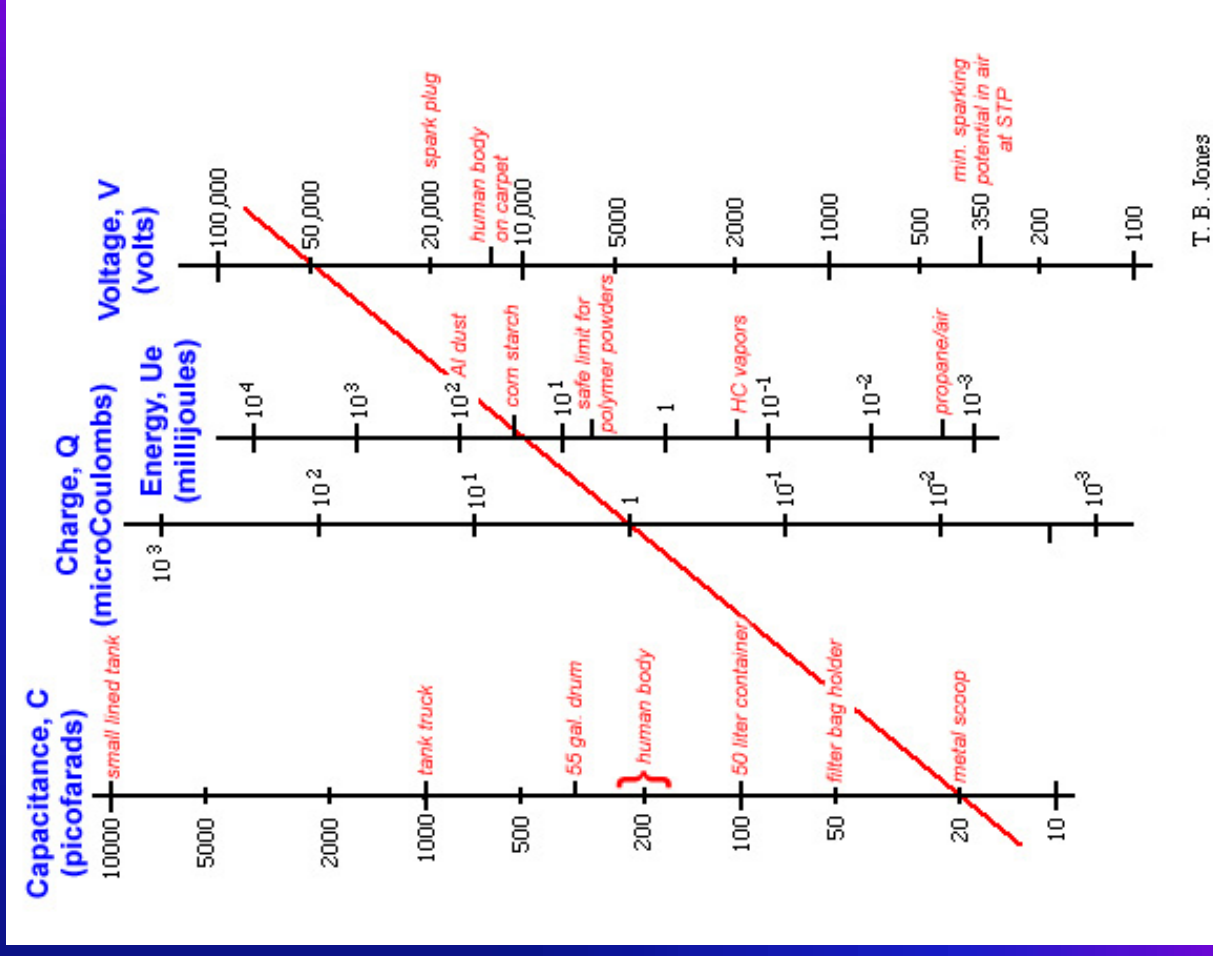
## 6.6.2.1 Minimum Ignition Energies

- ◆ **Hydrazine**
  - 2.5 milliJoules
- ◆ **MMH**
  - 2.8 milliJoules (2.2 volume percent)
- ◆ **UDMH**
  - 2.7 milliJoules (4.3 volume percent)
- ◆ **Propane**
  - 0.3 milliJoules (5.0 volume percent)

You walking on a carpet can generate a 10 millijoule spark

# 6.6.2.2 Ignition Energy Nomograph

Source: T. B. Jones  
University of Rochester



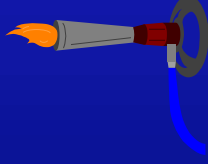


### 6.6.2.3 Electrical Ignition Sources

- ◆ Electrically ground fuel systems
- ◆ 24 VDC is preferred to 110 VAC
- ◆ Use explosion proof devices and connectors or place electrical equipment in explosion proof containers
  - sealed or inert gas purged box

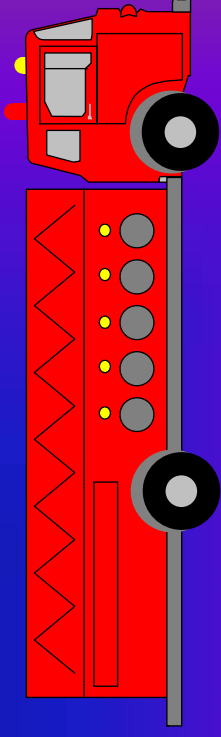
## 6.6.3 Ignition Sources

- ◆ Thermal
  - Open flames
  - Hot surfaces
  - Explosive charges (e.g. pyrovalves)



## 6.6.4 Fire Fighting

- ◆ Carbon dioxide
- ◆ Water
- ◆ Dry chemical (monoammonium phosphate)



## 6.6.4.1 Fire Fighting

- ◆ Use coarse water spray to dilute source, knock down vapors, and extinguish flames
- ◆ Attempt to shut off flow of any leaking propellant - **CAUTION**
- ◆ Cool exposed storage vessels and piping containing propellant
- ◆ Build dikes to contain fluids if possible

## 6.6.4.2 Fire Fighting


- ◆ By way of comparison and contradiction, a hypergol fire (both species present) cannot be extinguished without removing one or the other species.

QG-250-KSC video - “Hypergolic Fire Suppression”

# Course Outline

- ✓ Introduction
- ✓ Accidents
  - ✓ Examples of the “problems”
- ◆ Step 1 - Identify the Hazards
  - ✓ Toxicity Hazard
  - ✓ Reactivity Hazard
  - ✓ Fire Hazard
  - Explosion Hazard
  - Hypergol Properties, References & Other Information
- ◆ Step 4 - Manage the Risks
  - Primary Controls
    - Design
      - Material Compatibility
    - Build Up
    - Operation
  - Secondary Controls
    - PPE
    - Detectors/Monitors
- ◆ Course Evaluations

# Step 1 - Identifying the Hazards

- ✓ Toxicity
- ✓ Reactivity
- ✓ Fire
- ✓  Explosion

# What is the Hazard?

## Pressure

$$P \cdot \text{Area} = \text{Force}$$

$$\text{Force} = \text{mass} \cdot \text{acceleration}$$
$$\text{accelerating mass} = \text{RUDE}$$



# Terminology



- ◆ **Explosion**
  - A rapid equilibration of pressure between a system and its surroundings that can produce a shock wave.

# Explosion

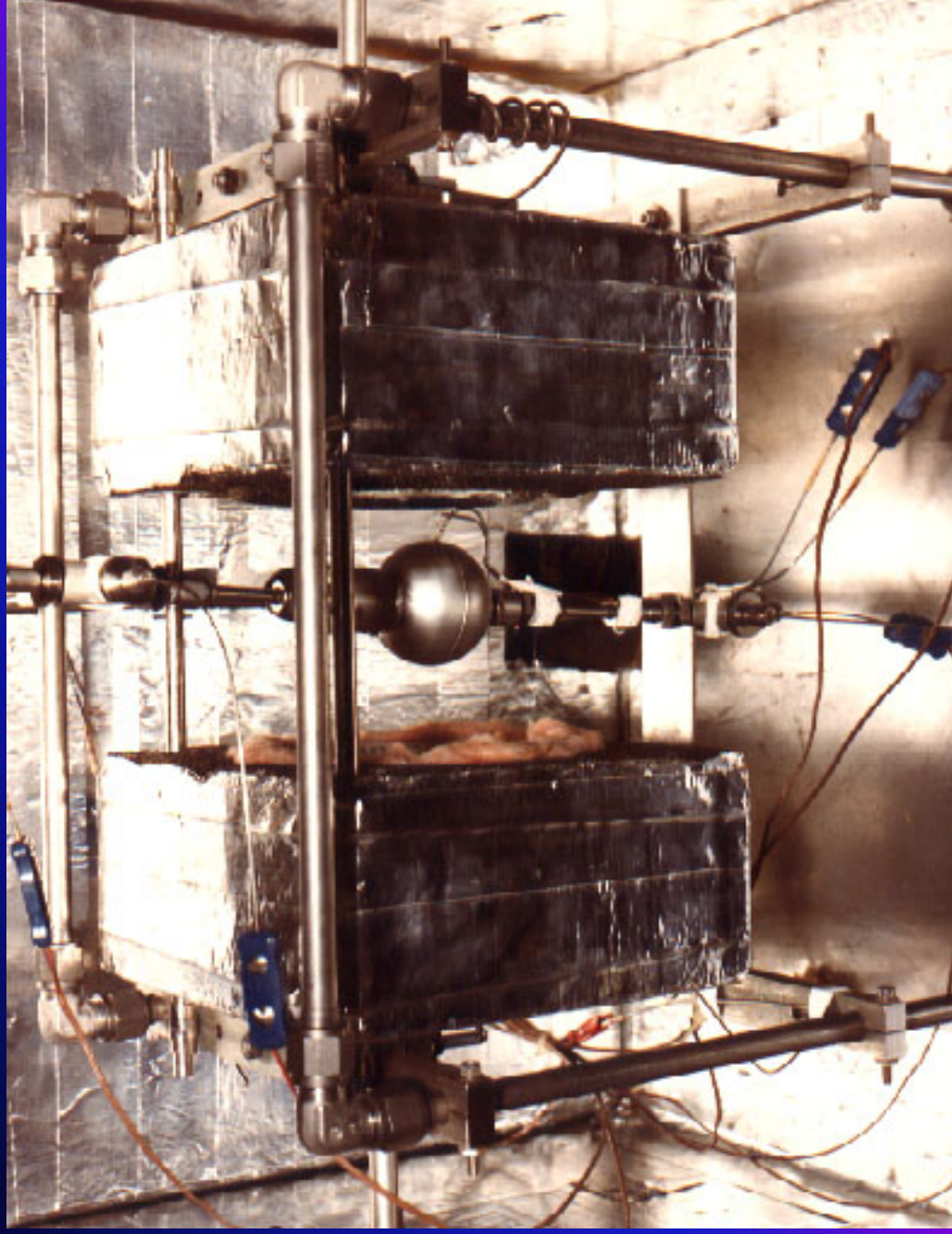
“I don’t care what you call it,  
the @#\$\$% thing blew up!”

- Witness to an explosion

# 7.0 Explosion Hazard

- ◆ Explosions involving the **hydrazine** fuels can occur three ways:
  - 1 ) Thermal runaway
    - External heat source (fire or other)
    - Heat generation from decomposition
      - Incompatible materials
      - Rapid compression
  - 2 ) Deflagration
  - 3 ) Detonation

## 7.1.1 Thermal Runaway Test



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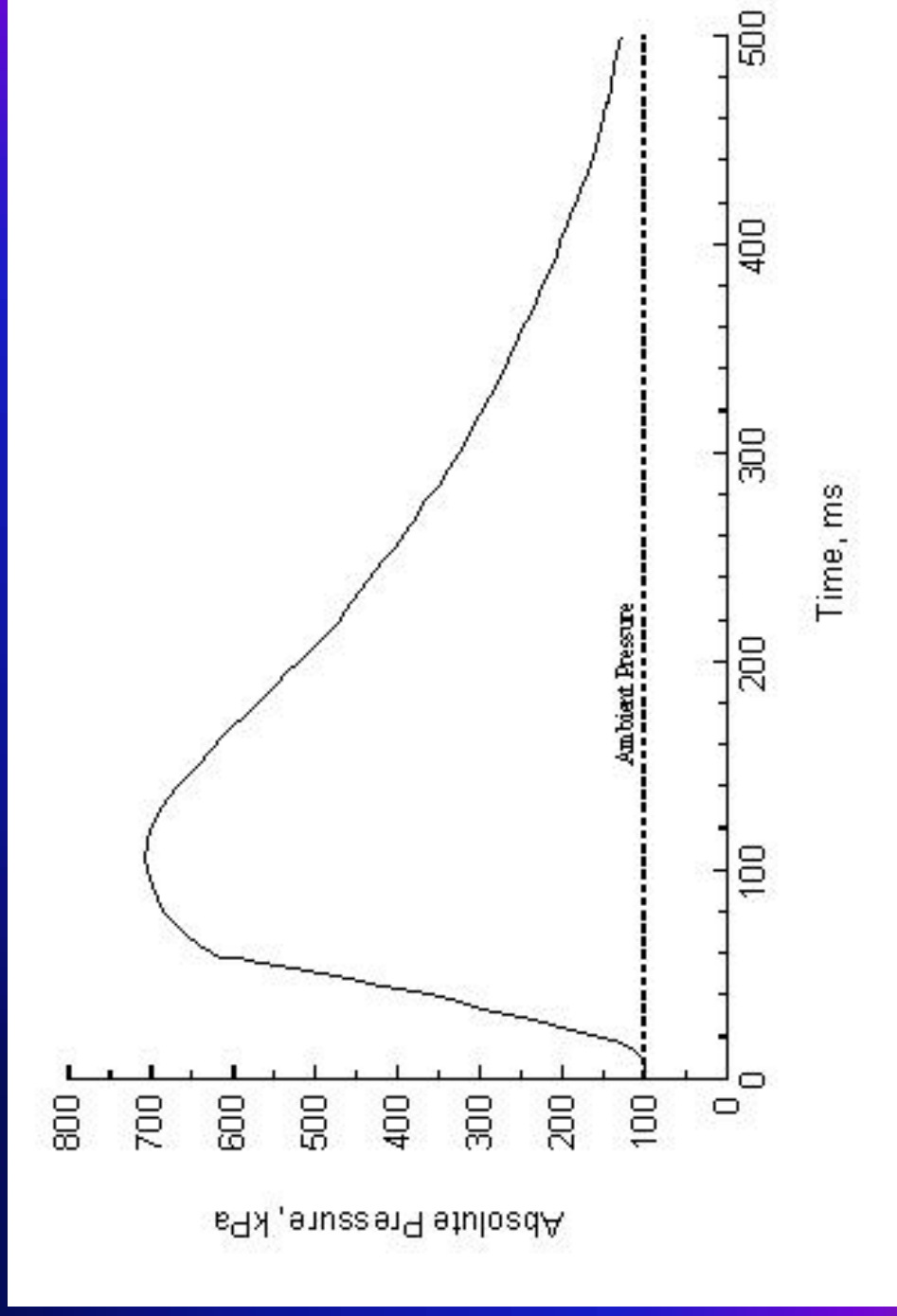
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## 7.1.2 Thermal Runaway Debris



## 7.1.3 Thermochemical Runaway

Typical pressure-time profile for confined thermal runaway.



## 7.1.4 Rapid Compression

- ◆ Liquid flow in a system can compress ullage gas, vapor, and/or froth formed at the liquid/gas interfaces
- ◆ When compression is rapid, hot spots can form accelerating **hydrazine** decomposition
- ◆ Hydrazine reaction can be explosive and cause system damage

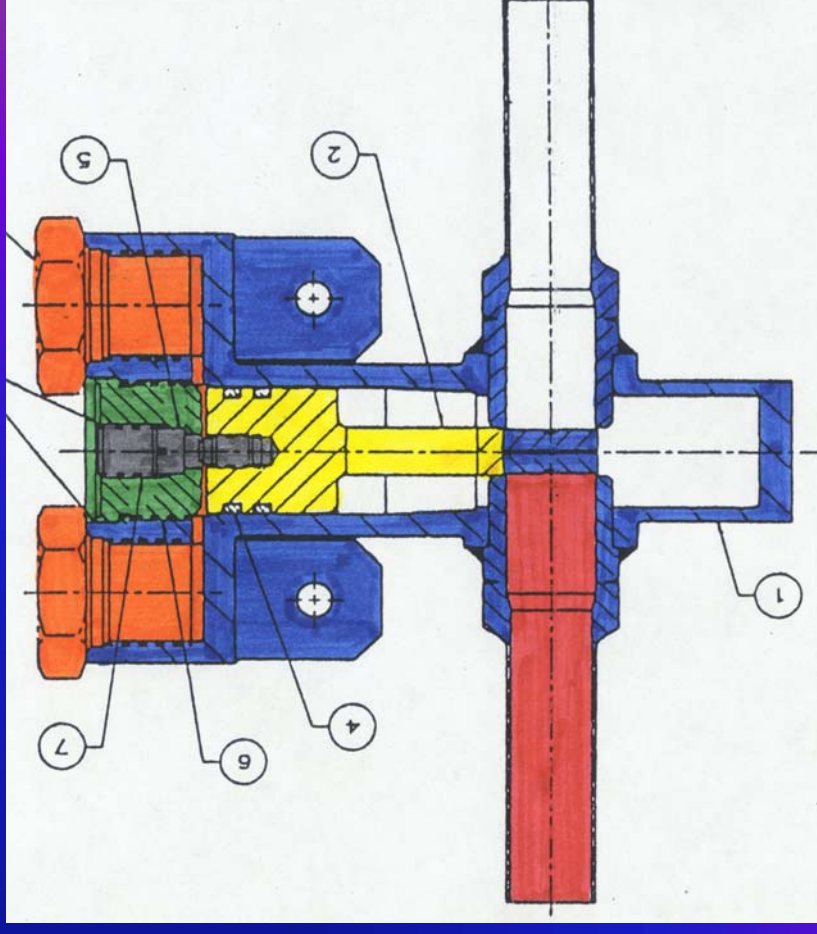
## 7.1.4.1 Factors Affecting Rapid Compression

- ◆ Surge pressure
  - Fluid velocity
  - Ullage gas
  - Ullage gas pressure
  - Ullage gas volume (line length)
  - Confinement



## 7.1.4.2 Same Mechanism?

- ◆ Explosive discharges from pyrovalves have resulted in explosions similar to those observed from rapid compression events



## 7.2 Explosion Hazards

- ◆ The other two processes that can cause an explosion are deflagration and detonation
  - Deflagration is subsonic
  - Detonation is supersonic

## 7.2.1 Deflagration - What's the Hazard?

- ◆ Fire
- ◆ Resulting pressure can be 5 to 10 times the initial pressure
- ◆ Confinement can lead to an explosion
- ◆ Can transition to detonation under certain conditions

## 7.2.2 Detonation - What's the Hazard?

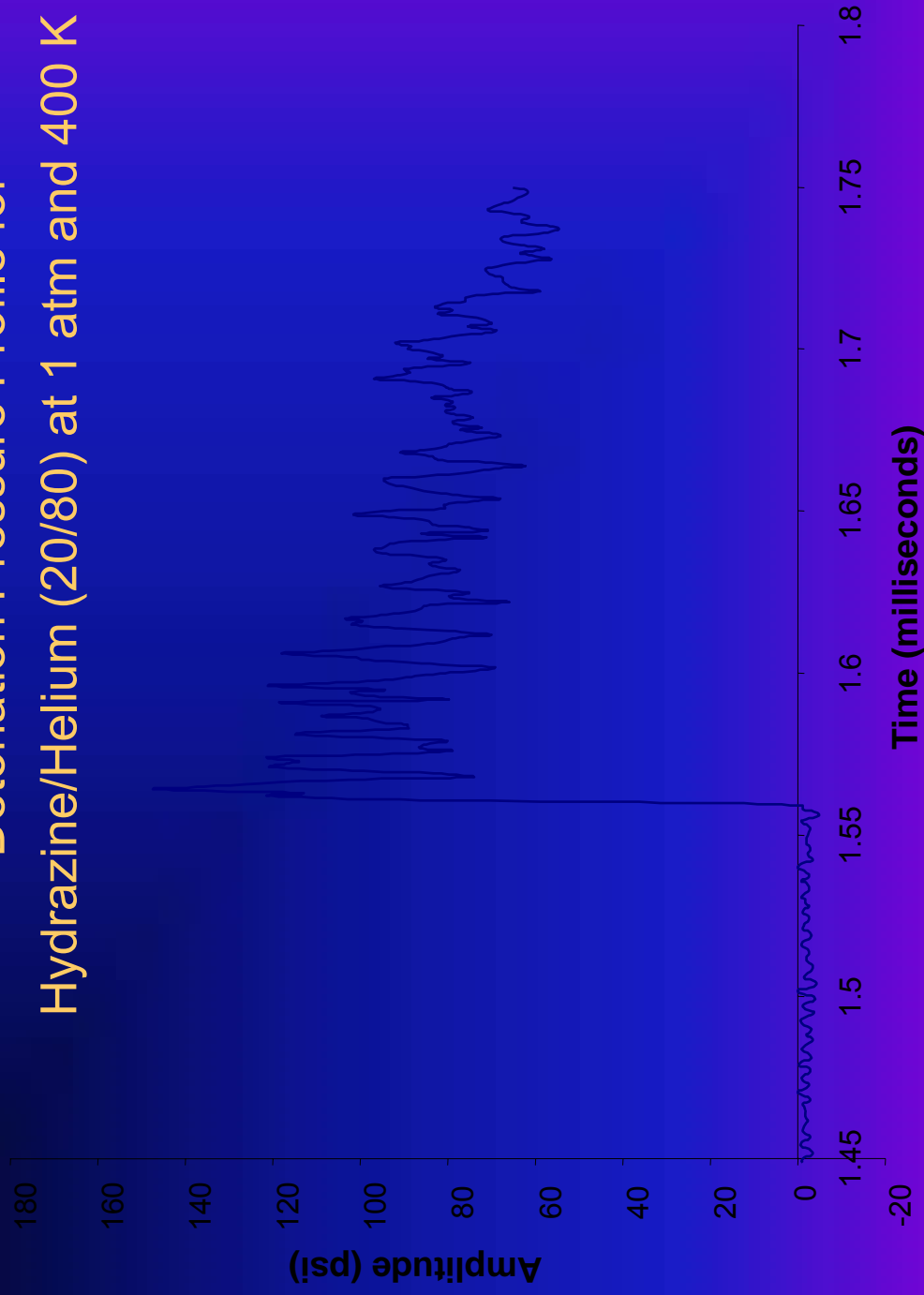
- ◆ Very rapid pressure increase
  - Relief protection cannot respond
- ◆ Resulting pressure can be 18 to 28 times the initial pressure

## 7.2.2.1 Hypergol Detonability

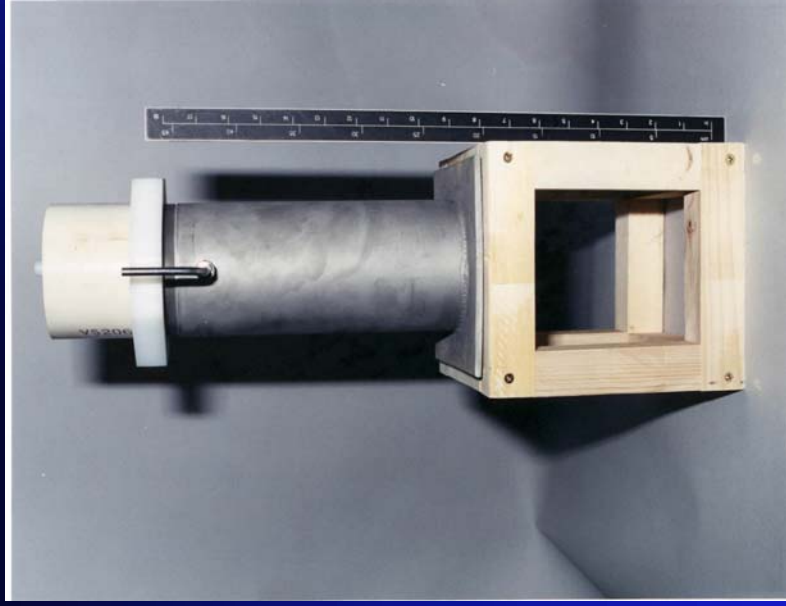
- ◆ **NTO** vapor is detonable with other non-hypergolic fuels
- ◆ **NTO** liquid is nondetonable
- ◆ **Hydrazine, MMH, and UDMH** vapors will detonate under certain conditions
- ◆ Liquid **hydrazine** and **MMH** have not been shown to be detonable

# Example

Detonation Pressure Profile for  
Hydrazine/Helium (20/80) at 1 atm and 400 K

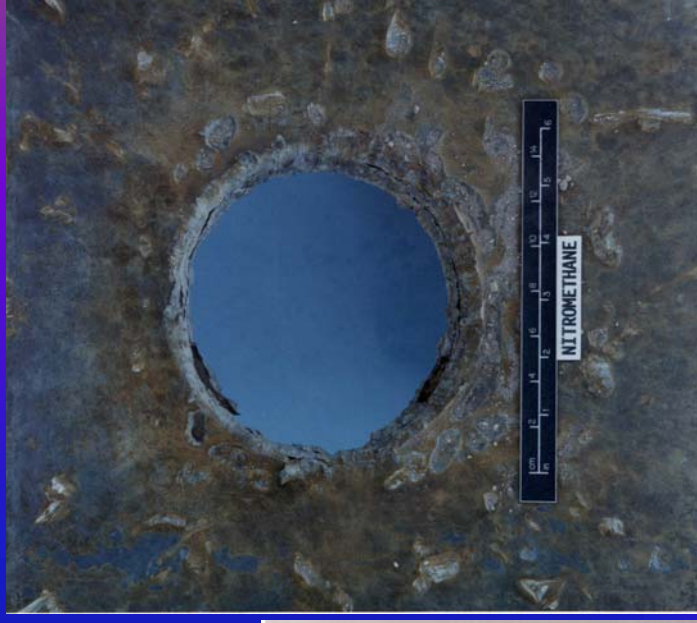


# 7.2.2.2.1 MCGT Photos



Test Article

Negative Result



Positive Result  
(Nitromethane)

# Course Outline

- ✓ Introduction
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    - PPE
    - Detectors/Monitors
- ◆ Course Evaluations



# 8.0 Hypergol Properties and Other Information

- ◆ See the *Properties & Other* Table in course book.

	HZ	MMH	UDMH	NTO
Chemical Formula	N <sub>2</sub> H <sub>4</sub>	CH <sub>3</sub> N <sub>2</sub> H <sub>3</sub>	(CH <sub>3</sub> ) <sub>2</sub> N <sub>2</sub> H <sub>2</sub>	N <sub>2</sub> O <sub>4</sub>
Boiling Point	237.5 °F	189.79 °F	144.45 °F	70.1 °F
Liquid Density	1.004 g/cm <sup>3</sup> (62.68 lb/ft <sup>3</sup> )	0.8702 g/cm <sup>3</sup> (50.397 lb/ft <sup>3</sup> )	0.7861 g/cm <sup>3</sup> (49.07 lb/ft <sup>3</sup> )	1.433 g/cm <sup>3</sup> (89.52 lb/ft <sup>3</sup> )

## 8.1 Other References

- ◆ Arch Chemicals, Inc.
  - Olin spin-off which manufactures the hydrazines.
  - See [www.archchemicals.com](http://www.archchemicals.com)
- ◆ Vicksburg Chemical Co. (former manuf.)
  - Filed for Chapter 11 in March 2002
- ◆ Mississippi Chemical Co. (current manuf.)
- ◆ Defense Energy Support Center (DESC)
  - See [www.desc.dla.mil](http://www.desc.dla.mil)
  - Email to [missilefuelsinfo@dla.mil](mailto:missilefuelsinfo@dla.mil)
  - (210) 925-2488 – technical info
  - (210) 925-9950 – general info

## 8.1.1 Other References

- ◆ AIAA Special Report SP-084-1999: Fire, Explosion, Compatibility, and Safety Hazards of Hypergols - **Hydrazine**
- ◆ AIAA Special Report SP-085-1999: Fire, Explosion, Compatibility, and Safety Hazards of Hypergols - **Monomethylhydrazine**
- ◆ AIAA Special Report SP-086-2001: Fire, Explosion, Compatibility, and Safety Hazards of **Nitrogen Tetroxide**
  - Available as PDF or hardcopy at <http://store.aiaa.org/>
    - Cost is \$49.95 (\$39.95 members)
  - Free to NASA personnel and NASA.gov contractors



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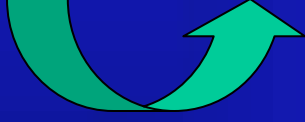
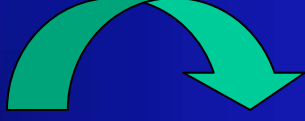
[Accessibility Statement](#)

## 8.2 Fluid Specifications

- ◆ Most specifications are based on Military Specifications
  - MIL-PRF-26536E (Hydrazine)
  - MIL-PRF-27404B (MMH)
  - MIL-PRF-25604C (UDMH)
  - MIL-PRF-26539D (NTO)
- Updated every 5 years, review process requires ~1 year

## 8.2 Fluid Specifications

- ◆ Military Specifications



- ◆ Shuttle  
SE-S-0073
- ◆ Space Station  
SSP-30573

## 8.2 Fluid Specifications

- ◆ What is covered?
  - Assay or purity
  - Concentrations of common contaminants
  - Appearance requirements
  - Allowable ranges of additives
  - Some contaminants of concern may not be covered
- ◆ May also include:
  - Different grades of propellants
  - The suggested method of analysis, calculation, and reporting

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## 8.2.1 Fluid Specification-Hydrazine

<u>Properties</u>	<u>Standard Grade</u>	<u>Monopropellant Grade</u>	<u>High Purity Grade</u>
Hydrazine (% by wt)	98 min	98.5 min	99.0 min
Water (% by wt)	1.5 max	1.0 max	0.5 – 1.0
Ammonia (% by wt)	---	---	0.3 max
Particulate (mg / L)	10 max	1.0 max	1.0 max
Chloride (% by wt)	---	0.0005 max	0.0005 max
Aniline (% by wt)	---	0.50 max	0.003 max
Iron (% by wt)	---	0.002 max	0.0004 max
Nonvolatile Residue (% by wt)	---	0.005 max	0.001 max
Carbon dioxide (% by wt)	---	0.003 max	0.003 max
OVCN	---	0.02 max	0.005 max

## 8.2.2 Fluid Specification - MMH

### Properties

Monomethylhydrazine  
(% by wt)

Water  
(% by wt)

Particulate  
(milligrams per liter)

### Limits

98.3 min

1.5 max

10 max

## 8.2.3 Fluid Specification - UDMH

Property	Limit
UDMH (% by weight)	98 min
Water (% by weight)	0.3 max
Amines (% by weight)	1.5 max
N-Nitrosodimethylamine (% by weight)	0.01 max
Chloride (% by weight)	0.003 max
Density (g/mL)	0.795 to 0.797
Particulate (mg/L)	10 max

## 8.2.4 Fluid Specification - MON3

Property	Limits
N <sub>2</sub> O <sub>4</sub> Assay (% by weight)	---
NO Assay (% by weight)	2.5 min to 3.0 max
N <sub>2</sub> O <sub>4</sub> + NO (% by weight)	99.5 min
Water Equivalent (% by weight)	0.17 max
Chloride Content (% by weight)	0.040 max
Iron Content (ppm)	1.0 max
Nonvolatile Residue	10 mg / liter

# Course Outline

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  - ✓ Reactivity Hazard
  - ✓ Fire Hazard
  - ✓ Explosion Hazard
  - ✓ Hypergol Properties, References & Other Information
- ◆ Step 4 - Manage the Risks
  - Primary Controls
    - Design
      - Material Compatibility
    - Build Up
    - Operation
  - Secondary Controls
    - PPE
    - Detectors/Monitors
- ◆ Course Evaluations

# Step 4 - Manage the Risks

- ◆ Primary (Engineering) Controls
  - Design
  - Build Up
  - Operation
- ◆ Secondary Controls
  - Personal Protective Equipment (PPE)
  - Detectors/Monitors

# 9.0 Design Controls

- ◆ Siting
- ◆ Paperwork
- ◆ Hardware

## 9.1 Siting (Where do we put it?)

- ◆ Objective/mission
- ◆ Life span
- ◆ Quantities
- ◆ Wind corridor
- ◆ Access controls
- ◆ Emergency Equipment
- ◆ Ignition Sources
- ◆ Fire Protection
- ◆ Secondary Containment
- ◆ Shock / Vibration Isolation



## 9.1.1 Objective / Mission

- ◆ What must the system do?
  - What resources are required?
  - What infrastructure is required to support?
- ◆ What is the intended use?
  - Fuel or oxidizer or both?
  - One shot or continuous use?

## 9.1.2 Life Span

- ◆ How long is the system going to be in service?
  - Temporary systems tend to last longer than the engineers that design them

## 9.1.3 Quantities

- ◆ What quantities of propellants are to be used?
  - Lab scale vs production scale
- ◆ What are the quantity-distance requirements?

## 9.1.4 Wind Corridor

- ◆ What are the prevailing winds?
- ◆ Establish a safe wind corridor to ensure personnel will not be exposed to released vapors
  - Wind speed and direction

## 9.1.5 Access Controls

- ◆ Hypergol systems should be located in areas that offer controlled-access entry
- ◆ Access controls include barricades, exclusion areas, public address announcements, and warning signs, lights, and/or sirens



**Area Access Control Light & Sign**

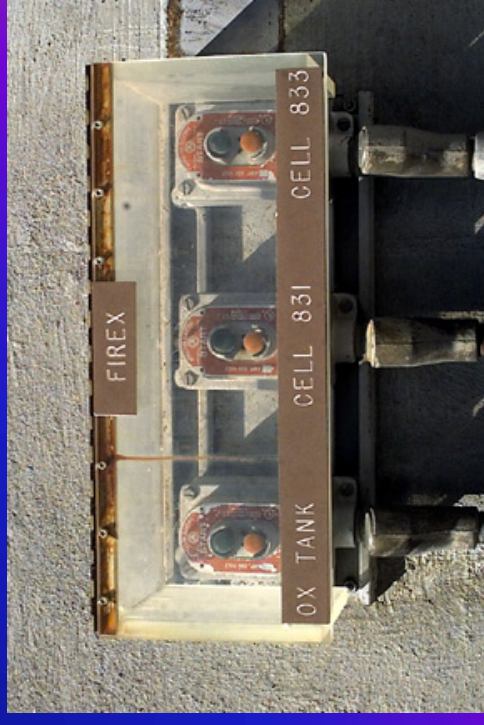
## 9.1.6 Emergency Equipment

- ◆ Emergency shower, eyewash, breathing-air source, alarm activation, and fire suppression systems should be available near hypergol systems
  - If it's not close by then it won't get used



## 9.1.7 Fire Protection

- ◆ Incorporate fire alarms, fire and/or smoke detectors, and fire extinguisher systems into the facility or system design
  - Must know when and how to use



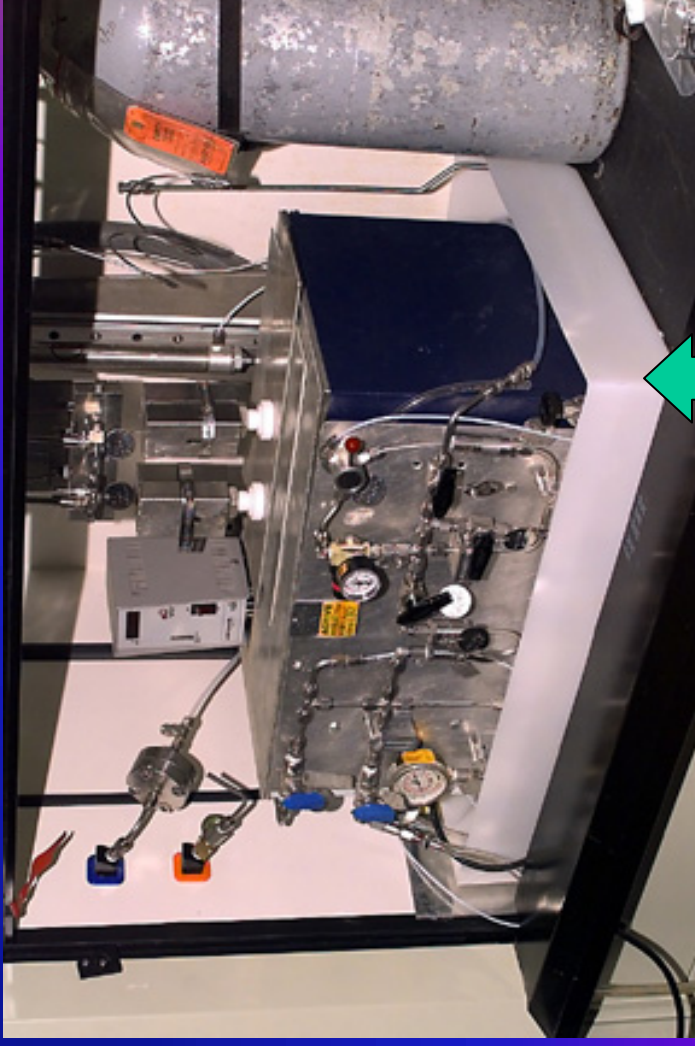
## 9.1.8 Ignition Sources

- ◆ In laying out the facility/system design, keep ignition sources away from hypergol systems and hypergol vents
  - Open flames
  - Hot surfaces
  - Sparks, arcs, electrical discharges
  - Incompatible materials



## 9.1.9 Secondary Containment

- ◆ Include provisions for secondary containment of hypergols around storage systems and test systems
- ◆ Containment should be sufficient to capture any released liquid and an appropriate volume of water to dilute the spill





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# 9.0 Design Controls

- ✓ Siting
- ◆ Paperwork
- ◆ Hardware

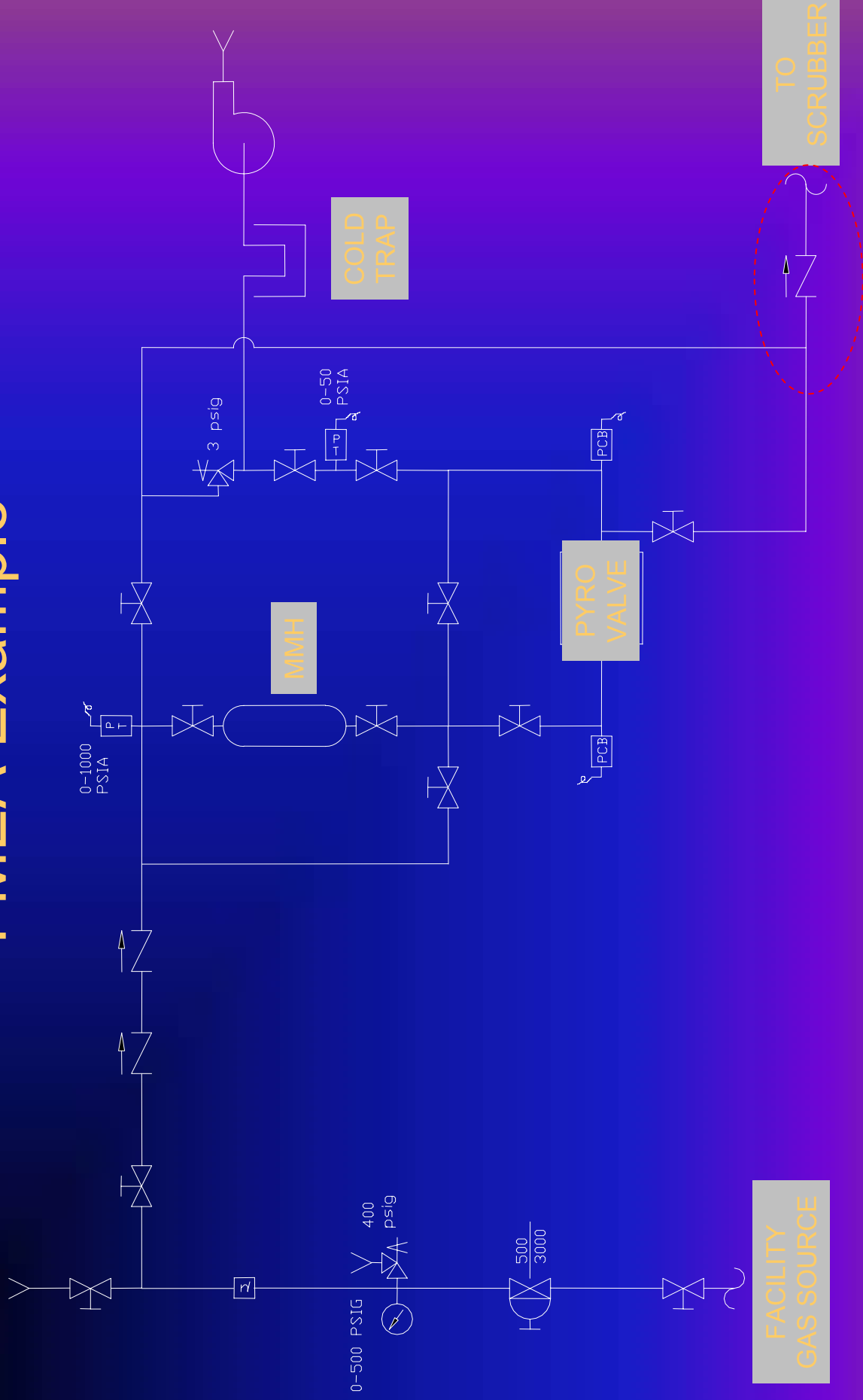
## 9.2 Paperwork (How do we describe it?)

- ◆ Design Reviews
- ◆ Failure Modes Effects Analysis (FMEA)
- ◆ Hazards Analysis
- ◆ System Safety Analysis
- ◆ Readiness Reviews
- ◆ Process Safety Management (PSM)
- ◆ Procedures
  - Build up
  - Operating
  - Maintenance
  - Emergency

## 9.2.1 FMEA Purpose

- ◆ Ensures systems are designed such that, at a minimum, two components must fail to produce a hazardous situation (single fault tolerant)
- ◆ In case of power loss, assures that valves fail in a safe mode to contain propellant or vent system pressure
- ◆ Design the system to preclude entrapment of liquid propellant in low points or in places that cannot be purged or evacuated

# FMEA Example

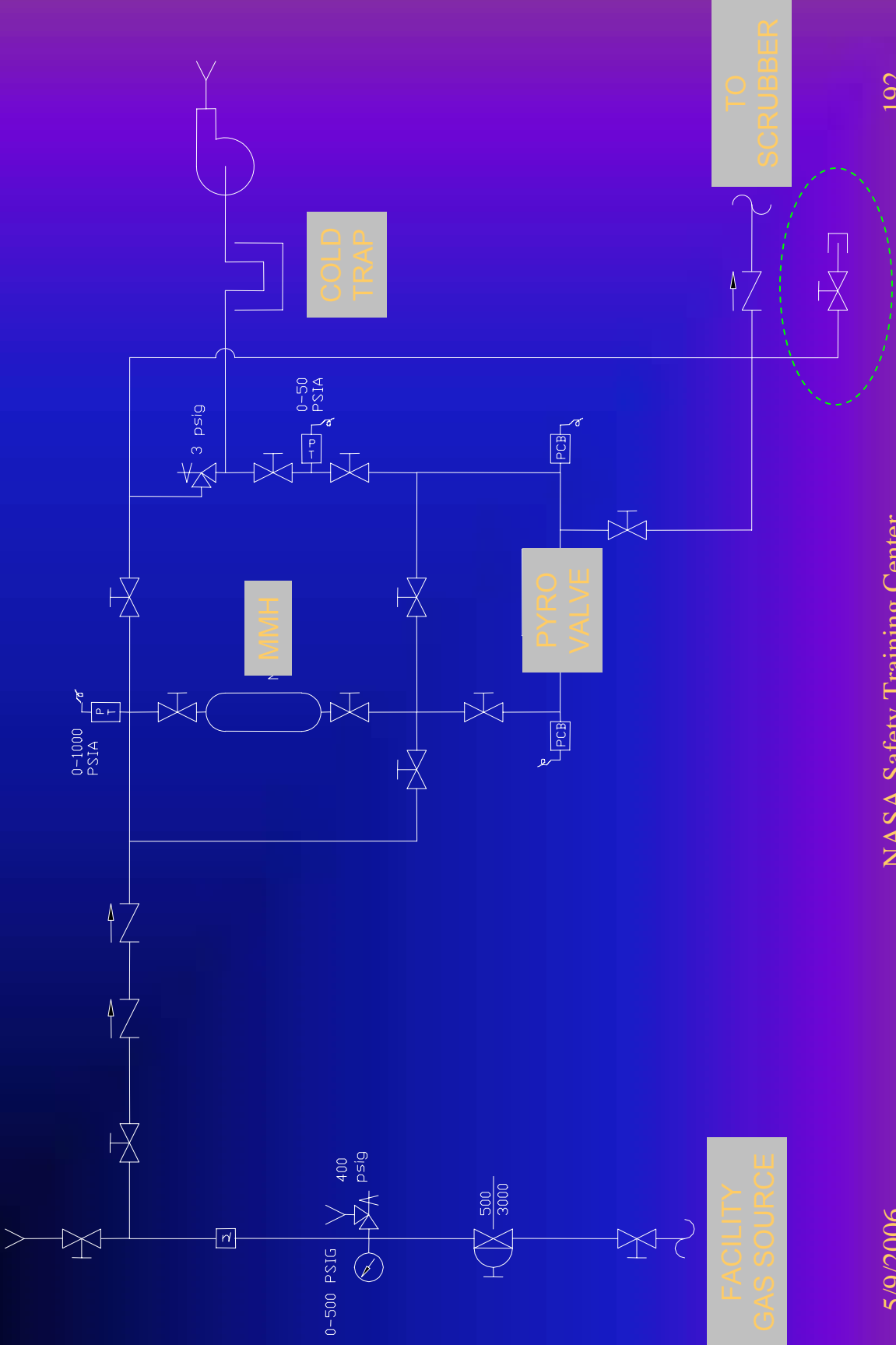


# FMEA Example

COMPONENT	FAILURE MODE	FAILURE EFFECT	CORRECTIVE ACTION AND REMARKS
CV-80X-BF11	Fails Open / Leaks Internally	Loss of isolation from ox drain system	.....
	Fails Closed	Unable to vent system through this valve	.....
	Leaks Externally	Vents oxidizer to cell atmosphere	.....



# Resulting Design Change



## 9.2.2 Process Safety Management

29 CFR 1910.119

- ◆ Purpose is to prevent or minimize the consequences of catastrophic releases of toxic, reactive, flammable, or explosive chemicals.
- ◆ Threshold quantities
  - **UDMH** 1000 lbs
  - **MMH** 100 lbs
  - **Hydrazine** - not listed (assumed 100 lbs)
  - **NTO** 250 lbs

## 9.2.2.2 PSM Elements

- ◆ Employee Participation
- ◆ Process Safety Info.
- ◆ Process Hazard Analysis
- ◆ Operating Procedures
- ◆ Training
- ◆ Contractors
- ◆ Pre-Startup Safety Review
- ◆ Mechanical Integrity
- ◆ Hot-Work Permit
- ◆ Management of Change
- ◆ Incident Investigation
- ◆ Employee Planning & Response
- ◆ Compliance Audits
- ◆ Trade Secrets

# 9.0 Design Controls

- ✓ Siting
- ✓ Paperwork
- ◆ Hardware

## 9.3 Hardware (What do we use?)

- ◆ Compatible Materials
  - Metals
  - Softgoods
  - Lubricants
- ◆ Components
  - Various types
- ◆ Storage and Transport Containers

## 9.3.A Material Compatibility

- ◆ The Material Compatibility Assessment
- ◆ Test Methods
- ◆ Materials for Hypergol Service

### 9.3.A.1 What is a Material Compatibility Assessment?

- ◆ A systematic consideration of how a material would be used and whether it should be used in contact with a reactive fluid, based on experience and applicable data.

## 9.3.A.1.1 Why Perform a Material Compatibility Assessment?

- ◆ Hydrazine fuels and NTO react with many materials that are desirable from a design standpoint.
- ◆ The question often is not, “Will they react?” but rather, “How fast?”
- ◆ A material compatibility assessment provides data to quantify the rates and types of reaction



## 9.3.A.1.2 Elements of a Material Compatibility Assessment

- ◆ Material and fluid designations
- ◆ Use environment(s)
- ◆ Possible fluid/material interactions
- ◆ Candidate compatibility tests
- ◆ Analysis of test results
- ◆ Final compatibility assessment

## 9.3.A.1.3 Material and Fluid Designations

- ◆ **Manufacturer / supplier**
- ◆ **Specification sheet**
  - Normal range of use specifications
- ◆ **Chemical constituents / formulation information**
- ◆ **Processing parameters**
  - Heat treats, molding parameters, etc.
- ◆ **MSDS**

## 9.3.A.1.4 Use Environments

- ◆ Temperature
- ◆ Pressure
- ◆ Flow Rate
- ◆ Duration of Contact
- ◆ Surface Area / Geometry
- ◆ Worst-case Extremes

## 9.3.A.1.5 Properties Possibly Affected by Fluid/Material Interactions

- ◆ Physical Properties
  - Tensile, Compressive Strength
  - Dimensional Changes, Corrosion
  - Visual Appearance
  - Permeability
  - Weight
  - Hardness
  - Solubility
  - Moduli
  - Embrittlement
  - Tackiness
- ◆ Chemical Properties
  - Composition Change
  - Flammability
  - Surface Catalysis
  - Bulk Decomposition
  - NVR Developement
  - Particulate Development
  - Outgassing
  - Impact Sensitivity

## 9.3.A.1.6 Candidate Compatibility Tests

- ◆ Expose material to fluid under appropriate conditions
  - Measure Pressure
  - Measure Heat / Temperature
  - Changes in Physical and Chemical Properties
  - Measure Corrosion Rates
    - Electrochemistry
    - Post test measurements

## 9.3.A.2 Standard Compatibility Test

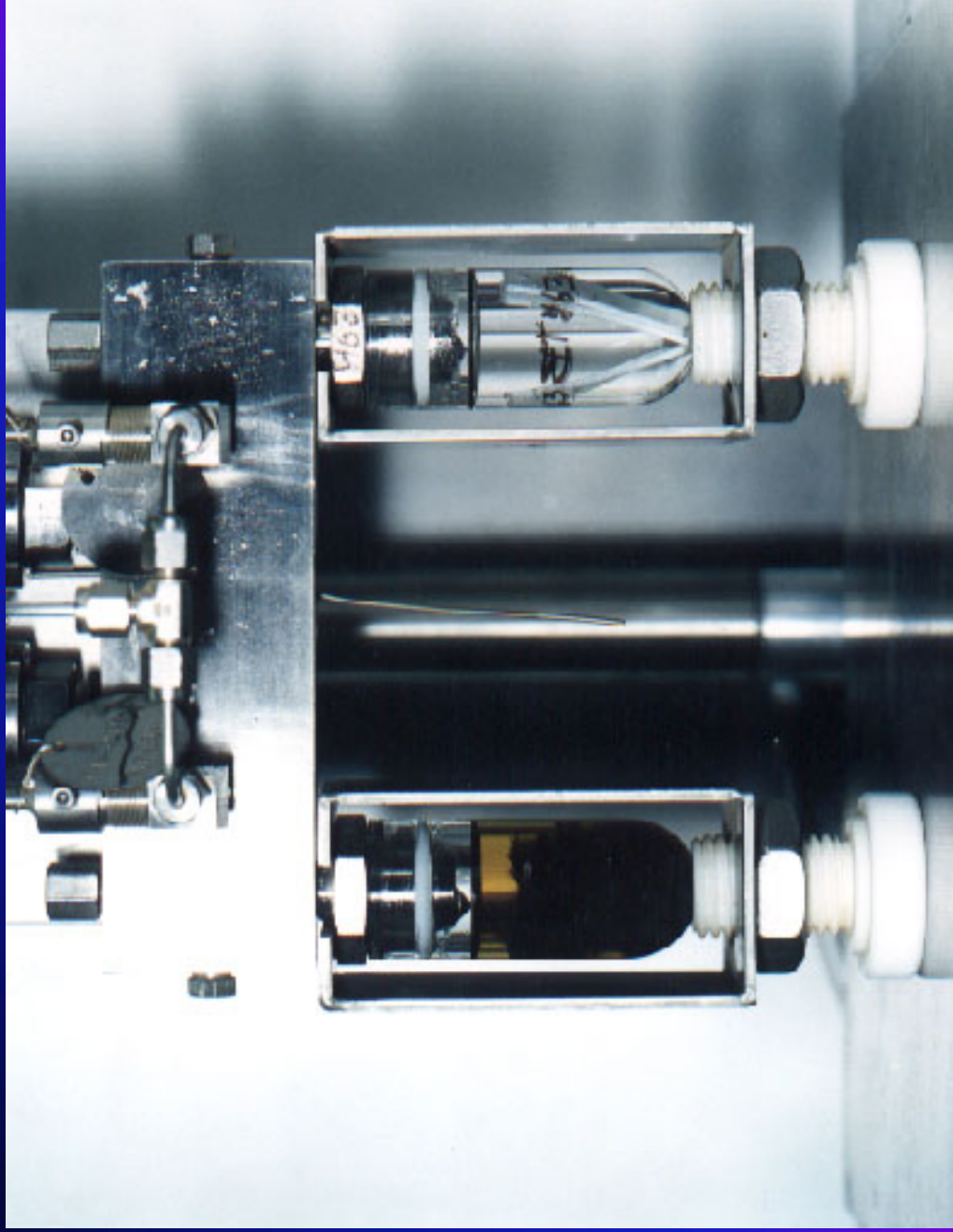
### Methods

- ◆ Differential Pressure Immersion Testing
- ◆ Microcalorimetry
- ◆ Accelerating Rate Calorimetry (ARC)

## 9.3.A.2.1 Differential Pressure Immersion Testing

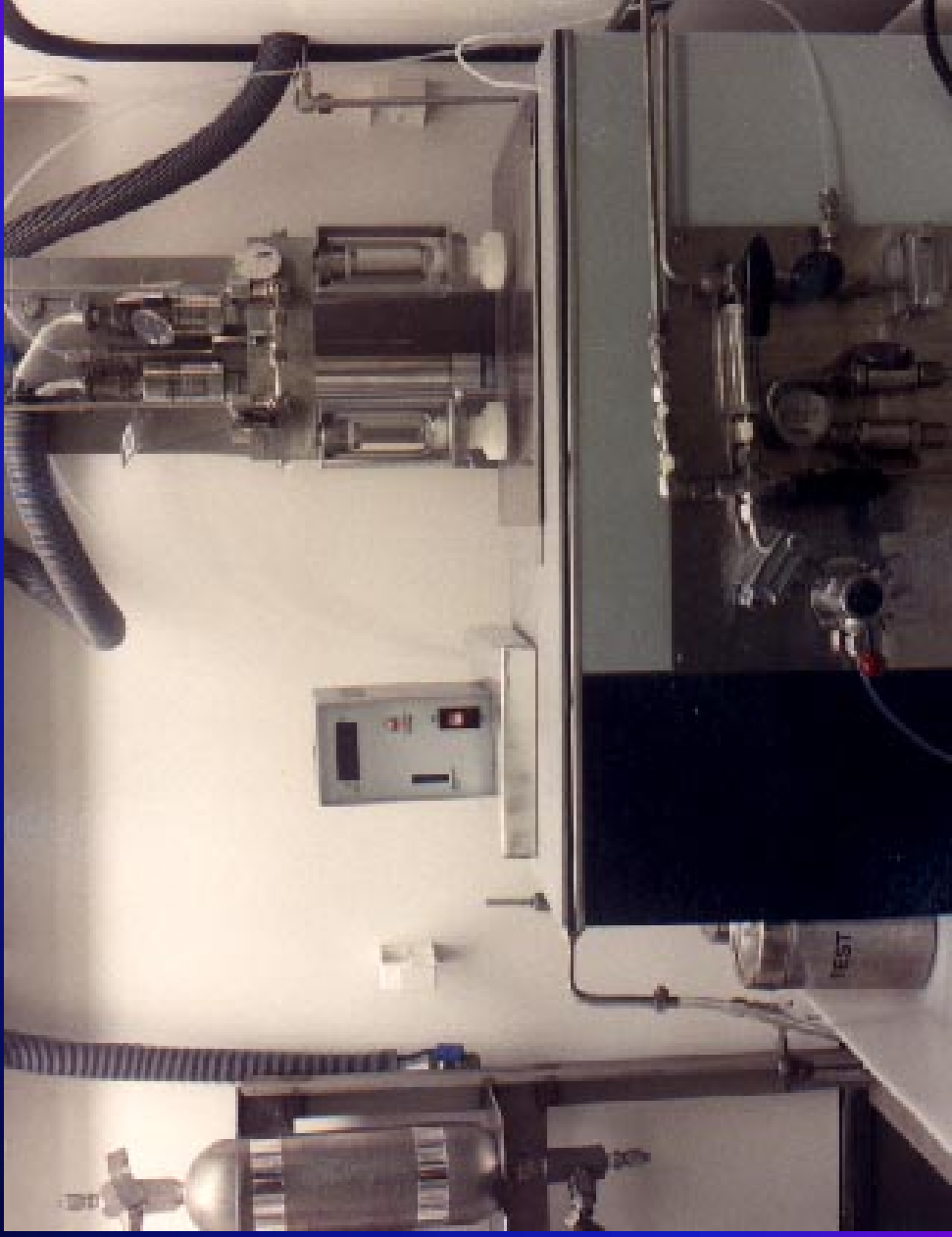
- ◆ NASA Technical Standard 6001 Test 15
  - Screening Test (“beaker” test)
  - Isothermal immersion at 71°C (160 °F)
  - Measure pressure of sample and reference material
  - Posttest analysis of material and fluid
  - Report results in system independent units
    - Standard cm<sup>3</sup> gas / cm<sup>2</sup> material
    - Mass of contaminant in fluid

# Test 15 Samples





# Test 15 System

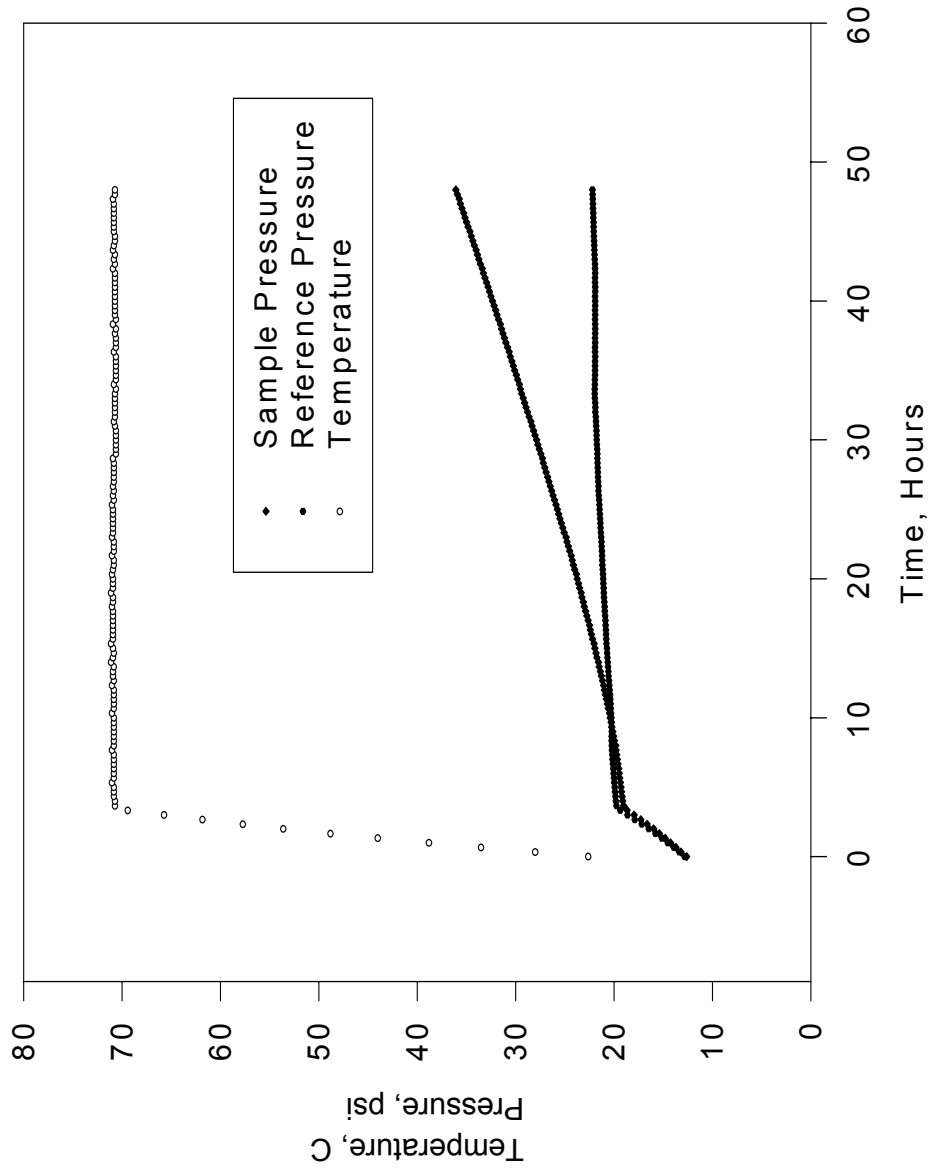


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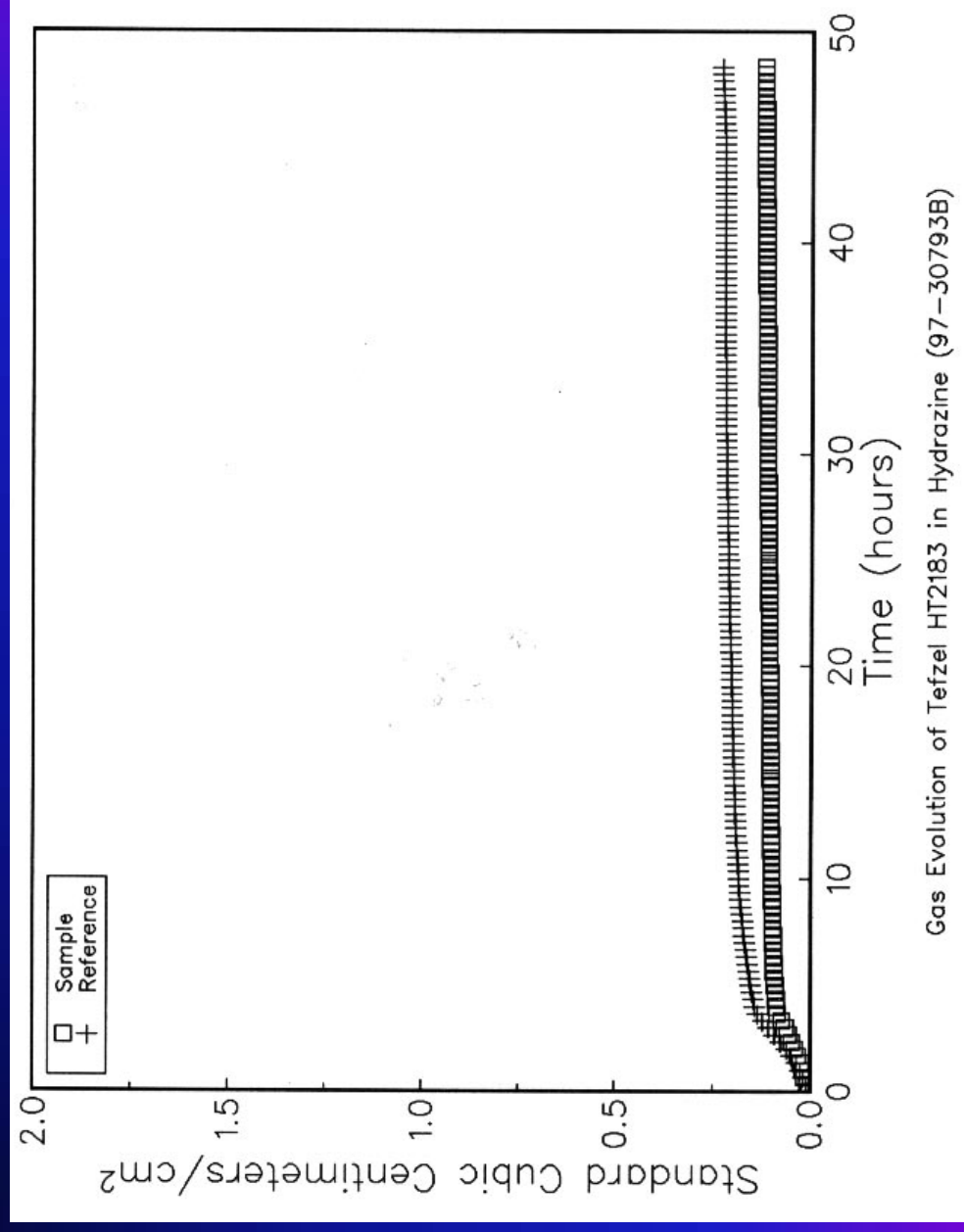
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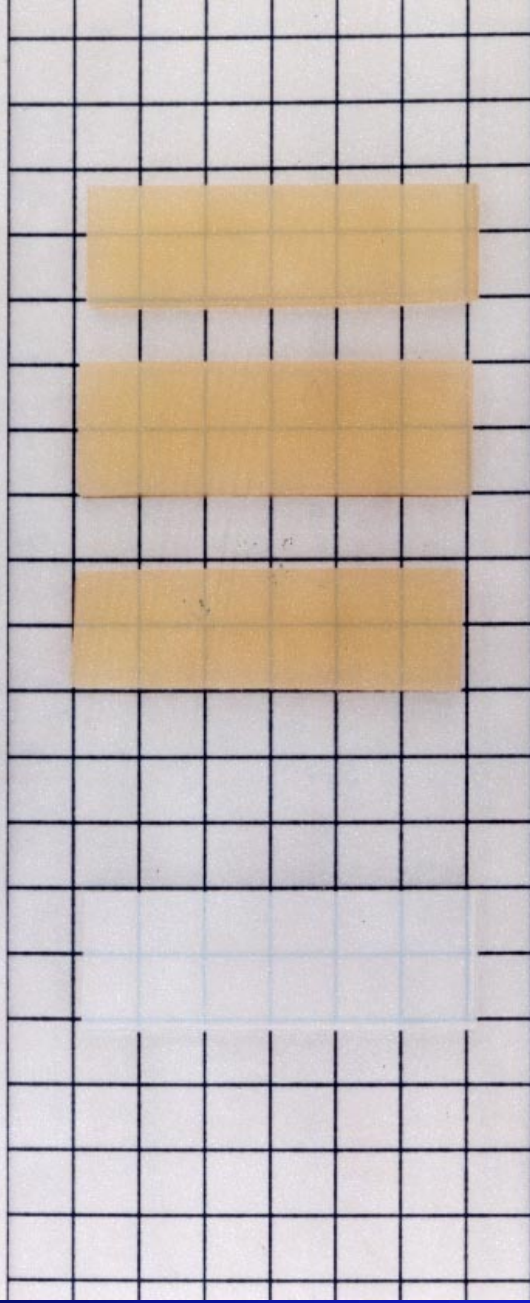
## Iron Powder Test 15



# Gas Generation from Tefzel



**WSTF NO. 97-30793**  
**Tefzel HT2183**  
**NHB 8060.1C TEST 15**  
**Liquid N<sub>2</sub>H<sub>4</sub>**



**COMPARISON**

**POSTTEST**

**1 Grid Length = 0.5 cm**

## 9.3.A.2.2 Posttest Analysis - Material

- ◆ Visual Observations
  - Discoloration
- ◆ Mass, Dimensions
  - Swelling
- ◆ Mechanical Properties
  - Hardness
  - Tensile strength
  - Elongation
  - Compression set
  - Compressive strength

### 9.3.A.2.3 Posttest Analysis - Fluid

- ◆ Color / Clarity
- ◆ Fluid Purity
- ◆ Carbon Dioxide
- ◆ Non-volatile Residue (NVR)
- ◆ Metals
- ◆ Halides - Anions

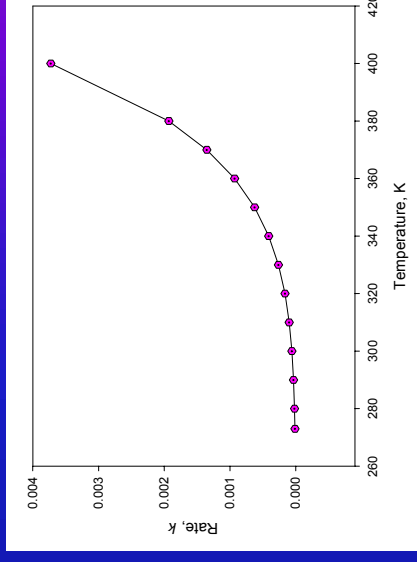
## Effect of Temperature on a Reaction Rate

- ◆ Raise temperature to match “worst-case” conditions
- ◆ Raise temperature to accelerate the effect
- ◆ Test at multiple temperatures to determine the temperature dependence of a reaction

# Effect of Temperature on a Reaction Rate

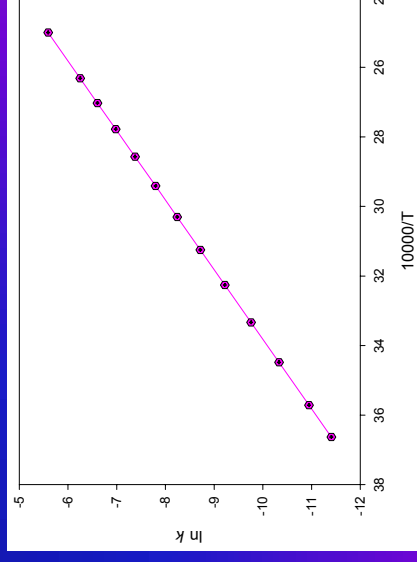
- ◆ Arrhenius Equation:

$$k = Ae^{E_a/RT}$$



- ◆ Log (ln) of both sides:

$$\ln k = -\frac{E_a}{R} \frac{1}{T} + \ln A$$





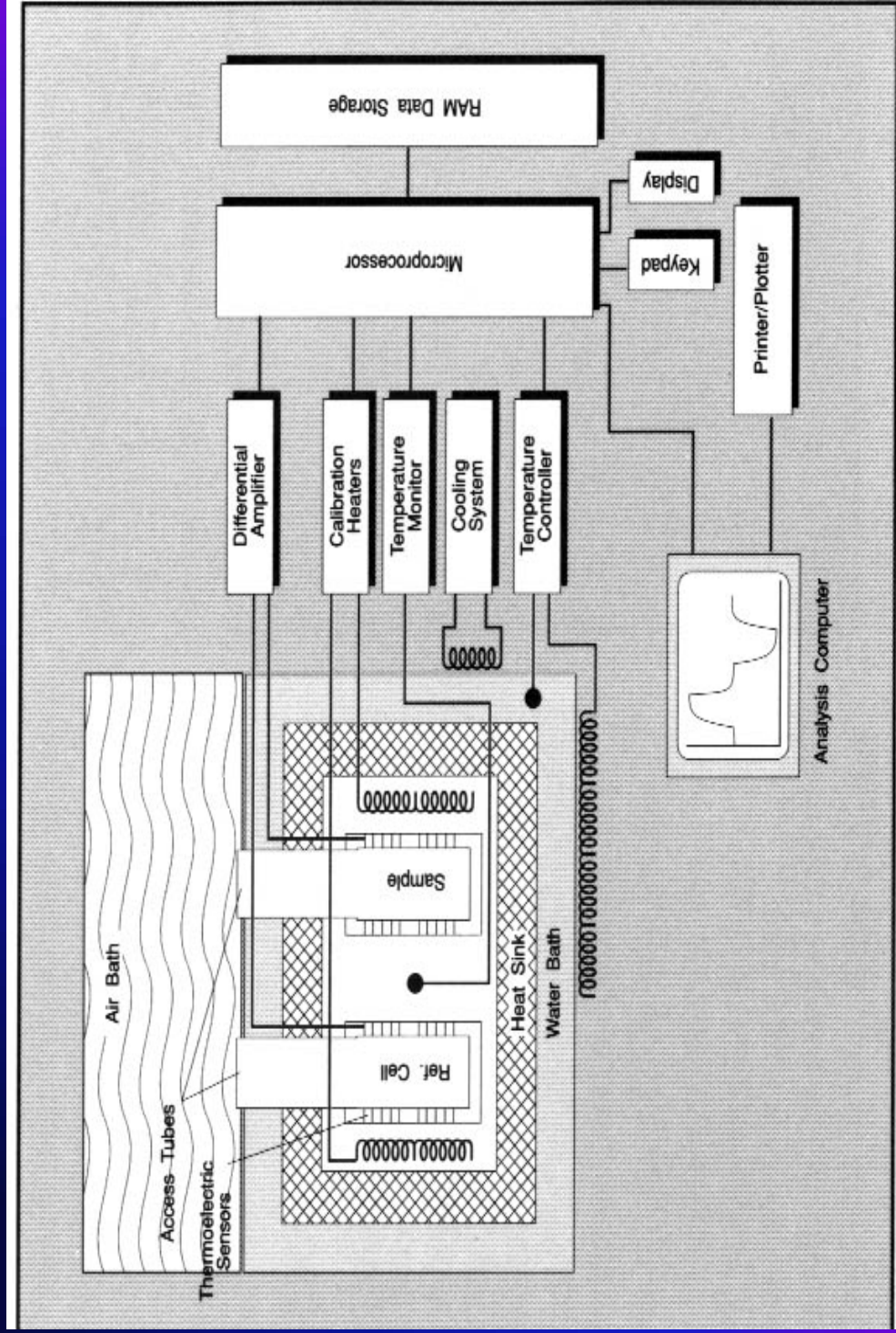
## 9.3.A.2.4 Microcalorimetry

- ◆ Isothermal
- ◆ Measure heat flow from sample to a heat sink
- ◆ Sample size up to 30 mL
- ◆ Heat from reaction of fluid with material

## 9.3.A.2.5 Microcalorimetry

- ◆ Ultra-sensitive, Real Time Kinetic Measurements
- ◆ Temperature Range 10 to 70 °C
- ◆ Thermal Activity  $\pm 2 \mu\text{Watts}$
- ◆ Kinetic Parameters  $E_a$ , A
- ◆ 24 Hours / Measurement on 3 samples

# Microcalorimeter



# Microcalorimeter

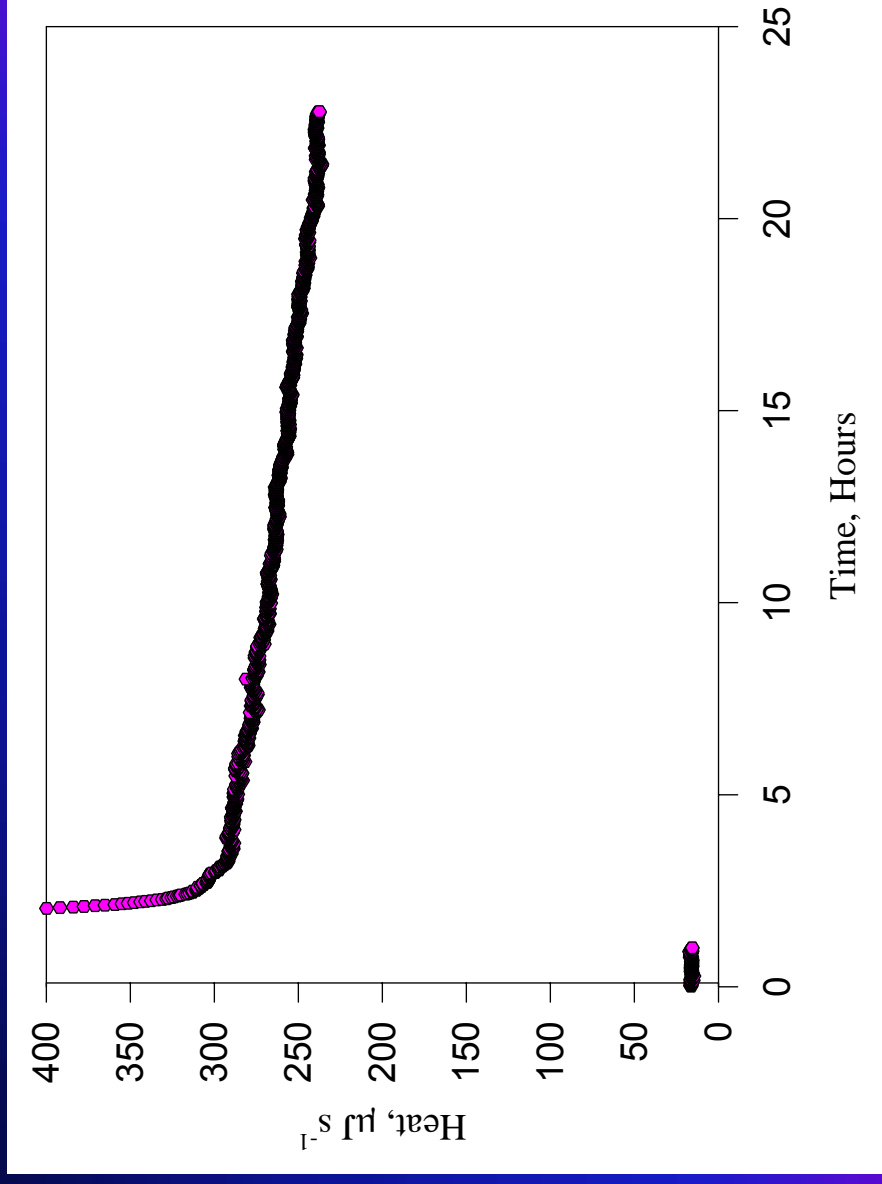


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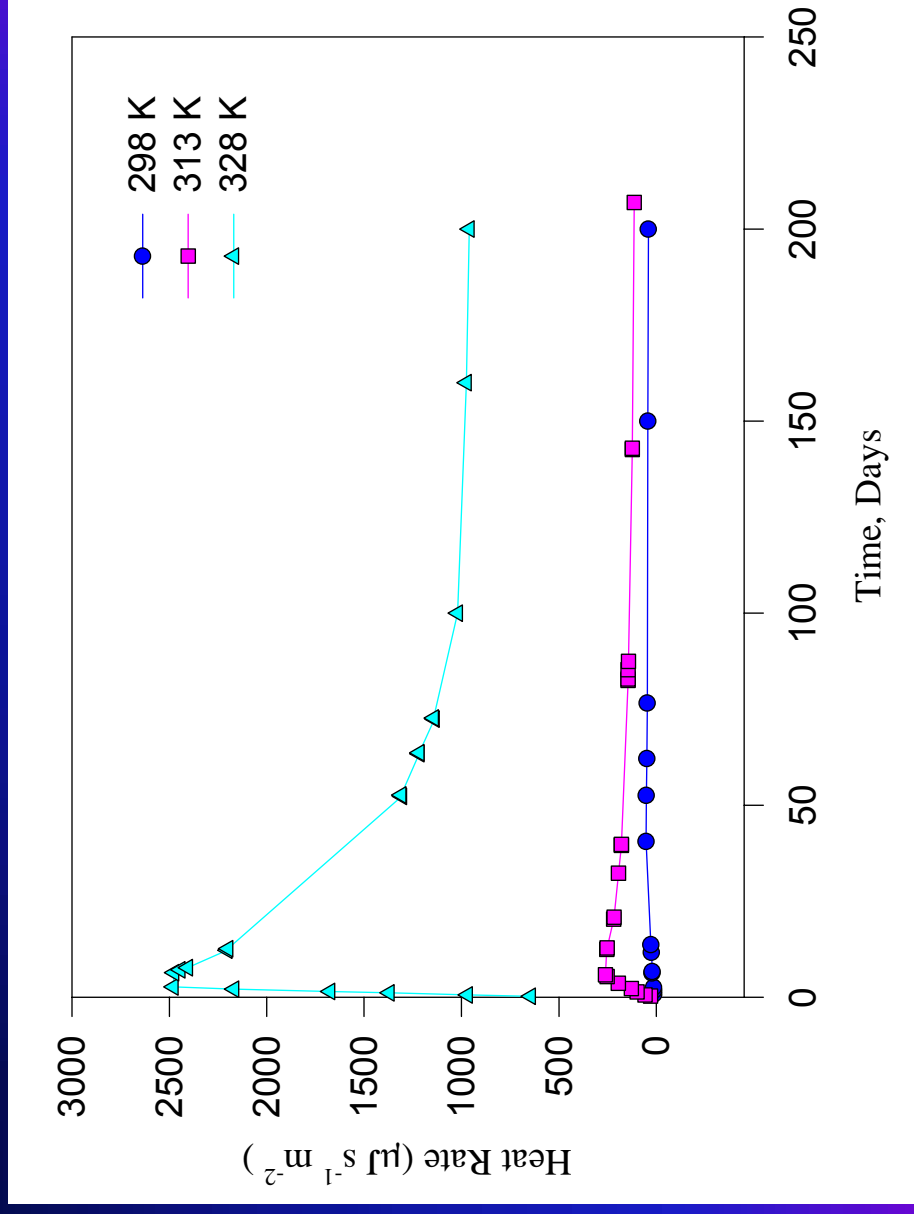
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# Microcal Data Trace



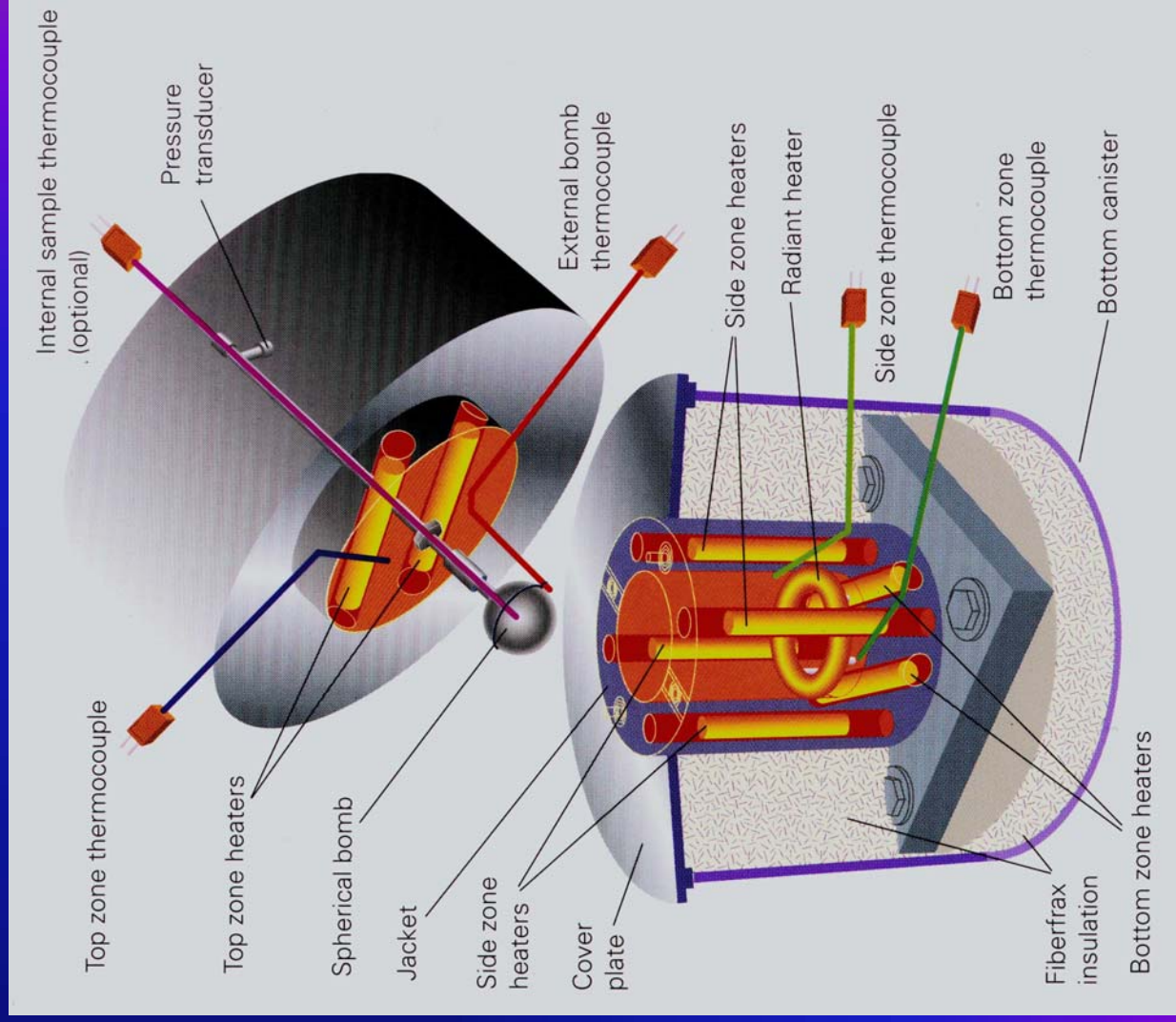
# Microcalorimetry Measurements for Inconel 600



## 9.3.A.2.6 Accelerating Rate Calorimetry

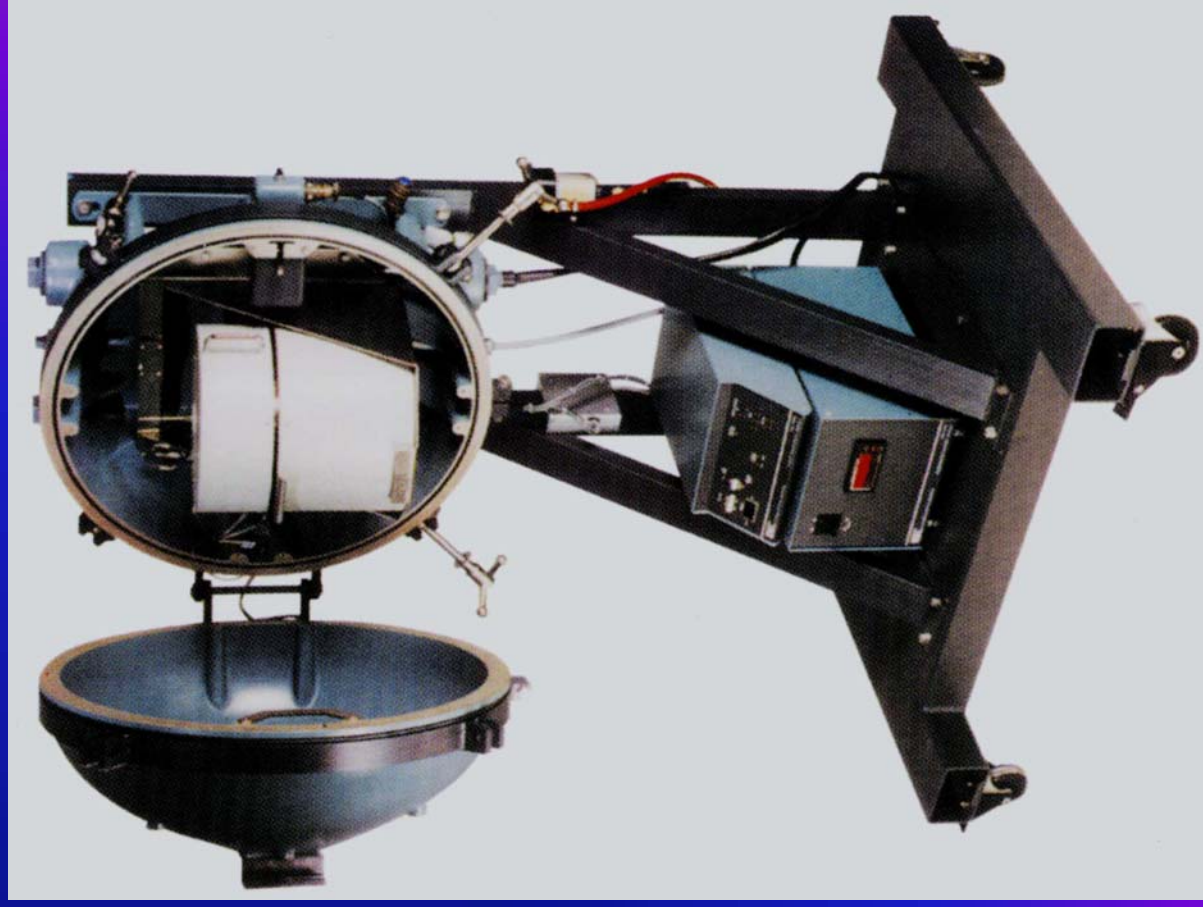
- ◆ Measures Adiabatic Self-Heating Rate
  - Surface Catalyzed Reaction
  - Kinetic Parameters,  $E_a$ ,  $A$
  - Extrapolate to Lower Temperatures
- ◆ Temperature Range 120 to 300 °C
- ◆ Testing With Thermally Stable Materials
- ◆ Relative Reactivity of Materials

# ARC Schematic

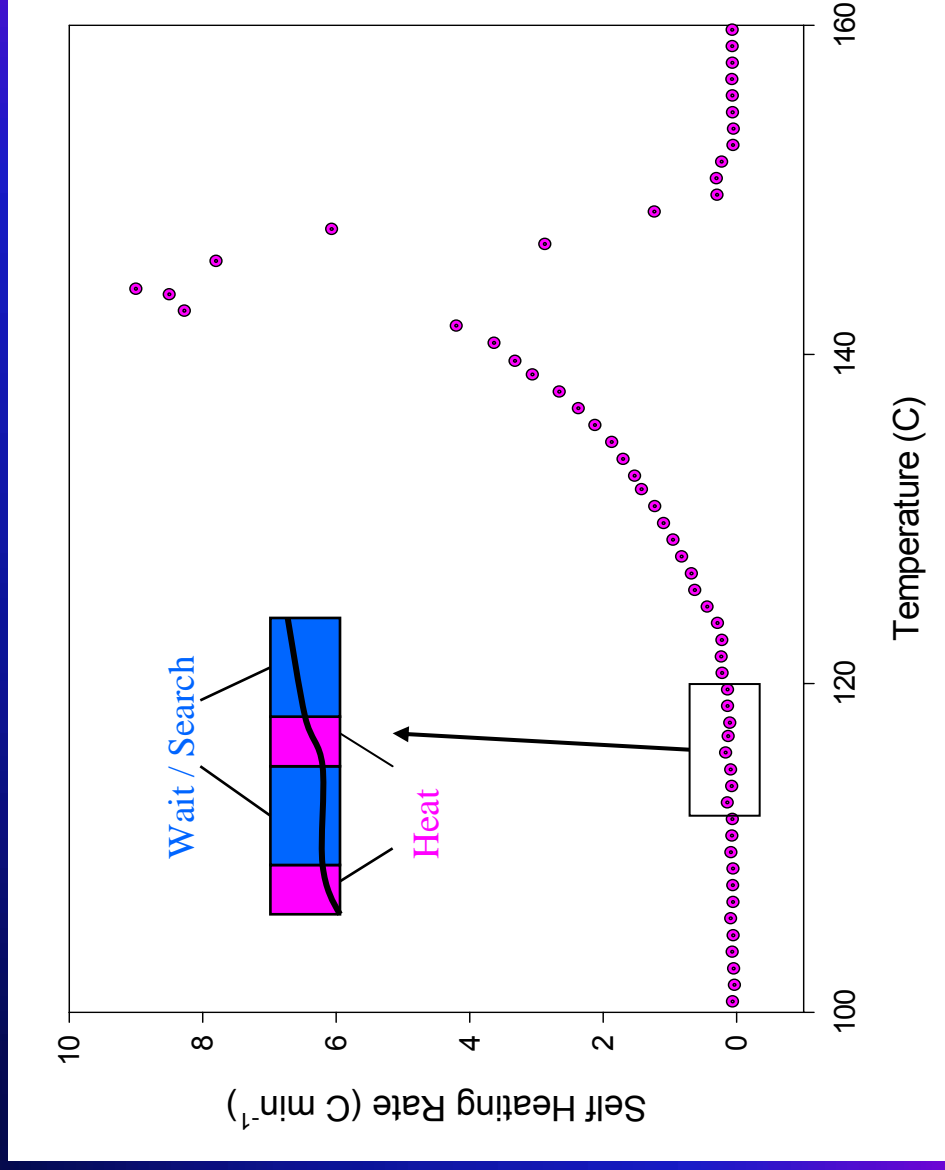




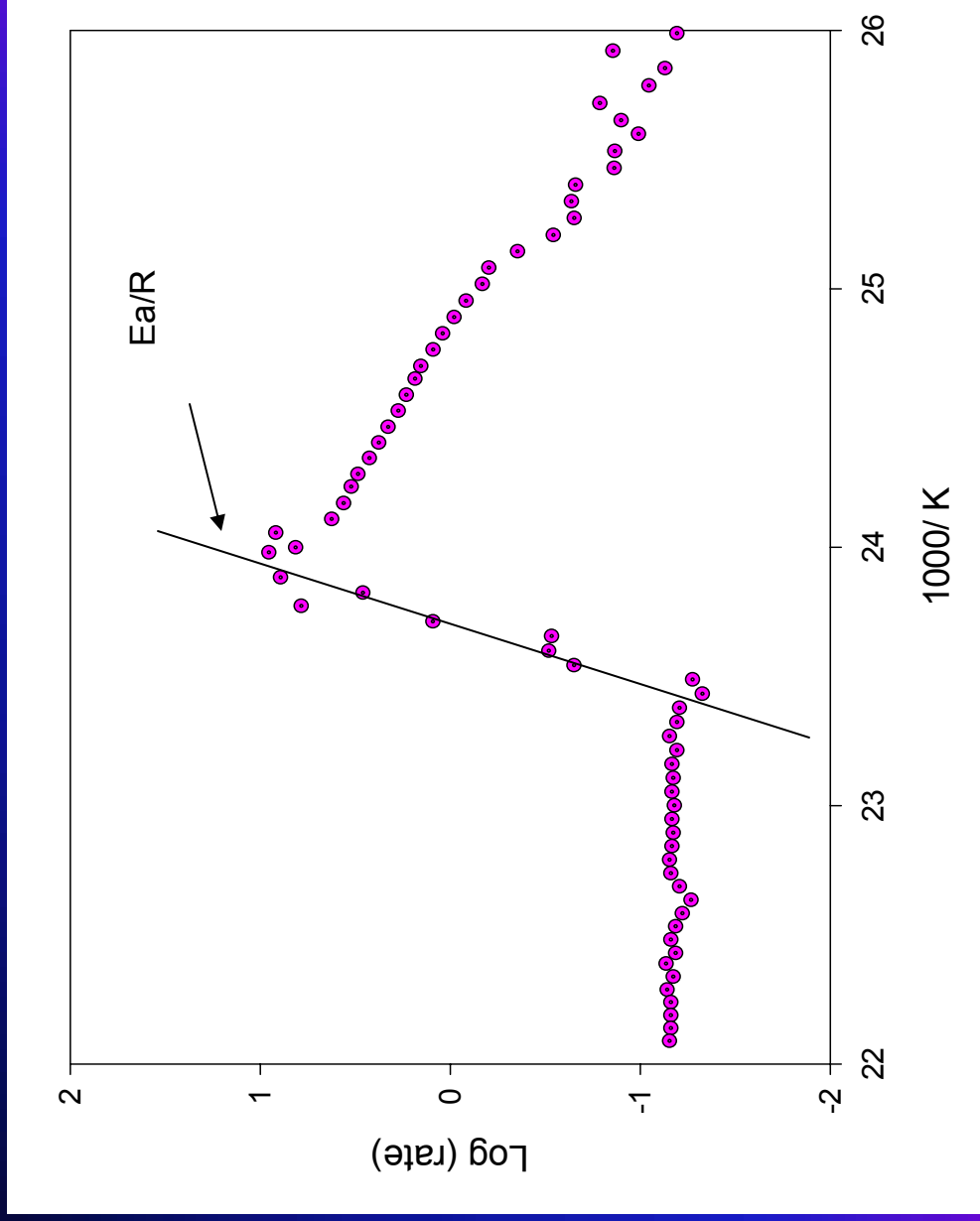
# ARC System



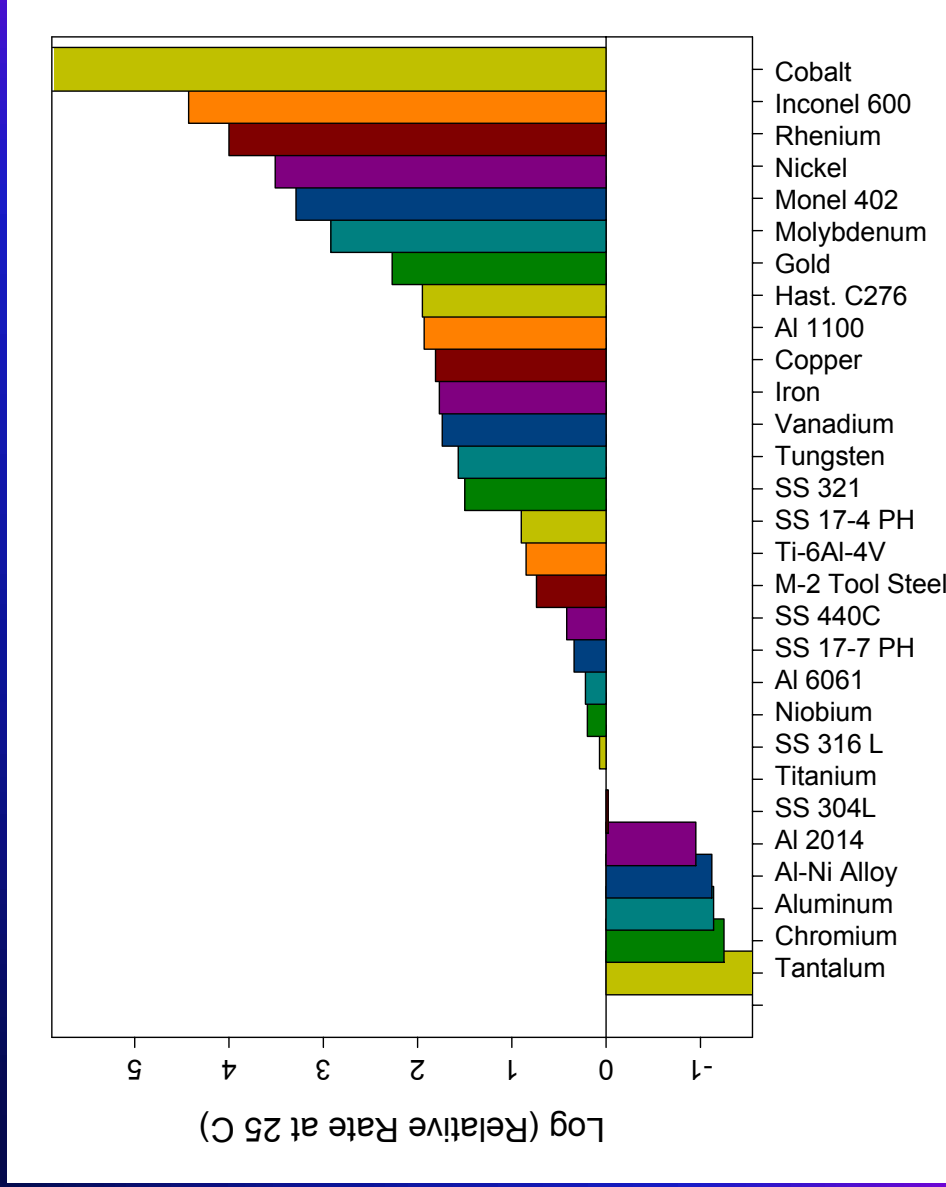
# ARC Data Trace



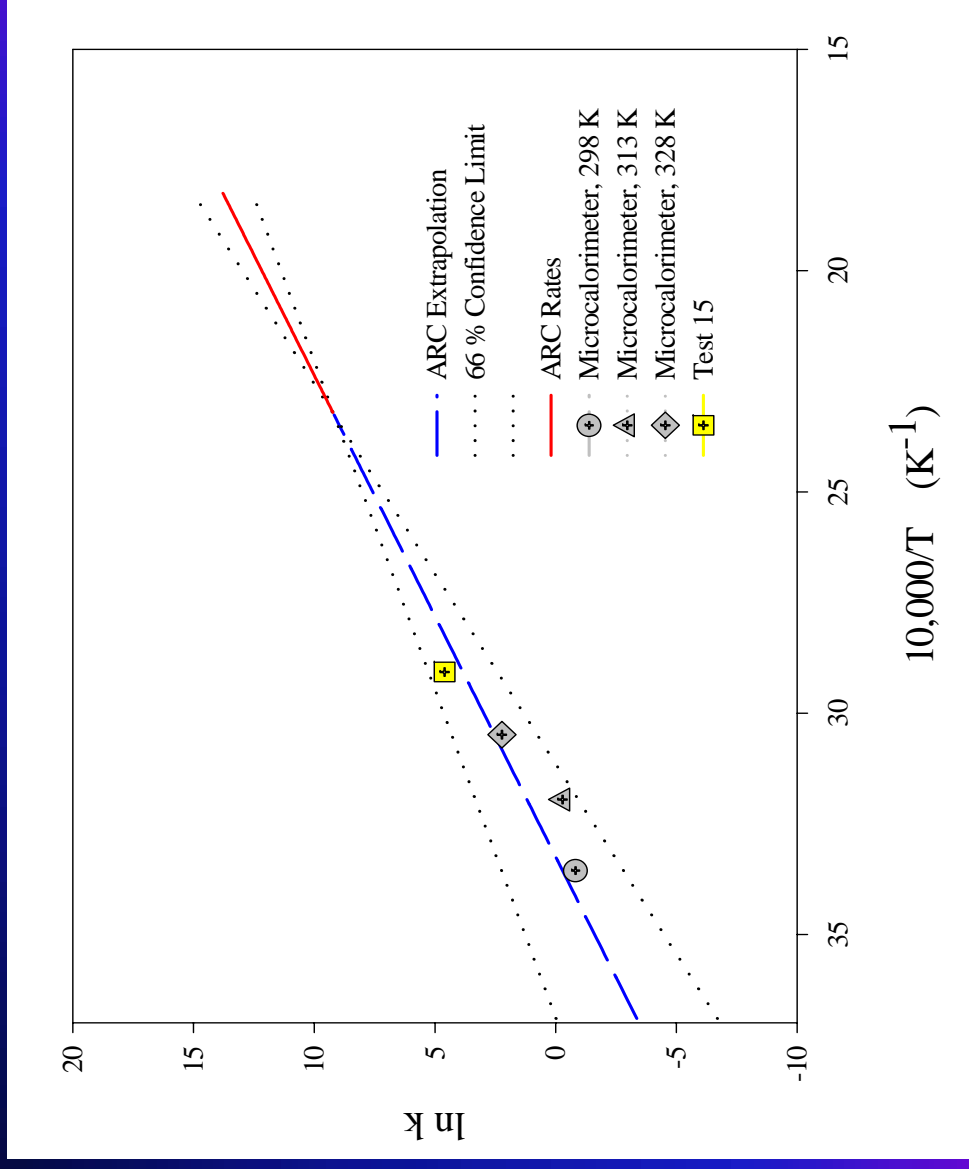
# ARC Plot



# Relative Decomposition Rates in Hydrazine



# Comparison of Rates by Technique



## 9.3.1.1 Approved Materials for Hydrazine

### Service at WSTF

Constant contact, 120 °F or less

- ◆ **Metals**
  - 304 and 316 Stainless Steel
  - 17-4 PH Stainless Steel
  - Monel 400 and 500
  - Ti 6-Al 4-V
- ◆ **Non-metals**
  - Teflon (TFE, PFA, FEP)
  - Fluorogreen (glass-filled Teflon)
  - AFE 332 (white EPR)
  - EPR 515
  - Kalrez 1045
  - Pyrex Glass
  - Polyethylene
  - Polypropylene
  - PEEK 450G (poly(etheretherketone))
- ◆ **Lubricants**
  - Braycote 601
  - Krytox 240AC
  - Fomblin Y25
  - Duoseal Pump Oil
  - Apiezon L

## 9.3.1.2 Approved Materials for NTO

### Service at WSTF

Constant contact, 120 °F or less

- ◆ **Metals**
  - 300 series Stainless Steel
  - Monel 500
  - Ti 6-Al 4-V
- ◆ **Lubricants**
  - Braycote 601
  - Krytox 240AC
  - Fomblin Y25
- ◆ **Non-metals**
  - Teflon (TFE and FEP)
  - Kalrez 1045
  - Pyrex Glass
  - Fluorogreen (glass-filled Teflon)

### 9.3.1.3 Softgood Considerations

- ◆ Choosing the right softgood
- ◆ Softgood integrity
- ◆ Absorbance and offgassing



### 9.3.1.3.1 Choosing the Right Softgood

- ◆ Material compatibility assessment
  - Engineering responsibility
- ◆ Compatible yes, but right for the application? - maybe not
  - Former WSTF policy - “Teflon only”
    - Indoor/outdoor temperature extremes
    - Cold flow

## Choosing the Right Sized Softgood

- ◆ Need to consider potential swelling of softgoods
  - Thermal
  - Absorption
- ◆ Effect
  - Seal material damage
  - Possible system contamination

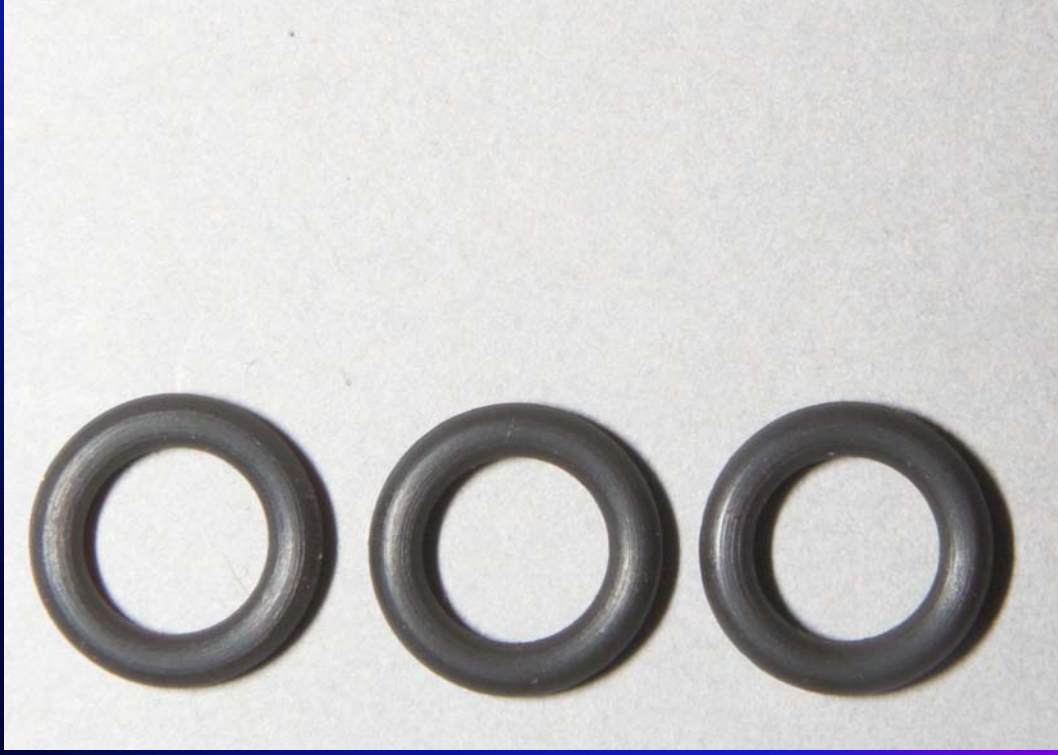


**Kalrez 1045 o-ring**

## 9.3.1.3.2 Softgood Integrity

- ◆ How do you know what you have is what has been approved?
  - Assuring formulation consistency
    - Manufacturer certifications
    - Batch-lot testing
    - Kel-F 81
    - Markings
      - EPR vs Buna N

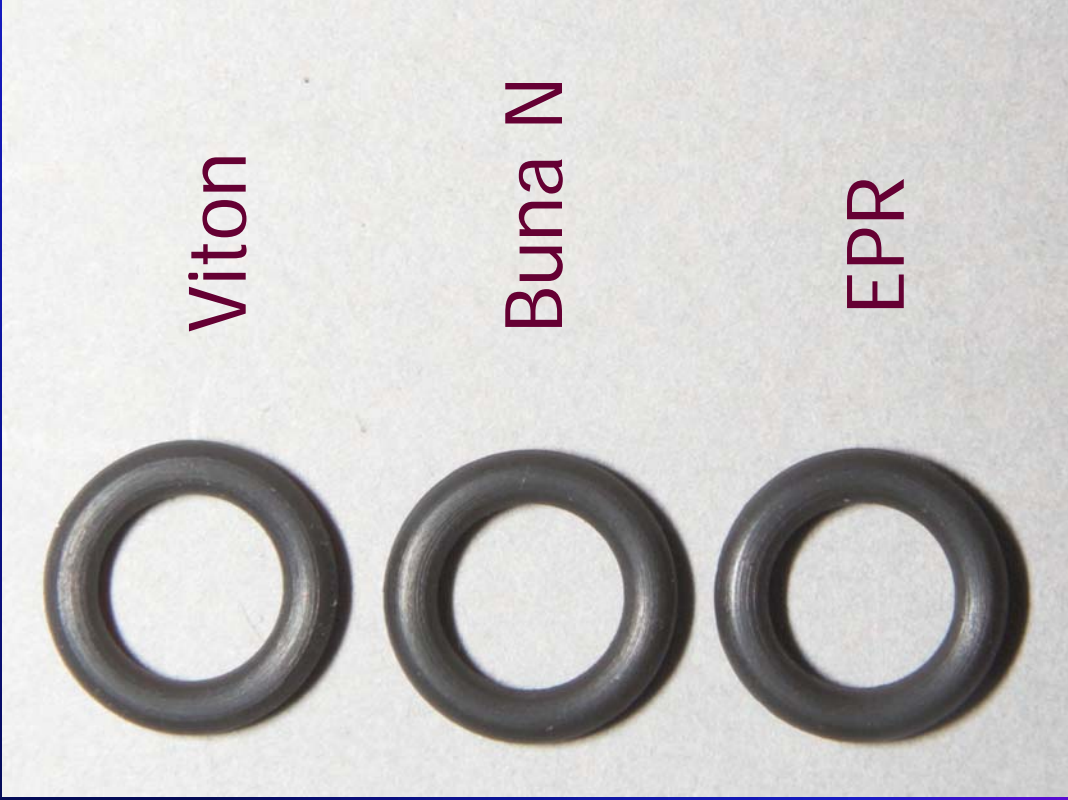
## Choosing the Right Softgood



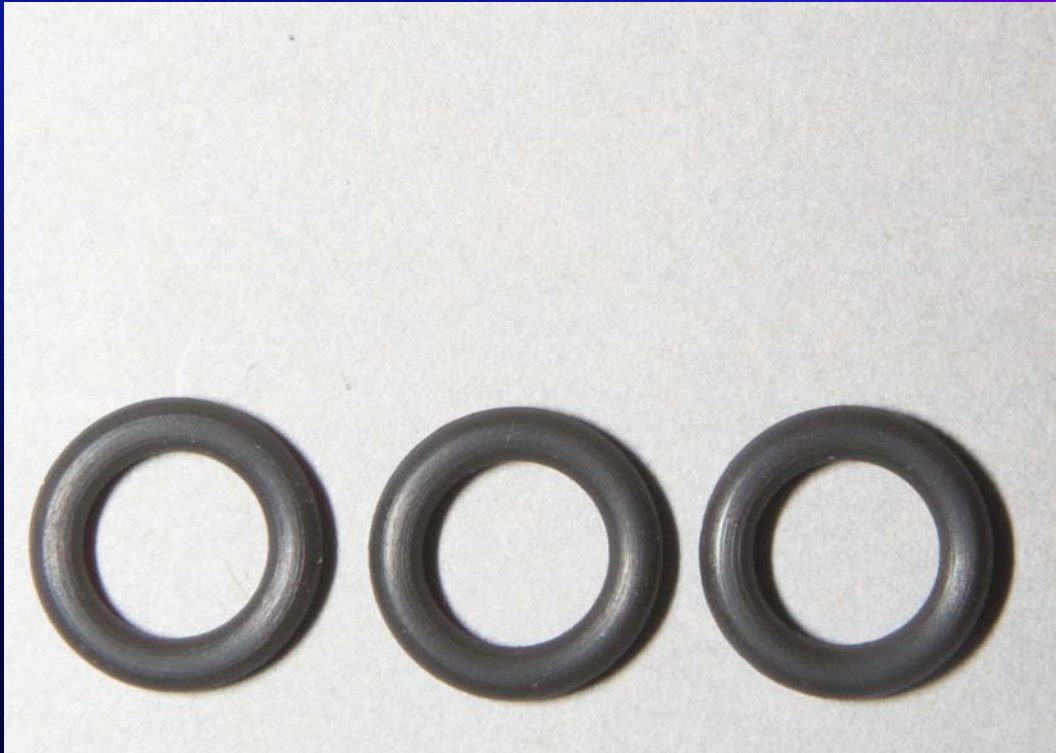
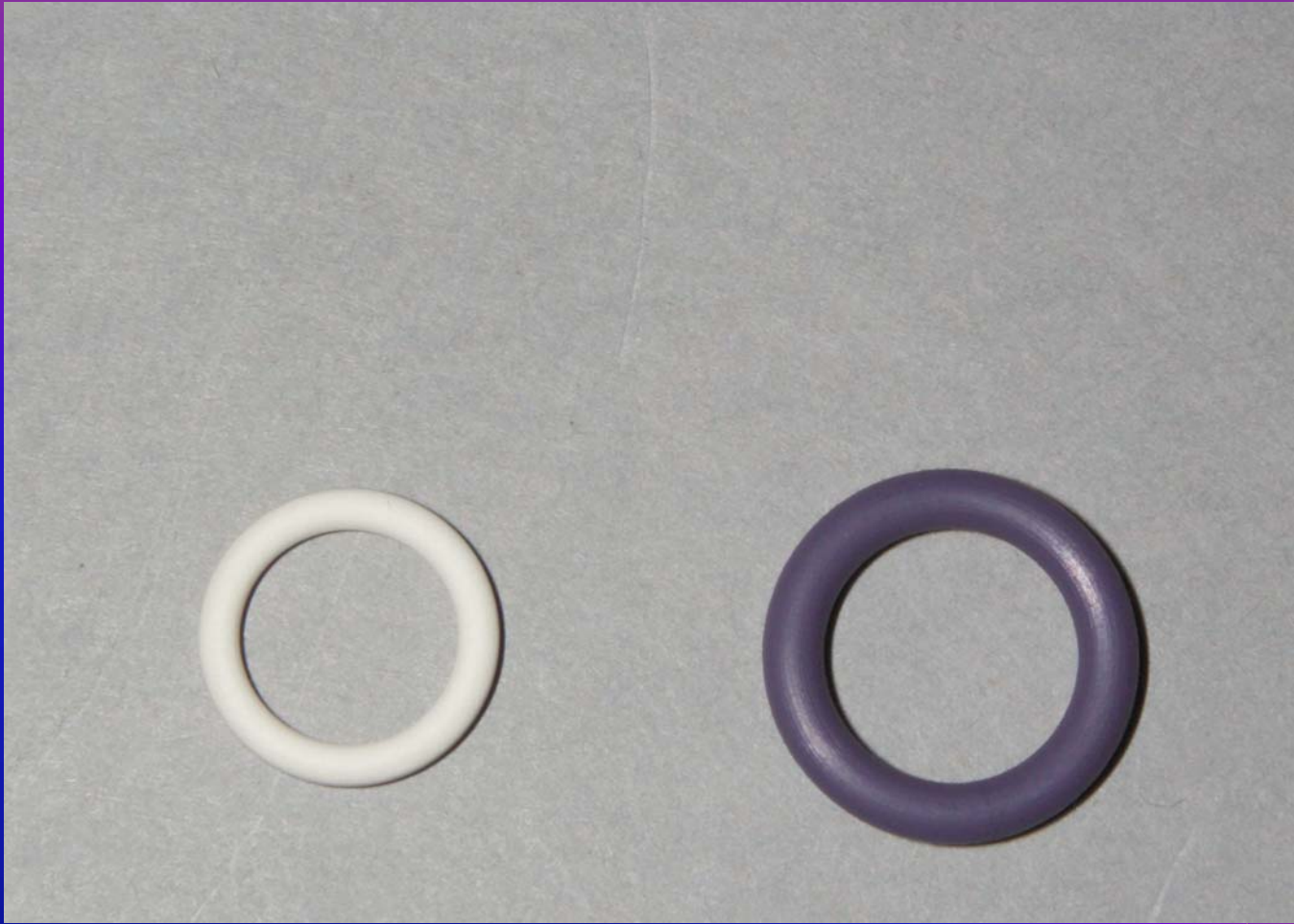
Which is which?

- EPR
- Viton
- Buna N

What types of  
O-rings are these?



Or are  
they?



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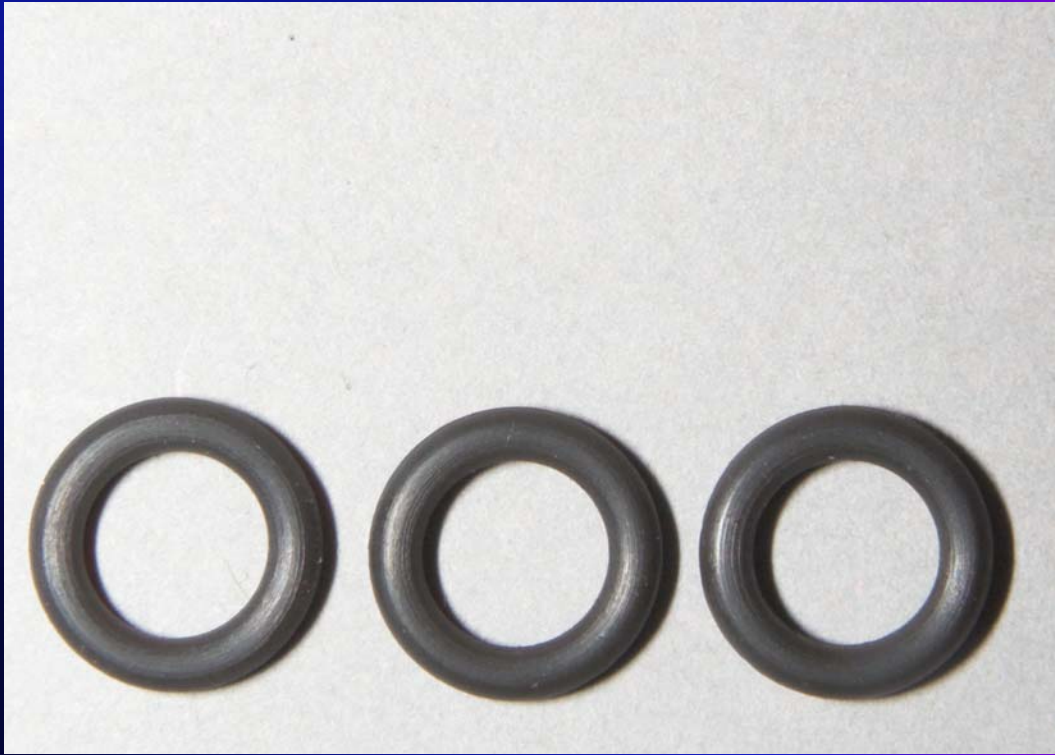
5/9/2006



Kalrez



Purple EPR



5/9/2006

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# Responsibility

- ◆ Project Engineer
- ◆ Project technician(s)
- ◆ Expediter(s)
- ◆ Valve Shop technician(s)



# Softgood Integrity

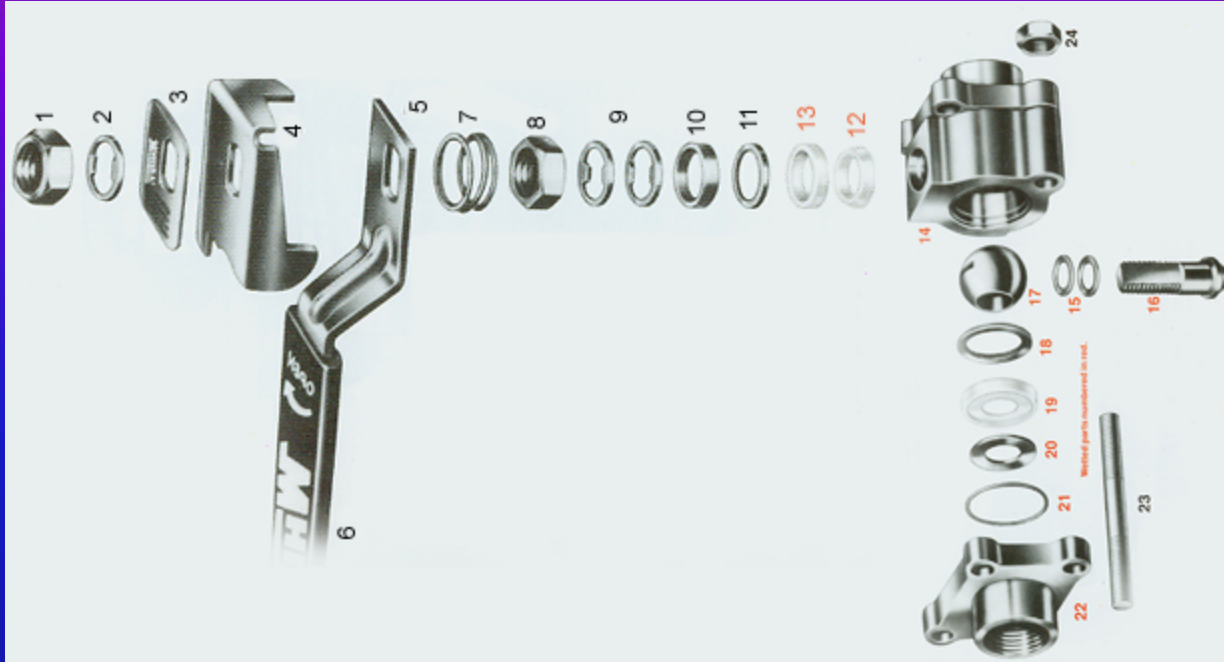
- ◆ How do we assure the Project Engineer requests the correct softgoods?
- ◆ How do we assure the project technician writes the correct softgoods on the work order?
- ◆ How do we assure the expeditor inputs the correct softgoods to the system?
- ◆ How do we assure that the Valve Shop technician selects the right softgoods for the component?
- ◆ How do we assure the softgood kits from the suppliers contain the right softgoods?

### 9.3.1.3.3 Absorbance and Offgassing

- ◆ All softgoods absorb
  - Don't mix media without changing softgoods
- ◆ All softgoods will offgas over time
  - Even after decon and cleaning
  - Vacuum bakeout - still need to check
- ◆ Dispose of properly
  - As hazardous waste

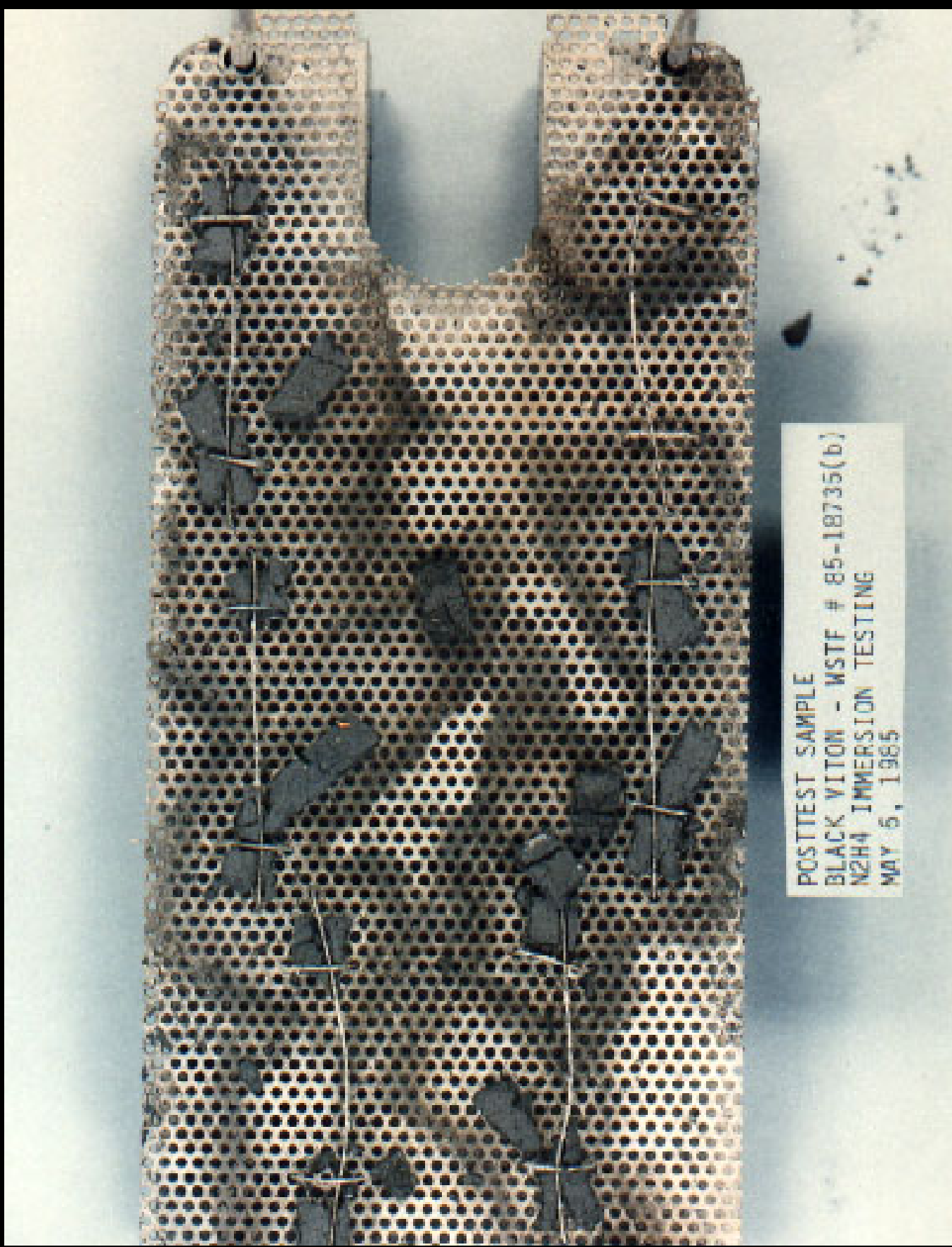
# The Swagelok 60 Series Ball Valve

- ◆ A good example of the bad things that can happen

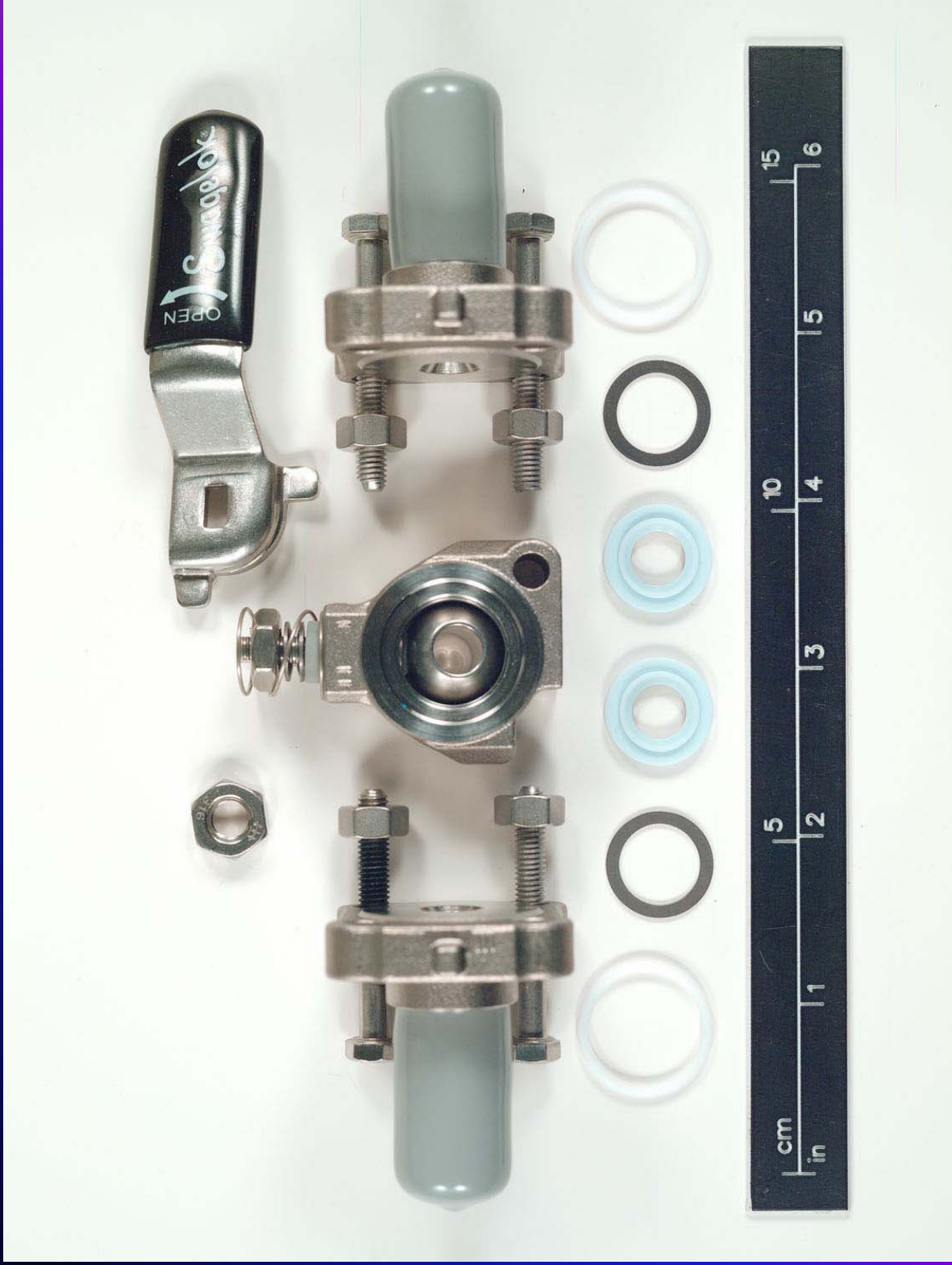


	Valve Body Materials		
	Stainless Steel	Carbon Steel	Brass
	Grade / ASTM Specification		
1 Stem Nut	Stainless Steel	Carbon Steel	Carbon Steel
2 Stem Spring	316SS/A167, Hard Tempered		
3 Name Plate (optional)	Stainless Steel		
4 Stop Plate <sup>①</sup>	Stainless Steel		
5 Handle	Stainless Steel		
6 Handle Sleeve	Vinyl		
7 Grounding Spring	Stainless Steel		
8 Stem Nut	Stainless Steel	Carbon Steel	Carbon Steel
9 Stem Springs (2)	316SS/A167, Hard Tempered		
10 Gland	Stainless Steel		Brass
11 Packing Support	PEEK (Polyetheretherketone)		
12 Top Packing	Reinforced TFE		
13 Bottom Packing	Reinforced TFE		
14 Center Body	316/A479 or CF3M or CF8M/A351	WCB/A216	Brass CDA 360/B16
15 Stem Bearings (2)	Alloy X750/AMS5542J		PEEK
16 Stem	316SS/A276 (62, 63, & 65 Series); 1018/A108 (67 & 68 Series)	316SS/A276	316SS/A276 CDA 360/B16 (63 & 65 Series)
17 Ball	316SS/A276		
18 Support Rings (2)	316SS/A276 or A167		
19 Seats (2)	Reinforced TFE		
20 Seat Springs (2)	316SS/A167, Hardened		
21 O-Rings (2)	Fluorocarbon FKM/Viton A		
22 Flanges (2)	316L/A479 or CF3M/A351	WCB/A216	Brass CDA 360/B16
23 Body Studs/Bolts (4)	304SS Gr. B8 C. 2/A193		Carbon Steel Grade 8/SAE J429
24 Body Nuts (8) (4)	303SS Gr. 8F Str. Hd./A194		Carbon Steel Grade 8/SAE J995

① "62" Series stop plate is integral with handle.  
**Lubrication:** Silicone base lube and TFE base lube.  
 Other lubricants are available for system compatibility.  
 Special alloy materials are available upon request. They include alloy 400, alloy C-276, alloy 20, alloy 600 and titanium. Consult your Authorized SWAGelok Sales & Service Representative.



POSTTEST SAMPLE  
BLACK VITON - MSTF # 85-18735(b)  
N2H4 IMMERSION TESTING  
MAY 5, 1985



## 9.3.2 Components

- ◆ Manual Valves
  - ball, shutoff, etc.
- ◆ Gas Operated Valves
- ◆ Electrically Actuated Valves
- ◆ Pressure Regulators
- ◆ Check Valves
- ◆ Pressure Safety Devices
  - relief valves vs burst disks
- ◆ Pressure Transducers
- ◆ Pressure Gauges
  - bleed tip
- ◆ Filters
- ◆ Flexhoses

## 9.3.2.1 Manual Valves

- ◆ **Ball Valves**
  - Little control over flow
    - Full open with 1/4 turn
  - Water hammered potential
  - Recommended for **NTO** service
    - self cleaning
  - Also used in hydrazine service
  - Drilling the ball
  - Examples of ...



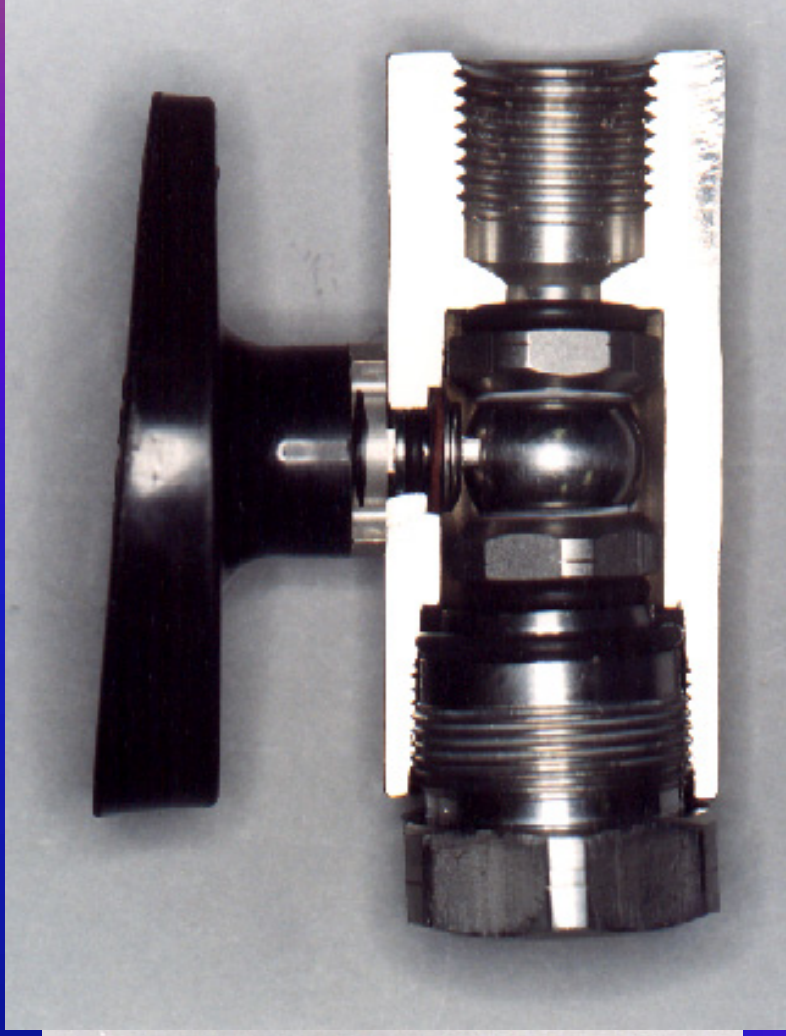
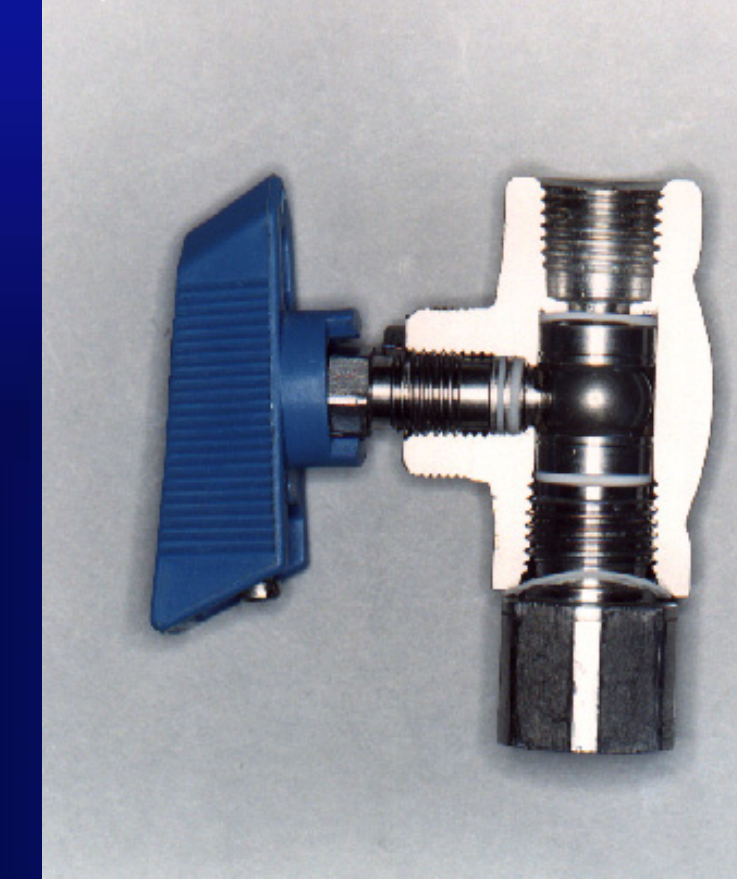
## 9.3.2.1.1 Liquid Lock

- ◆ Pressure in a “liquid lock” situation can rise dramatically as temperature increases
  - Hydrazine: 295 psi per °F
  - MMH: 148 psi per °F
  - UDMH: 53 psi per °F
  - NTO: 135 psi per °F
- ◆ Always provide ullage space or relief protection for liquid in a closed system

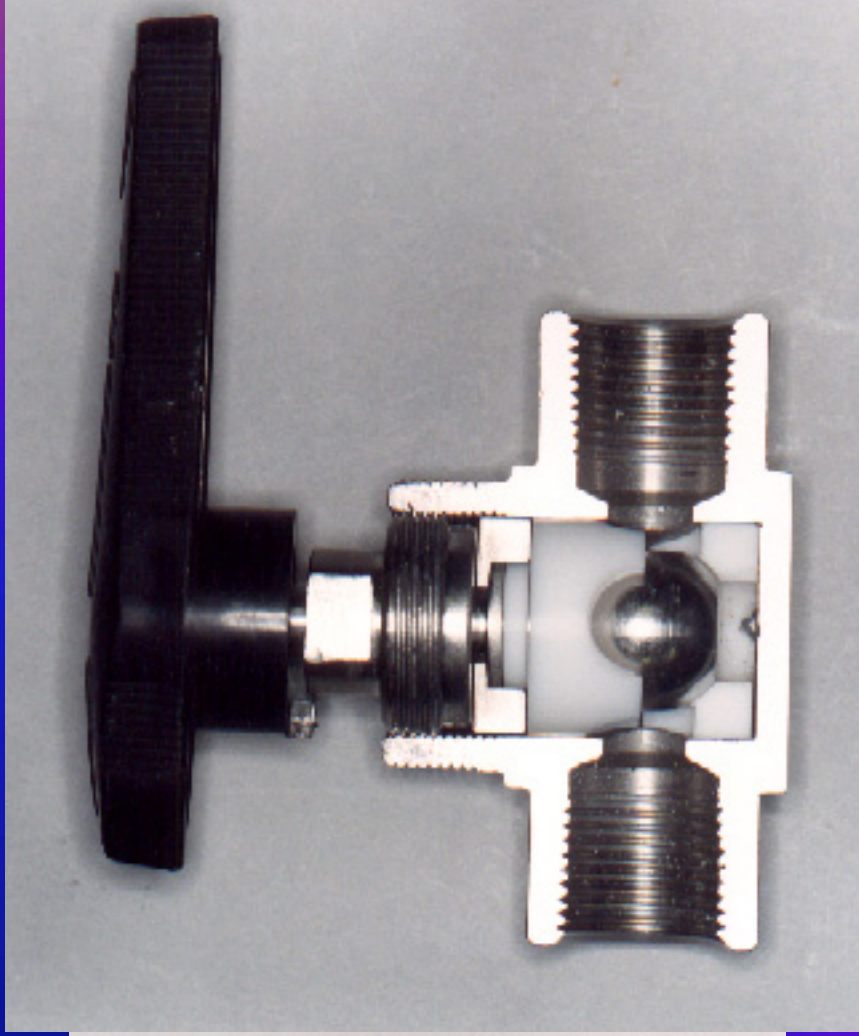
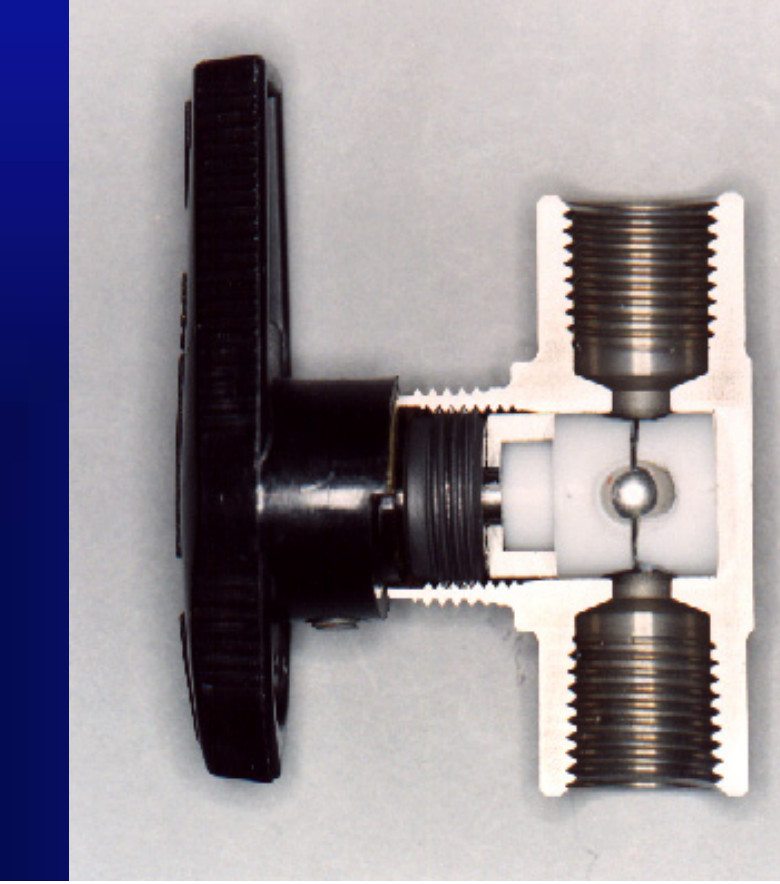
NOTE:

Worst case values

# Hoke Valves



# Whitey Valves



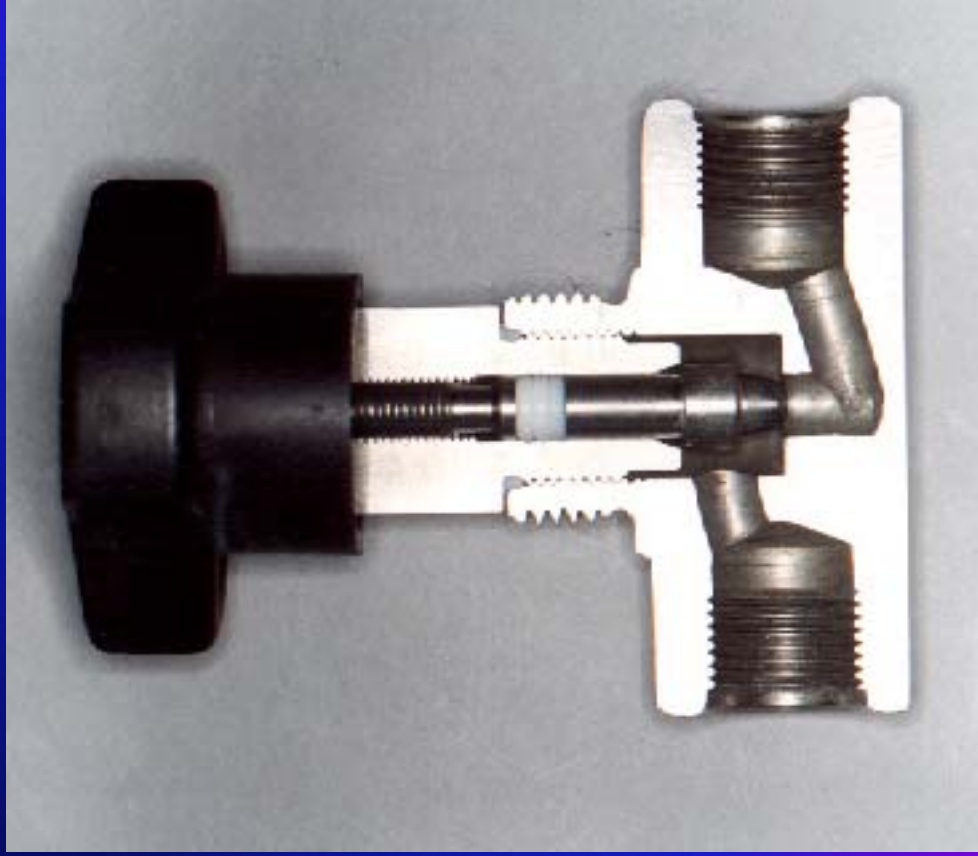
# Jamesbury Valve



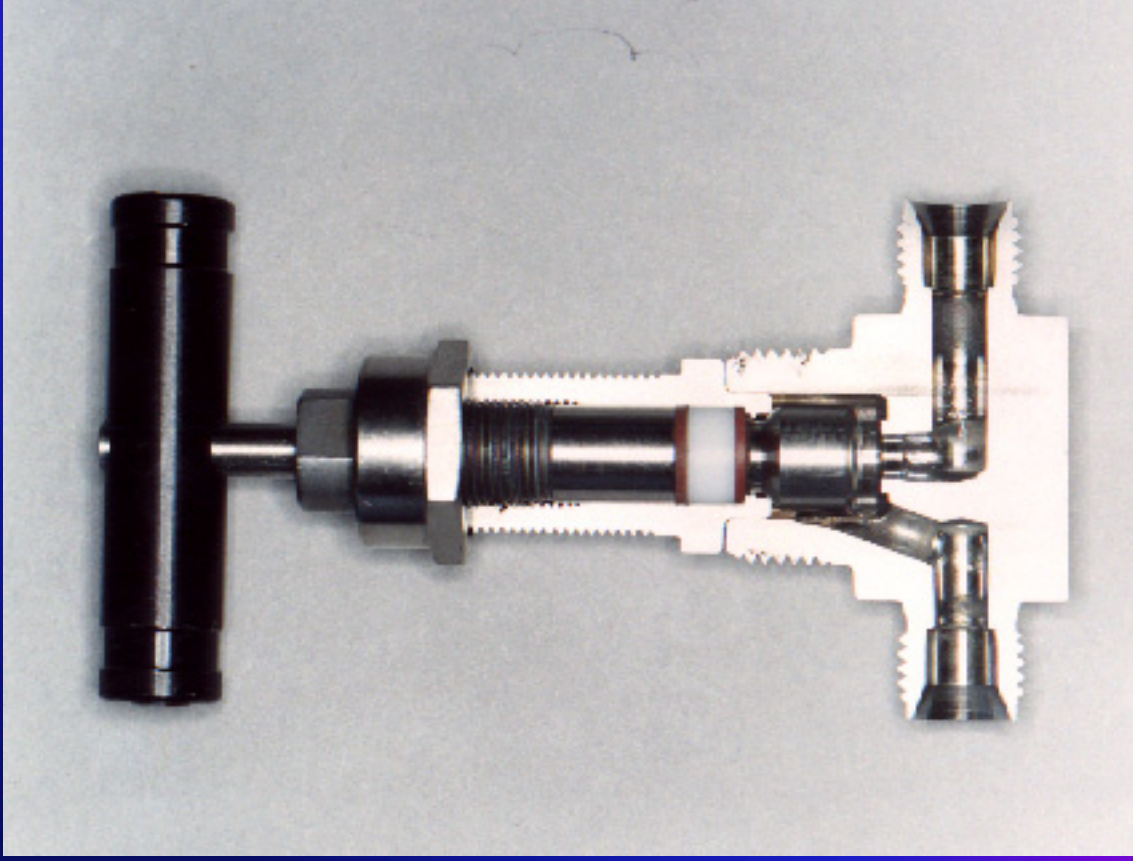
## 9.3.2.2 Manual Valves cont'd

- ◆ Shutoff Valves
  - Good flow control
    - Some vendors offer same model as shutoff or regulating
  - Minimal water hammer potential
  - Flow decay problem in **NTO** service
  - Difficult to obtain valves with **NTO** compatible softgoods that seal reliably
  - Examples of ...

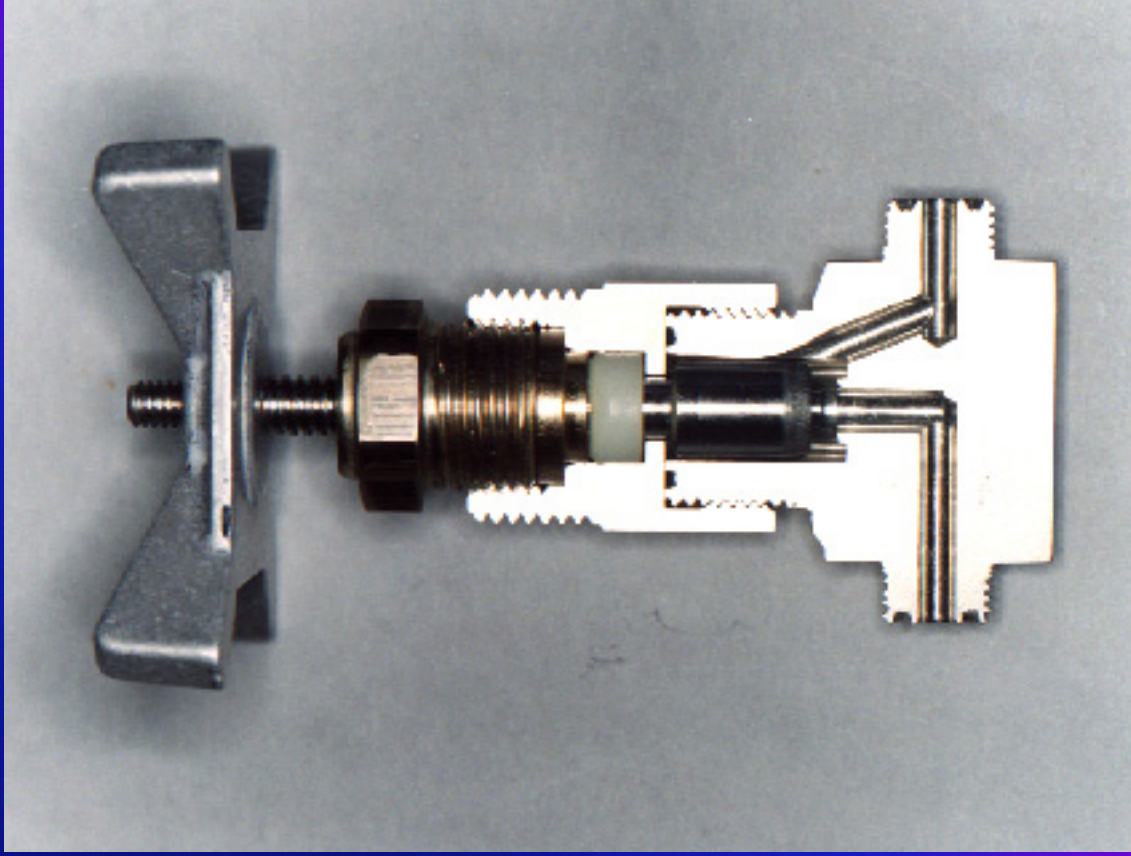
# Dragon Valve



# Whitey Valve

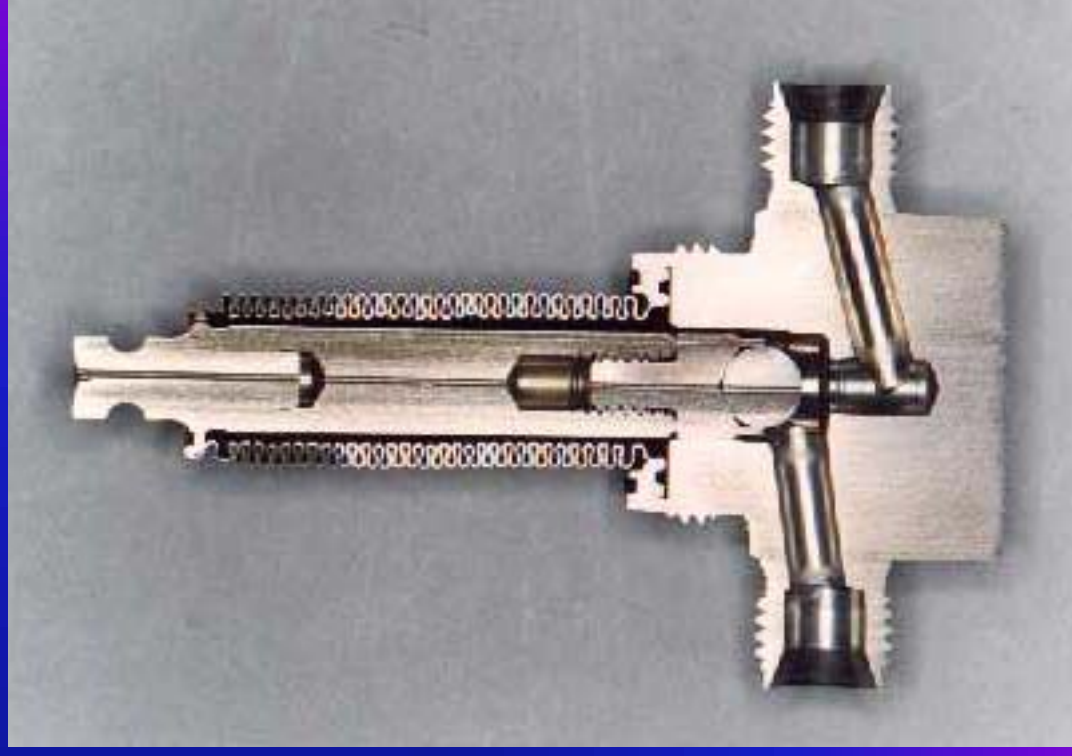
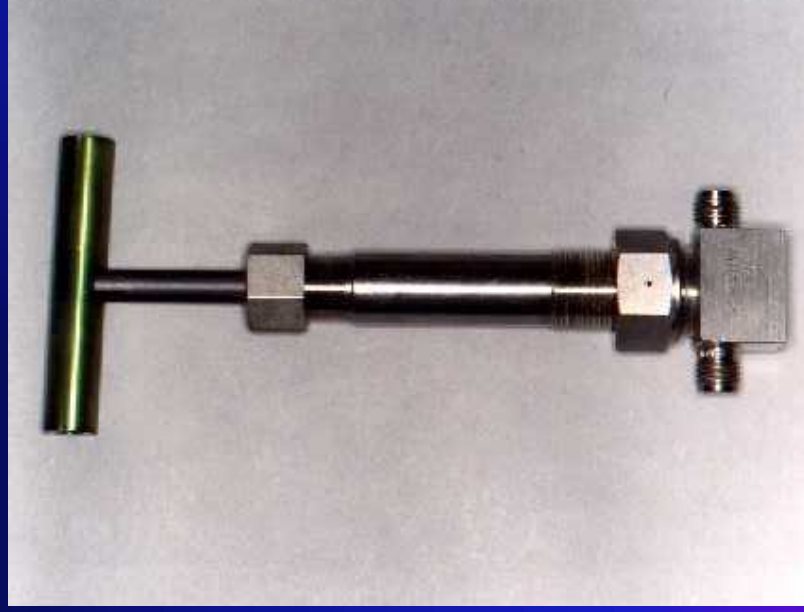


# CPV Valve





# Nupro Valve (bellows)



### 9.3.2.3 Gas Operated Valves

- ◆ Allows for remote operation
- ◆ Spring loaded return
  - Closes with loss of actuation pressure
- ◆ No ignition hazard
  - Controlling ECVs can be located safe distance away from system
- ◆ Requires regulated gas source

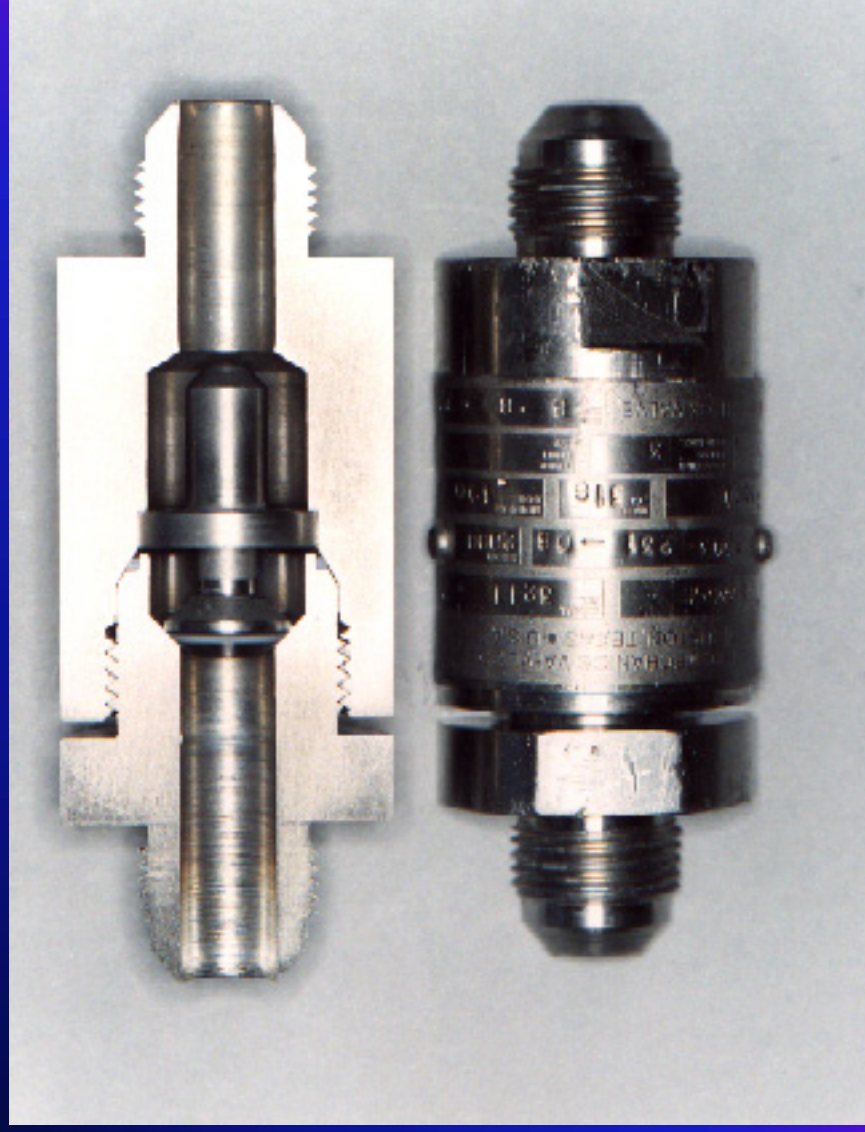
## 9.3.2.4 Electrically Actuated Valves

- ◆ Allows for remote operation
  - 110 VAC or 24 VDC solenoid
- ◆ Spring loaded return
  - Closes with loss of power
- ◆ No need for regulated gas source or controlling ECV
- ◆ Potential ignition hazard
  - Spark
  - Heat \* - Accident # 3

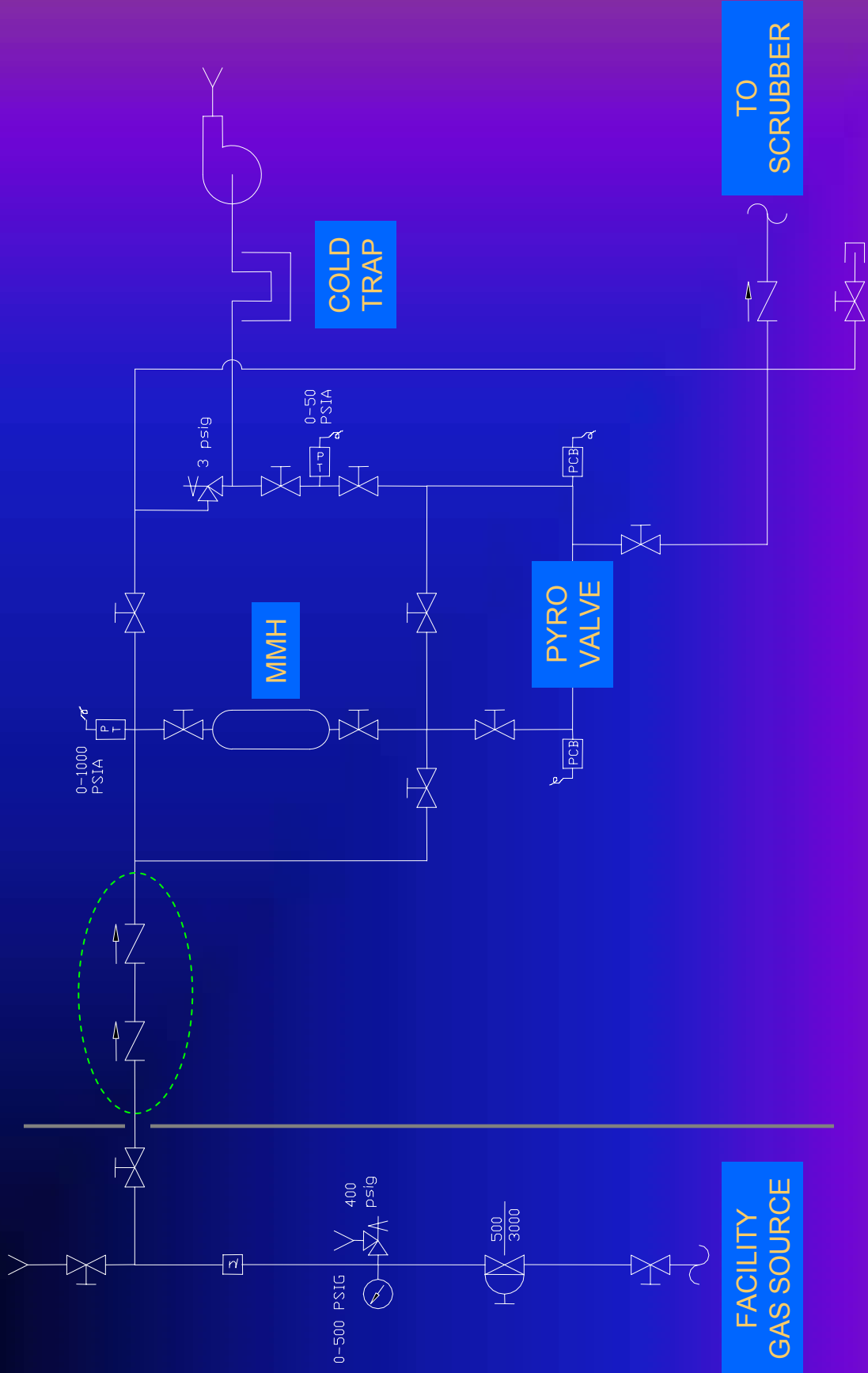
## 9.3.2.5 Check Valves

- ◆ Spring-loaded backflow prevention device
- ◆ Wetted portions of hypergol systems should be double isolated from non-wetted portions, such as gas sources, to prevent contamination

# Fluid Mechanics



# Double Isolation Example



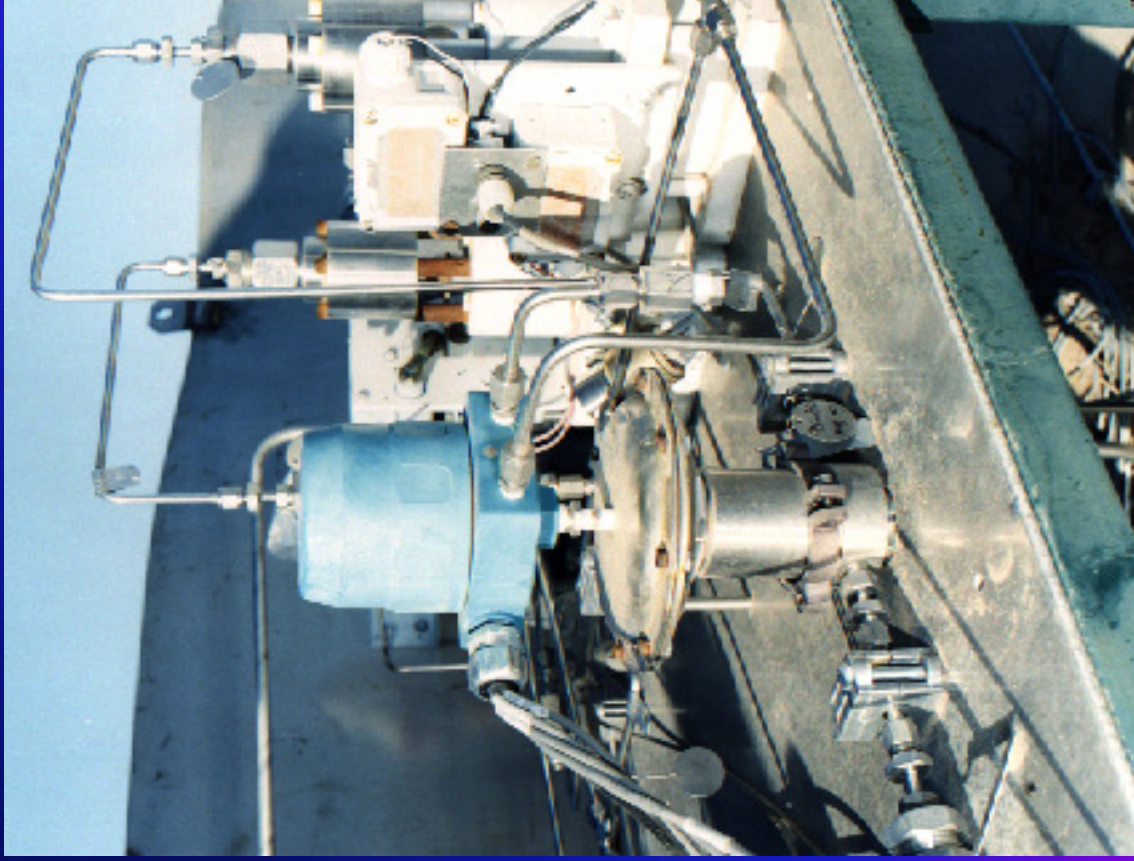
## 9.3.2.5.1 Check Valve Considerations

- ◆ Teflon softgoods will leak
  - Leak worse at lower pressures ...
    - As when system not in use
  - ... and at lower temperatures
- ◆ Maintenance
  - Back pressure leak check
  - 6 month interval
- ◆ Need to evaluate softgood selection
  - WSTF currently evaluating
    - Kalrez 1045 in check valves for **NTO** service
    - EPR 515 in check valves for **hydrazine fuels** service

### 9.3.2.6 Pressure Regulators

- ◆ Self venting preferred for easier pressure resets
- ◆ Types of vent ports
  - Out of bonnet under the handle
  - Captured (separate port on body)
    - Should be standard for hypergol systems
    - Accident #7
- ◆ Remote operation possible
  - Example: Tescom ER3000

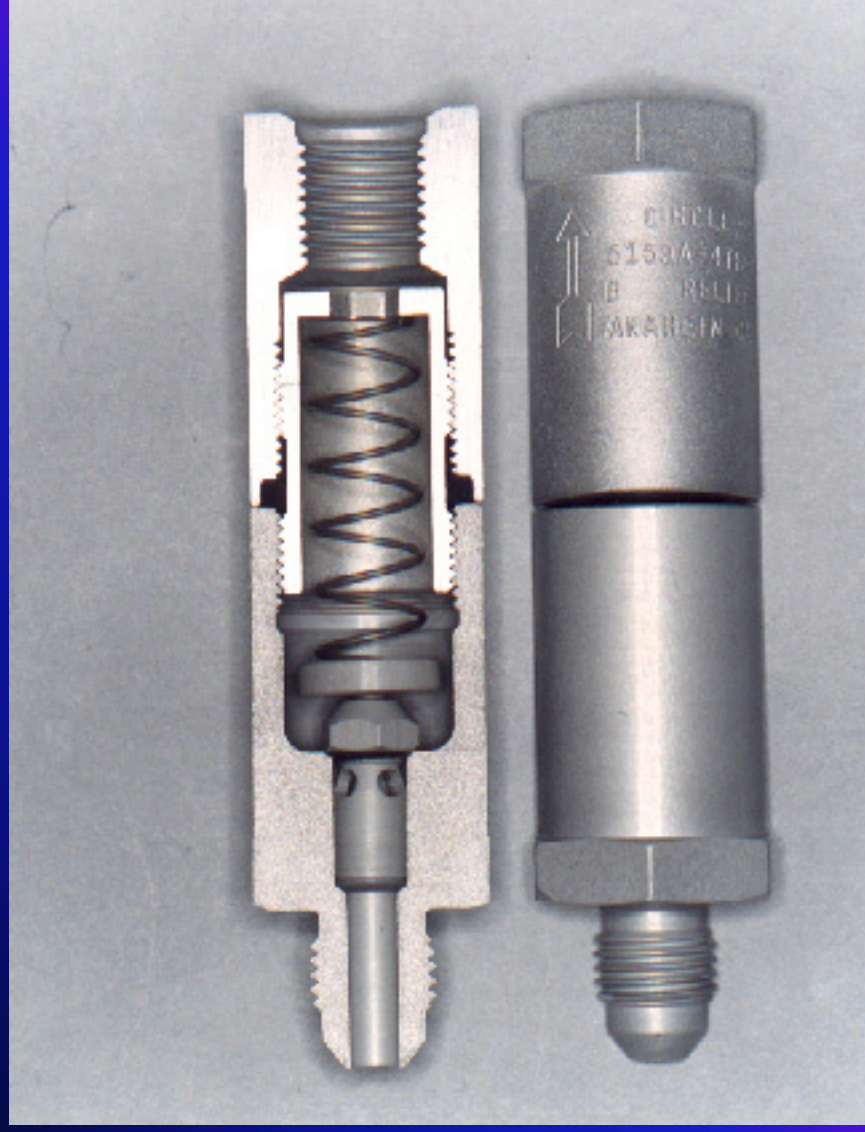




## 9.3.2.7 Pressure Safety Devices

- ◆ Relief valve
  - Potential for leakage
  - Chattering can cause leakage and generate particulate
  - Should capture outlets and vent to safe location ...

# Circle Seal



## 9.3.2.7.1 Vents

- ◆ Design vents to reduce or eliminate the possibility of personnel exposure, vapor accumulation or ignition, and contamination of surrounding equipment, such as ventilator air intakes
  - This could mean using scrubbers or burners to condition gases and vapors before release to the environment

## 9.3.2.8 Pressure Safety Devices

- ◆ Burst disk
  - “Leak proof”
  - Corrosion can degrade set pressure
    - Teflon lined
  - Only rated to hold pressure in normal direction
  - Actuation generates particulate
    - Consider effects on downstream hardware
  - Should capture outlets and vent to safe location

## 9.3.2.9 Pressure Transducers

- ◆ 24 VDC
- ◆ Stainless steel diaphragms
  - 316 and 17-4 PH for hypergol service
- ◆ No oil!
- ◆ Ensure electronics are sealed
  - Corrosion
- ◆ If one is good, are two better?

### 9.3.2.9.1 Note on Instrumentation

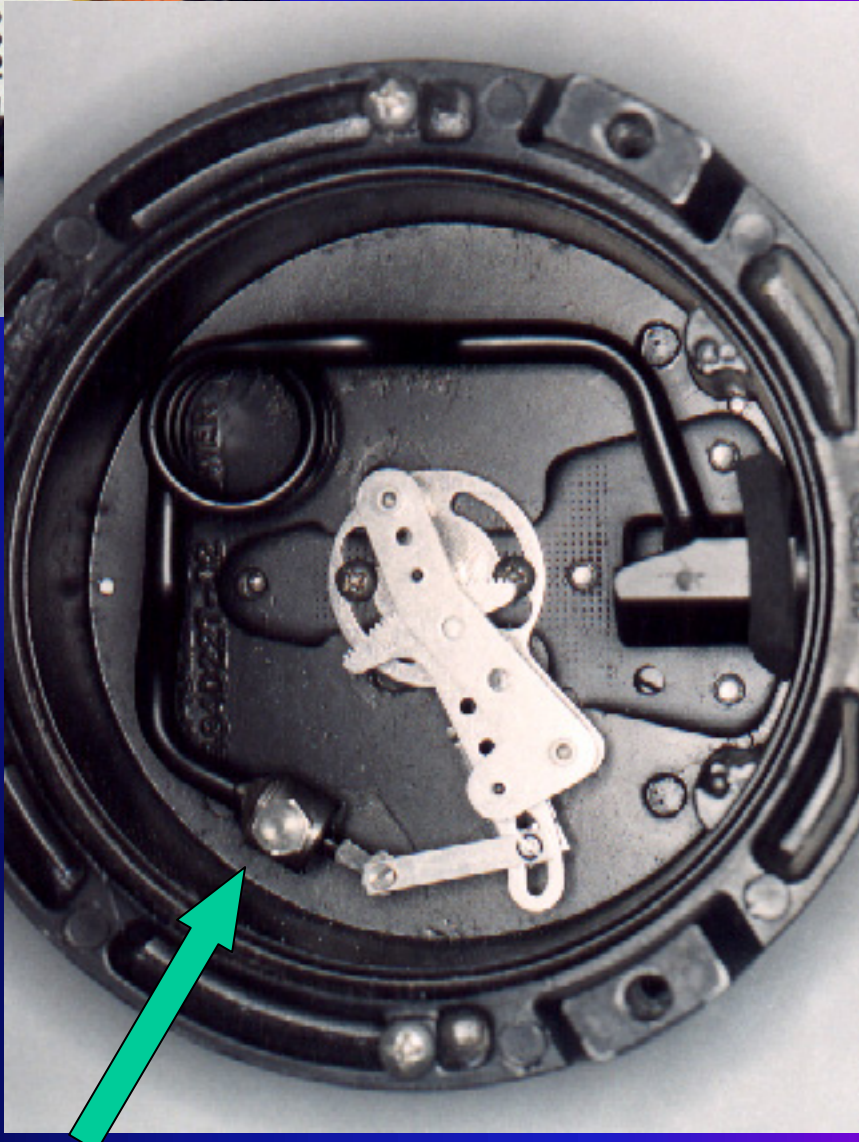
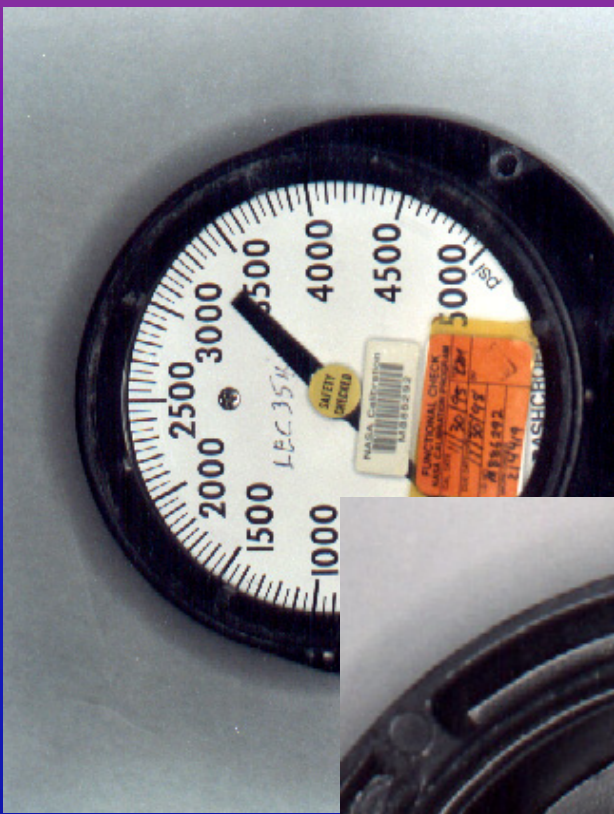
- ◆ Ensure systems are adequately instrumented to determine and monitor operating conditions
  - Redundancy
  - Proper instrument ranges and tolerances

## 9.3.2.10 Pressure Gauges

- ◆ Bourdon tube with tip bleed port for cleaning
- ◆ Do not block blow out ports on back
- ◆ Ensure proper ranges and tolerances

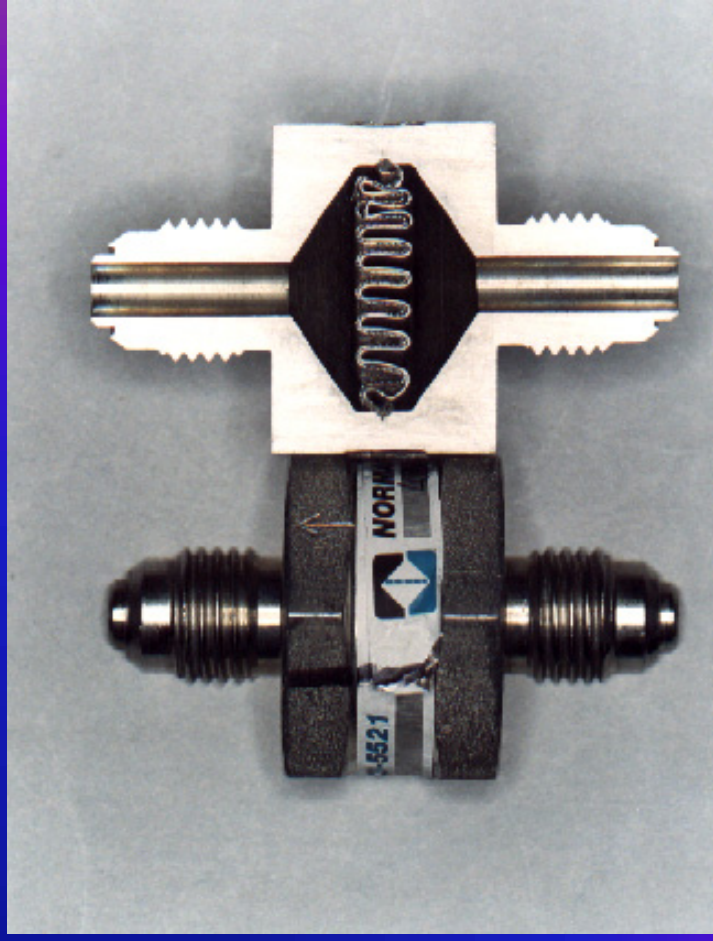


Example of Bourdon Tube with  
Tip Bleed Port



## 9.3.2.11 Filters

- ◆ Need all stainless steel construction
  - Example: Norman mini inlines
- ◆ Other types with removable elements and Teflon softgoods available



## 9.3.2.12 Flexhoses

- ◆ Avoid use when possible
  - Teflon lined
    - Hypergols will permeate
- ◆ Don't mix media
  - Should be clearly marked for **hydrazine fuels, NTO, OR** inert gas service
- ◆ Cannot be completely deconned and cleaned
  - Orange cloud in the bag

# Aside

- ◆ Component Standardization
  - Softgoods
  - Safety issues
  - Cost issues
  - Logistics issues

## 9.3.3 Examples of Storage and Transport Containers

- ◆ Choice depends on type and quantity of fluid, distance to travel, mode of transport, ...
  - I-Chem vial
  - Nalgene bottle
  - Fischer-Porter bottles
  - Hoke bottle
  - 4BW cylinders

# Transport and Lab Scale Containers



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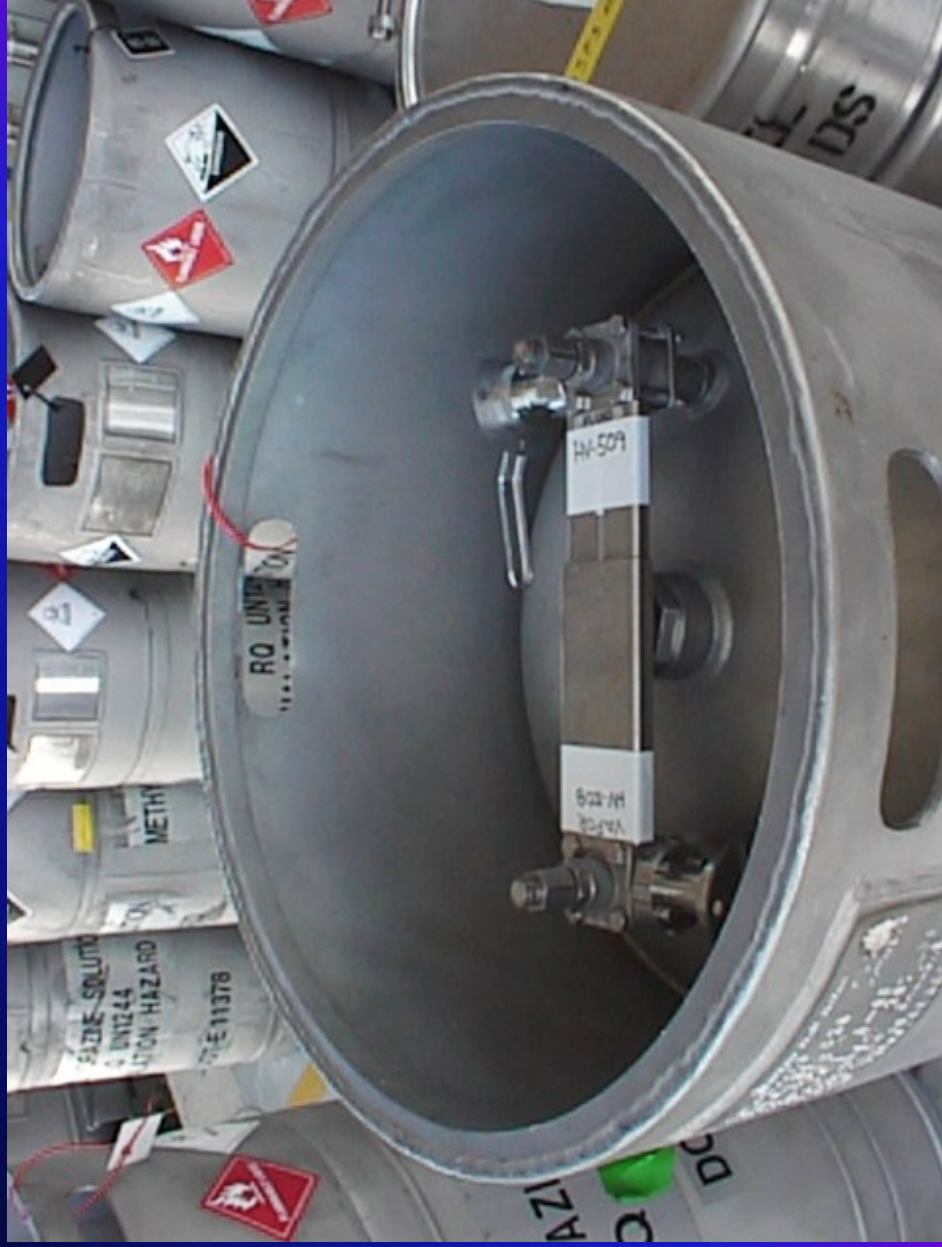
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# DOT 4BW Cylinders



KSC Propellants & Life Support Office  
<http://propellants.ksc.nasa.gov/dot4bwfront.htm>

# Top of 4BW





# N<sub>2</sub>O<sub>4</sub> DOT110 One Ton Cylinder



KSC Propellants & Life Support Office  
<http://propellants.ksc.nasa.gov/dot110a500w.htm>

# Propellant Tanker



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# Course Outline

- ✓ Introduction
- ✓ Accidents
  - ✓ Examples of the “problems”
- ✓ Step 1 - Identify the Hazards
  - ✓ Toxicity Hazard
  - ✓ Reactivity Hazard
  - ✓ Fire Hazard
  - ✓ Explosion Hazard
  - ✓ Hypergol Properties, References & Other Information
- ◆ Step 4 - Manage the Risks
  - Primary Controls
    - ✓ Design
      - ✓ Material Compatibility
    - Build Up
    - Operation
  - Secondary Controls
    - PPE
    - Detectors/Monitors
- ◆ Course Evaluations

# Step 4 - Manage the Risks

- ◆ Primary (Engineering) Controls
  - ✓ Design
  - Build Up
  - Operation
- ◆ Secondary Controls
  - Personal Protective Equipment (PPE)
  - Detectors/Monitors

# 10.0 Build Up Sequence

- ◆ System Construction
- ◆ Reassemble
- ◆ Considerations
- ◆ Torque and tag
- ◆ Paperwork
- ◆ Integrity check
- ◆ Mockup
- ◆ system
- ◆ Document physical
- ◆ Leak check
- ◆ Disassemble
- ◆ Flow check relief valves
- ◆ Clean and proof
- ◆ Paperwork

# 10.1 System Construction Considerations

- ◆ Life Span
- ◆ Location
- ◆ Mode of Operation
  - Hands-on vs remote
  - Water checkouts?
- ◆ Tubing
  - Diameter
  - Material
  - Wall thickness
- ◆ Choice of Fittings
  - Weld
  - Swagelok
  - Flanged
  - AN
  - NPT
  - Dynatube
- ◆ Cleanliness Requirements
- ◆ ASME Code compliance
  - Lethal Service

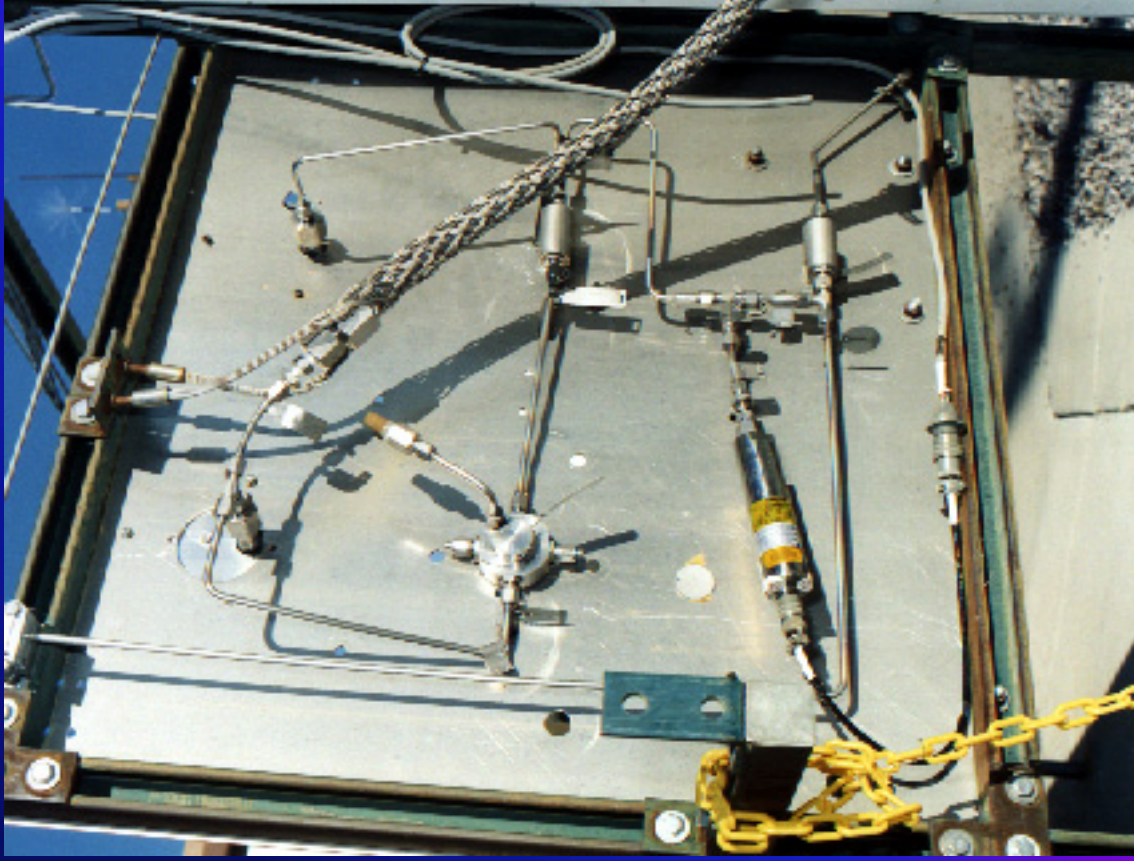
## 10.2 Paperwork

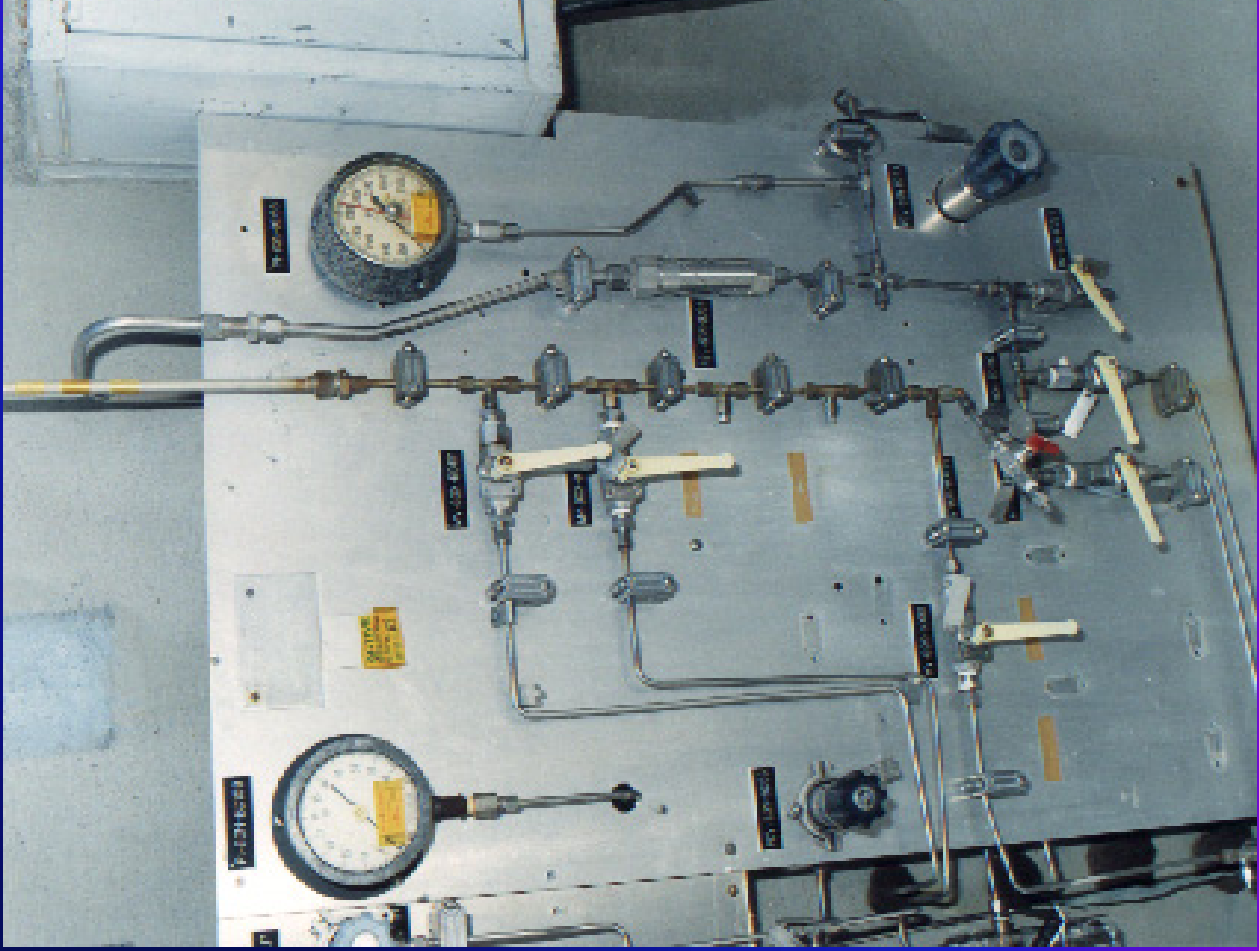
- ◆ Schematic
  - Sketches
  - Released drawings
- ◆ Design specifications
- ◆ Work authorizing document(s)
  
- ◆ How does it work here?

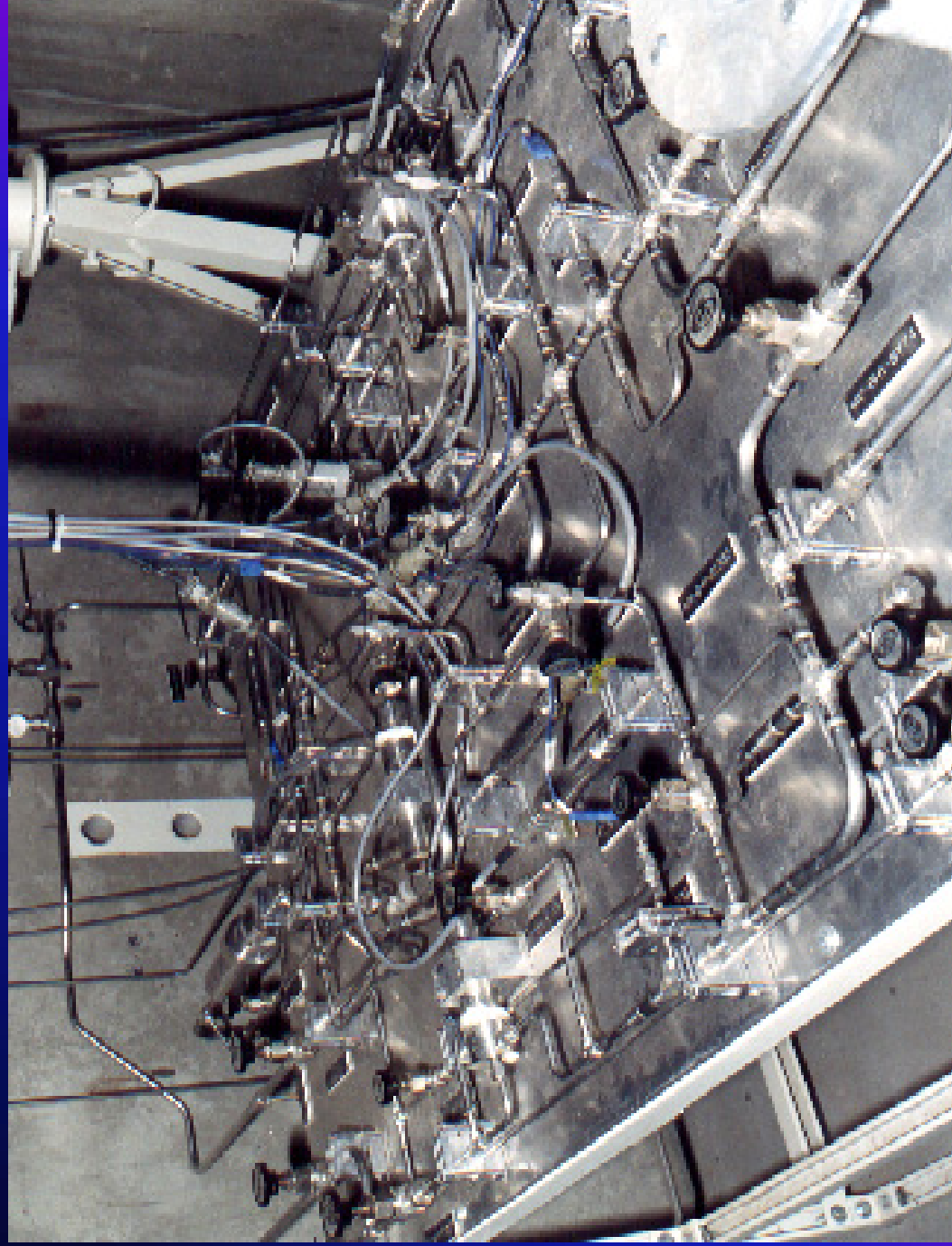
## 10.3 Mockup

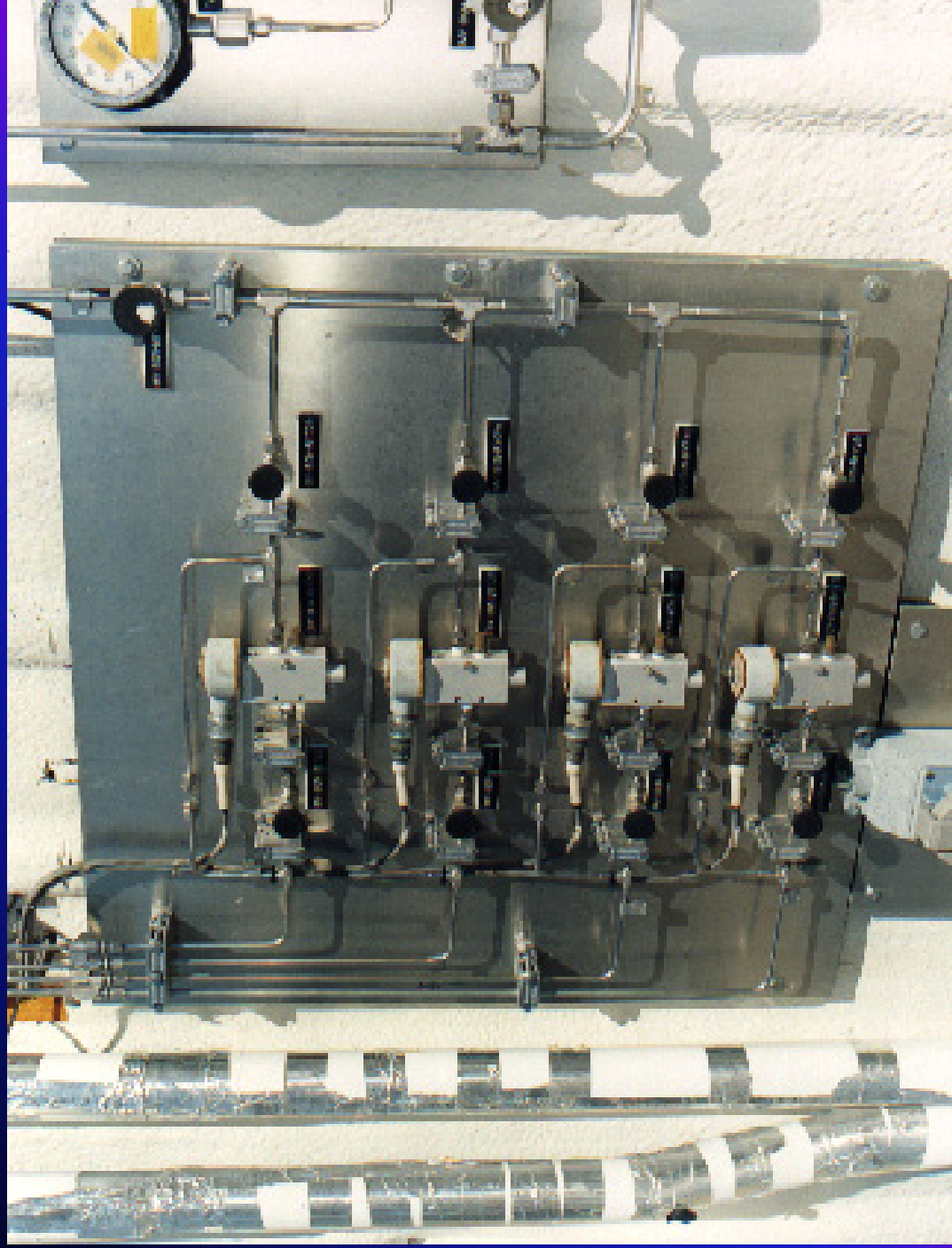
- ◆ How will system be used by the operator?
- ◆ Ergonomics
  - Panel or table?
  - Front or back?
  - Sit, stand, or squat?
  - Inside or outside?
  - Required PPE?
- ◆ Perform water checkouts (if permitted)
  - Must stay below 150 psi

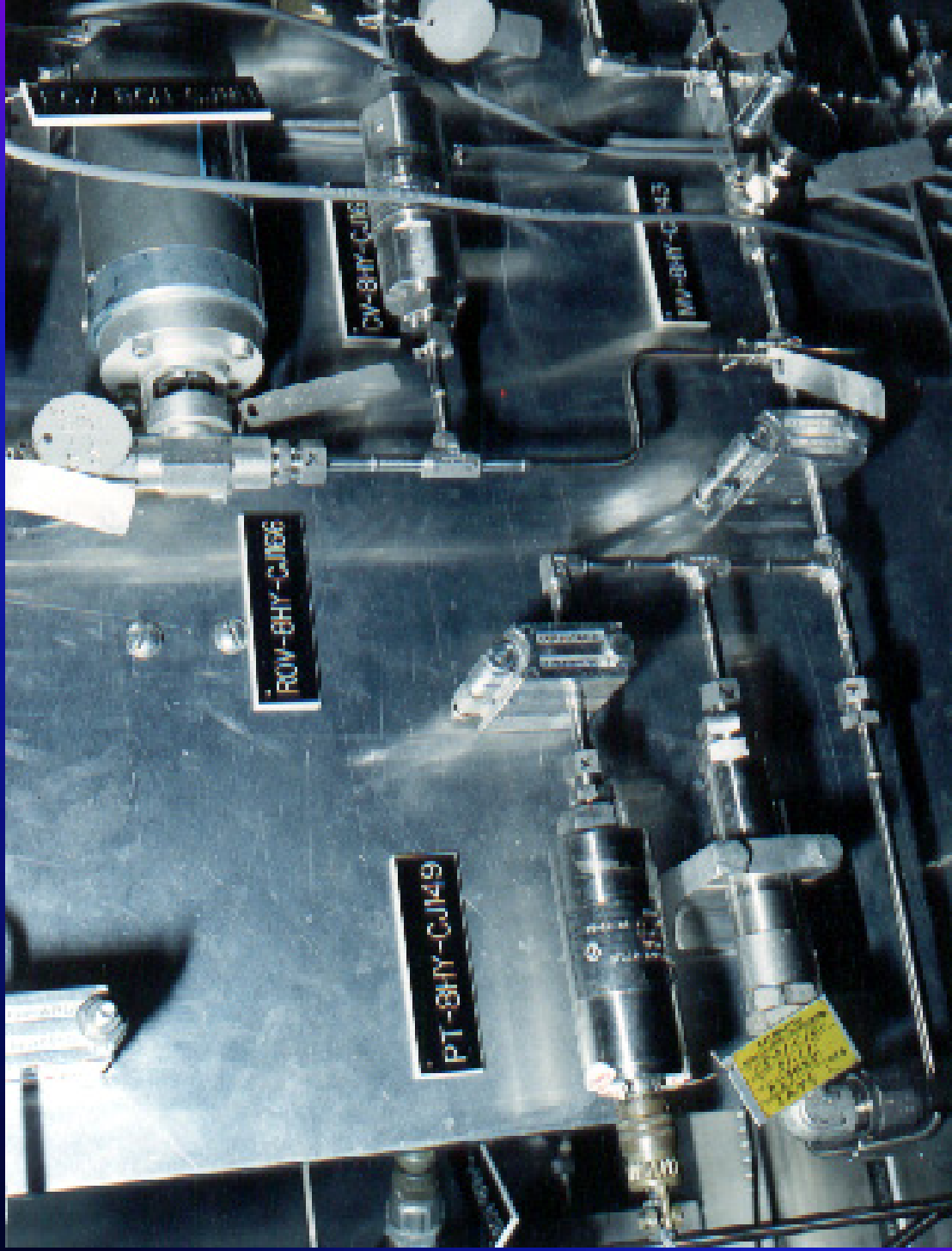












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## 10.4 Document

- ◆ Before disassembling for cleaning, document physical system so you will know how to put it back together
  - Temp tags on hardlines
  - Photos
  - Hand sketches

## 10.5 Disassemble

- ◆ Polish flares?
- ◆ Protect flares & face seals
- ◆ Make a list of your parts

## 10.6 Cleaning

- ◆ What clean levels are required for the various systems and subsystems?
  - Level 50, 100, 200, 300, VC
    - **Fuel** systems should be cleaned to remove particulate and metallic oxides
    - Example: fuel system, level 100
  - Level 50A, 100A, 200A, 300A, VC
    - **Oxidizer** systems should be cleaned to remove particulate and organic materials
    - Example: oxidizer system, level 300A



# Examples



## 10.6.1 Cleaning Levels - Particulate

- ◆ Gives number of particles allowed in each size range
- ◆ Example of Level 200:
  - Unlimited particles below 50 microns
  - 50 through 100 154 max
  - 100 through 200 16 max
  - > 200 0 max

## 10.6.2 Cleaning Levels - NVR

- ◆ Nonvolatile residue levels


- A - 1 mg / ft<sup>2</sup>
- B - 2 mg / ft<sup>2</sup>
- C - 3 mg / ft<sup>2</sup>
- D - 4 mg / ft<sup>2</sup>

Going metric every inch of the way.

## 10.7 Reassemble

- ◆ **Maintain clean as you reassemble**
  - Avoid wind, water, and dust
  - Wear powder-free gloves
    - Change gloves often
- ◆ **Unbag as you go**
- ◆ **Use lubricants and Teflon tape sparingly**
- ◆ **Use proper seals**

## 10.7.1 Seals

- ◆ K-seals
- ◆ KC seals
- ◆ AN nose-seals
  - Stainless steel or Teflon coated stainless
  -  NO copper
- ◆ Weld fitting face seals
  - Swagelok (formerly Cajon)
  - CPV

## 10.8 Torque

- ◆ Follow torque specs
- ◆ Use a back-up wrench to avoid bending hardlines
- ◆ Mark fittings as you go

## 10.9 Tag

- ◆ Separate systems or subsystems should be clearly delineated from one another by a documented tagging scheme
- ◆ Individual components should be clearly identified with tags
- ◆ Components should also be tagged to identify media, MAWFP, and softgoods

## 10.10 Remote Integrity Check

- ◆ Purpose is to prove pressure integrity as a system after assembly
- ◆ If individual components have not been proof tested, ...
  - Remove system relief devices.
  - Install relief device to ensure pressure does not exceed 110% of integrity test pressure
    - Pneumastat to 110% of MAWP for at least 10 minutes
    - Hydrostat to 150% of MAWP



## 10.10.1 Remote Integrity Check

- ◆ If each component and hardline have been proofed individually ...
  - Pneumastat to only 90% of MAWP for at least 10 minutes
  - No need to remove relief devices

## 10.11 Leak Check

- ◆ Reinstall relief devices (if necessary) and torque
- ◆ Pressurize to 90% of MAWP
  - Hold for at least 10 minutes if relief devices have been reinstalled
- ◆ Perform pressure decay check, bubble leak check, and/or use He leak detector

## 10.12 Flow Check

- ◆ Flow check relief valves to verify flow capacity is sufficient to protect system unless proven by calculation
  - Hearing protection req'd
  - Fully increased regulator is full flow (at WSTF)
  - Not to exceed 110% of lowest rated component
  - Install orifice upstream of regulator if necessary

## 10.13 Paperwork

- ◆ Pressure Vessel/System Package
  - System schematic
  - Component summary list
  - Pressure vessel data
  - Recall list
  - Weld map
  - Weld examination sheets
  - System assembly and qualification procedures
    - Relief device flow calculations or flow check procedures
    - Pressure qualification procedures

# Course Outline

- ✓ Introduction
- ✓ Accidents
  - ✓ Examples of the “problems”
- ✓ Step 1 - Identify the Hazards
  - ✓ Toxicity Hazard
  - ✓ Reactivity Hazard
  - ✓ Fire Hazard
  - ✓ Explosion Hazard
  - ✓ Hypergol Properties, References & Other Information
- ◆ Step 4 - Manage the Risks
  - Primary Controls
    - ✓ Design
      - ✓ Material Compatibility
    - ✓ Build Up
    - Operation
  - Secondary Controls
    - PPE
    - Detectors/Monitors
- ◆ Course Evaluations

# Step 4 - Manage the Risks

- ◆ Primary (Engineering) Controls
  - ✓ Design
  - ✓ Build Up
  - Operation
- ◆ Secondary Controls
  - Personal Protective Equipment (PPE)
  - Detectors/Monitors

# 11.0 Operation Controls

- ◆ Before → Pretest
  - ◆ During → Test
  - ◆ After → Post test
- 
- ◆ The following are offered as operation controls and job design considerations

## 11.1.1 Training Certification Plan

- ◆ Train all personnel who will be working with or around hypergols on the properties and hazards. A training plan identifies the level and content of training required depending on the type of work to be performed.
  - Class room
  - Mentoring
  - On-the-job



## 11.1.1.2 Test Team

- ◆ Test Conductor
- ◆ At least two personnel equipped with identical personal protective equipment
- ◆ Safety Observer

## 11.1.1.3 Written Procedures

- ◆ Ensure that procedures for hypergol operations are written down, reviewed, dry run, and approved. These procedures should be based on defined processes or standard procedures.
- ◆ Written procedures should be reviewed periodically to ensure content is up to date.

## 11.1.1.4 Pretest Briefing

- ◆ Brief test team personnel on the work to be performed
- ◆ This should include a dry run of the actual procedures
- ◆ Ensure each person knows what is required of them during the operation

## 11.1.4.1 PPE Assessment

- ◆ Identify potential hazards and specify the required PPE
- ◆ Is the PPE in good condition and functioning properly?



## 11.1.4.2 Tools & Materials

- ◆ Ensure the required tools and materials are on hand for the given operation
  - Wrenches
  - O-rings, nose seals, Teflon tape, lubricant
  - Monitors/detectors
  - Water bucket(s), hoses
  - etc.

## 11.1.5 Wind Corridor

- ◆ Identify and establish a safe, sustained wind corridor that will carry released vapors away from test personnel and inhabited buildings or areas.
- ◆ Continually monitor the wind speed and direction so that operations may continue safely.

## 11.1.6 Time

- ◆ Hypergol operations should not be rushed. Ensure there is ample time to complete operations without compromising safety.
  - Avoid shift changes when possible
    - Accident #1, OV105 Fire
- ◆ Accidents happen when the normal routine is interrupted.

## 11.1.1.7 Access Controls

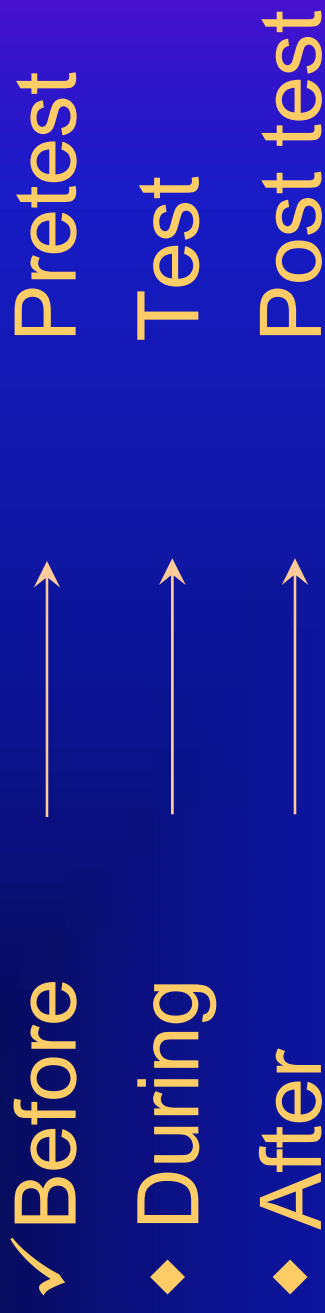
- ◆ Ensure access control has been established prior to performing a hypergol operation.
  - Warning lights
  - Barricades
  - Announcements



## 11.1.8 Communication

- ◆ Ensure that all members of the test team are in communication with the test conductor
- ◆ Ensure access control restrictions have been communicated to other personnel in the area
- ◆ Ensure emergency services personnel have been notified about the performance of a potentially hazardous operation

# 11.0 Operation Controls



# 11.2 During

## Oxidizer PSV replacement

### Discussion



# 11.0 Operation Controls



## 11.3.1 Decontamination

- ◆ Decon procedures should be part of the written operational procedure, and not left as something to do at the end
- ◆ Personnel should be trained on proper decon procedures
  - Disassemble
  - Triple rinse / actuate valves
  - Label as fuel or ox contaminated

## 11.3.1.1 Decontamination

- ◆ Decontamination facilities for fuel and oxidizer should be available near hypergol systems and/or operations to support clean up activities



Fuel and Oxidizer  
Decon Sinks

## 11.3.1.2 Decontamination

- ◆ Neutralizing rinses can be used to decon hardware
  - Citric acid solution used for **hydrazines**
  - Sodium bicarbonate or other basic solution used for **NTO**

## 11.3.2 Disposal

- ◆ Waste products from propellant operations need to be disposed of in accordance with local, state, and federal environmental regulations



90 Day Storage Waste Accumulation Area



# 11.3.2.1 Disposal

## Label on Hazardous Waste Drum

1193 DRUM # 1193  
CONTENTS  
WASTE FUEL & WATER  
ENVIRONMENTAL DEPARTMENT  
NASA JSC WHITE SANDS TEST FACILITY  
GENERATOR HFTA  
ACCUMULATION START DATE 10/26/00  
CONTACT ED HAVENOR 5168  
MISCELLANEOUS HAZARDOUS WASTE  
WSTF HAZARD CLASS 1  
LDC Safety Supply, Inc. CREATION

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## Waste Accumulation Area Instructions and Log Books

## 11.3.3 Hypergol Detection

- ◆ Use monitors to verify safe propellant vapor concentrations before allowing unprotected personnel to re-enter the area

## 11.3.4 Safe Configuration

- ◆ After operations, hypergol systems should be safed to:
  - Contain propellant
  - Vent pressure, but maintain inert pad pressure
  - Shut down electrical equipment
  - Maintain access control

## 11.3.5 Maintenance

- ◆ Ensure that maintenance on systems is performed as planned \*
- ◆ Ensure that system configuration and cleanliness are sustained during maintenance procedures
- ◆ Ensure maintenance is performed by personnel familiar with the system and/or trained on the hazards of hypergols

# 11.0 Operation Controls



# Course Outline

- ✓ Introduction
- ✓ Accidents
  - ✓ Examples of the “problems”
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  - ✓ Toxicity Hazard
  - ✓ Reactivity Hazard
  - ✓ Fire Hazard
  - ✓ Explosion Hazard
  - ✓ Hypergol Properties, References & Other Information
- ◆ Step 4 - Manage the Risks
  - Primary Controls
    - ✓ Design
      - ✓ Material Compatibility
    - ✓ Build Up
    - ✓ Operation
  - Secondary Controls
    - PPE
    - Detectors/Monitors
- ◆ Course Evaluations

# Step 4 - Manage the Risks

- ◆ Primary (Engineering) Controls
  - ✓ Design
  - ✓ Build Up
  - ✓ Operation
- ◆ Secondary Controls
  - Personal Protective Equipment (PPE)
  - Detectors/Monitors

# 12.0 Personal Protective Equipment

- ◆ Engineering controls
  - Primary means of reducing occupational exposures to hazards
- ◆ Personal Protective Equipment (PPE)
  - Supplementary control for
    - Emergencies (see [Accident #8](#))
    - Failed engineering controls
    - Unproven or in-process controls/practices
    - Mobile or short-term work



## 12.1 Chemical Exposure Protection

- ◆ PPE is divided into 4 categories based on the degree of protection afforded (29 CFR 1910.120 App. B Subpart H)
  - Level A
    - Selected when the greatest level of skin, respiratory, and eye protection is required.
  - Level B
    - Provides highest level of respiratory protection but a lesser level of skin protection

# 12.1 Chemical Exposure Protection

- Level C
  - The concentration(s) and type(s) of airborne substance(s) are known and the criteria for using air purifying respirators are met.
  - ⊘ NOT suitable for handling hypergols.
- Level D
  - A work uniform affording minimal protection

## 12.1.1 Level A Equipment

- ◆ Positive pressure, full face-piece self-contained breathing apparatus (SCBA), or positive pressure supplied air respirator with escape SCBA (NIOSH approved)
- ◆ Totally-encapsulating chemical-protective suit
- ◆ Coveralls (optional)
- ◆ Long underwear (optional)
- ◆ Gloves, outer, chemical-resistant
- ◆ Gloves, inner, chemical-resistant
- ◆ Boots, chemical-resistant, steel toe and shank
- ◆ Hard hat (under suit) (optional)
- ◆ Disposable protective suit, gloves and boots (depending on suit construction, may be worn over totally-encapsulating suit)

# 12.1.1.1 Modified Level A Example KSC Propellant Handler Ensemble



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## 12.1.1.2 Modified Level A Example KSC Propellant Handler Ensemble



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## 12.1.1.3 Propellant Handler Ensemble

- ◆ **Features**
  - Fully encapsulating
  - Continuous air supply or SCBA
  - Positive pressure
  - Locking cuff mechanism for glove and boot change out
  - Good chemical resistance
- ◆ **Limitations**
  - Tethered by airline or weighted down by SCBA
  - Movement
    - Standing quickly
  - Dexterity
  - Visibility
    - Face shield

## 12.1.1.3 Modified Level A Example



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## 12.1.1.4 Modified Level A Example



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## 12.1.1.5 ILC Dover Ensemble

- ◆ **Features**
  - Fully encapsulating
  - Continuous air supply or SCBA
  - Positive pressure
  - Cloropel™ material protects against wide range of chemicals
- ◆ **Limitations**
  - Tethered by airline or weighted down by SCBA
  - Movement
    - Standing quickly
  - Dexterity
  - Visibility
    - Face shield
  - UDMH permeability
  - Hot/cold weather
  - Butyl gloves

## 12.1.1.6 Respirix Gas Tight Suit



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## 12.1.1.7 Respirer Suit Features

- ◆ Adjustable internal support belt
- ◆ Locking cuff mechanism for glove and boot change out
- ◆ Larger visor for greater visibility
- ◆ Distributed air flow throughout suit
- ◆ Bromobutyl rubber coated polyester
- ◆ Good permeability
- ◆ Resistance to hydrazine fuels
- ◆ Good protection against NTO splash + vapor

## 12.1.2 Level B Equipment

- ◆ Positive pressure, full-facepiece self-contained breathing apparatus (SCBA), or positive pressure supplied air respirator with escape SCBA (NIOSH approved)
- ◆ Hooded chemical-resistant clothing (overalls and long-sleeved jacket; coveralls; one or two-piece chemical-splash suit; disposable chemical-resistant overalls)
- ◆ Coveralls (optional)
- ◆ Gloves, outer, chemical-resistant
- ◆ Gloves, inner, chemical-resistant
- ◆ Boots, outer, chemical-resistant steel toe and shank
- ◆ Boot-covers, outer, chemical-resistant (disposable) (optional)
- ◆ Hard hat (optional)
- ◆ Face shield (optional)

# 12.1.2.1 Level B Example



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## 12.1.2.2 “Full Splash Gear”

- ◆ Features
  - Easy to don
  - Lightweight
  - Ease of movement
  - Airline respirator or SCBA
  - Disposable
- ◆ Limitations
  - Vinyl material provides smaller range of chemical protection
  - Potential for skin exposure
  - Hot/cold weather

## 12.1.3 Level C Equipment

- ◆ Full-face or half-mask, air purifying respirators (NIOSH approved)
- ◆ Hooded chemical-resistant clothing (overalls; two-piece chemical-splash suit; disposable chemical-resistant overalls)
- ◆ Coveralls (optional)
- ◆ Gloves, outer, chemical-resistant
- ◆ Gloves, inner, chemical-resistant
- ◆ Boots (outer), chemical-resistant steel toe and shank (optional)
- ◆ Boot-covers, outer, chemical-resistant (disposable) (optional)
- ◆ Hard hat (optional)
- ◆ Escape mask (optional)
- ◆ Face shield (optional)

## 12.1.4 Level D Equipment

- ◆ Coveralls
- ◆ Gloves (optional)
- ◆ Boots/shoes, chemical-resistant steel toe and shank
- ◆ Boots, outer, chemical-resistant (disposable) (optional)
- ◆ Safety glasses or chemical splash goggles (optional)
- ◆ Hard hat (optional)
- ◆ Escape mask (optional)
- ◆ Face shield (optional)

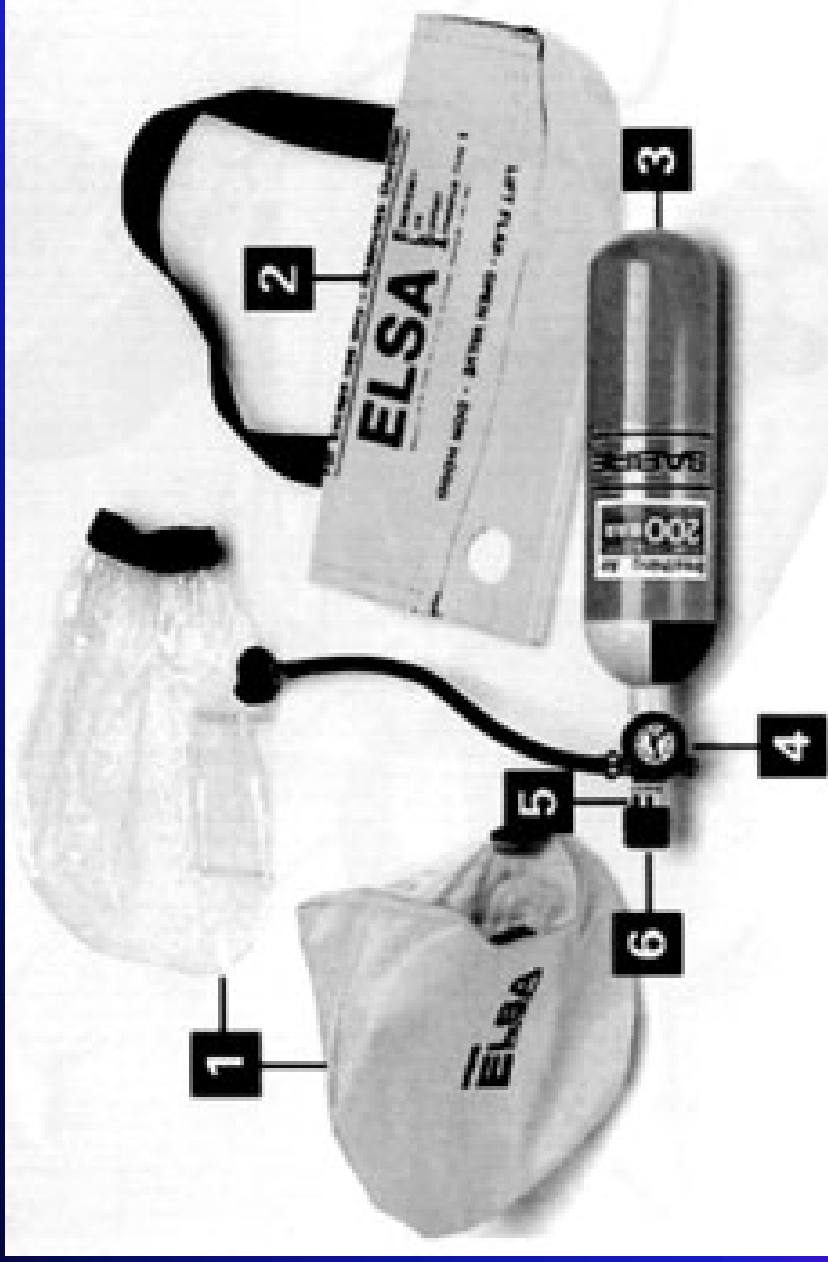


## 12.1.4.1 Level D Example



# ELSA

## Emergency Life Support Apparatus



- Small cylinder
- 5 to 15 minute air supply
- supply hose to air hood

# Aside

- ◆ Combinations of PPE other than those described for Levels A, B, C, and D protection may be more appropriate and may be used to provide the proper level of protection.

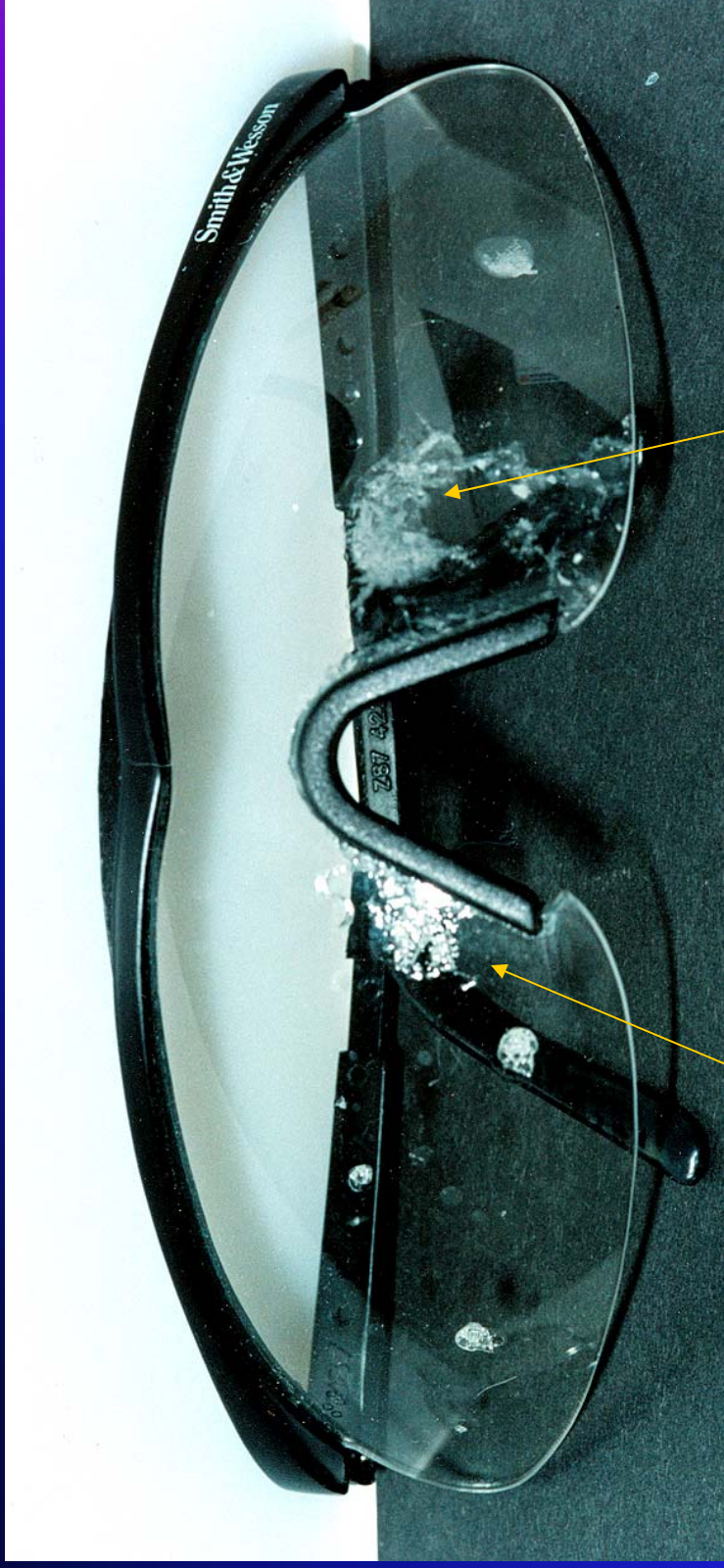
## 12.2 Improper PPE

- ◆ Use of improper PPE can be more dangerous than not using PPE.
  - Karen Wetterhahn, Chemist, Dartmouth Univ.

## 12.2 “T”PPE?

- ◆ Maybe the term should be changed to:  
“Temporary” Personal Protective Equipment
- ◆ If selected properly PPE will protect you,  
but its not completely impervious
- ◆ Look for signs of damage
- ◆ Be aware of limitations
- ◆ Consider replacing after use
  - Change/decon gloves periodically during  
use

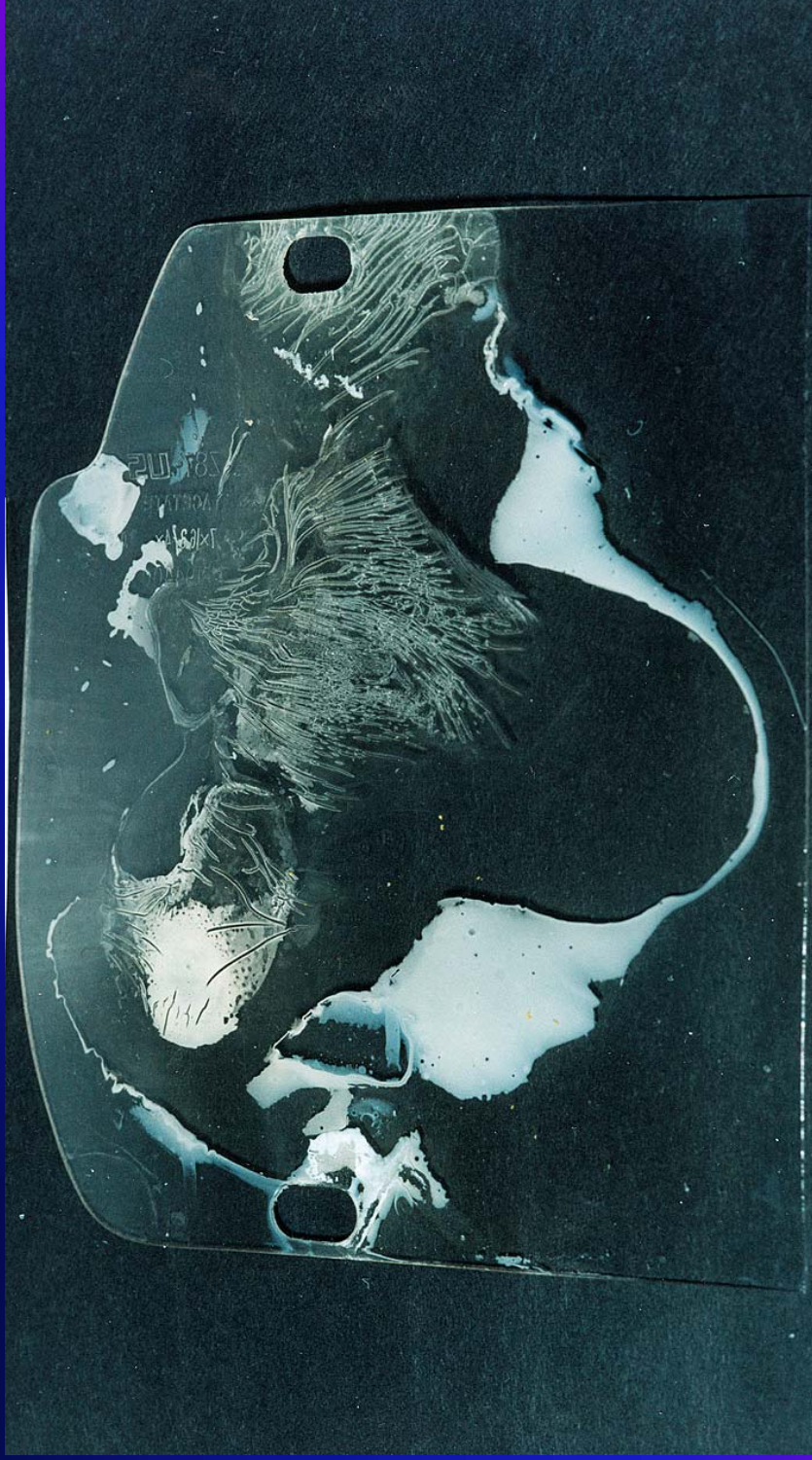
Safety glasses, poly-dimethylsiloxane compound, exposed to fuels



MMH

Hydrazine

# Safety shield, acetate compound exposed to NTO



## 12.3 PPE Removal

- ◆ Getting out of PPE can be hazardous if not done properly
  - Rinse off
  - Don't touch contaminated surfaces while removing
  - Dispose of properly
  - Training on proper donning and removal should be provided by employer



# Video Version of “What’s Wrong with this Picture?” The fume hood and the syringe.

## Discussion



# Course Outline

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# Step 4 - Manage the Risks

- ◆ Primary (Engineering) Controls
  - ✓ Design
  - ✓ Build Up
  - ✓ Operation
- ◆ Secondary Controls
  - ✓ Personal Protective Equipment (PPE)
  - Detectors/Monitors

## 13.0 Hypergol Detection

- ◆ Detection is an issue because:
  - Toxicity and inhalation hazard
  - Significant vapor pressure at ambient temperatures
  - Low vapor exposure limits

# Authority for the NASA Environmental Health Program

- ◆ NPD 1820.1 NASA Environmental Health Program and subservient documents establish:
  - The KSC IH Program is a key element in the overall Environmental Health Protection Program
  - APPLICABLE EXPOSURE LIMITS: In accordance with NPD 1820.1, NASA has adopted health standards promulgated by the Occupational Safety and Health Administration (OSHA) or the American Conference of Governmental Industrial Hygienists (ACGIH), whichever is more stringent.
  - In addition, their responsibilities include implementing health hazard controls when exposure levels exceed the "Action Level" for the hazardous material or agent of concern.

# WSTF Interim Policy for the Hydrazine Family of Fuels - 1996

- ◆ Referenced new TLV-TWA of 0.01 ppm
- ◆ Noted lack of required sensitivity for 0.01 ppm
- ◆ Implemented:
  - The TLV will be treated as a time-weighted average.
  - When hydrazines are detected PPE or additional engineering controls (fume hoods, point source ventilation) will be applied.
  - Personal dosimeters, when established as a valid measurement device, will be worn in areas where potential exposure conditions exist.

## 13.0 Vapor Exposure Limits

- ◆ **Hydrazine Fuels**
  - Threshold Limit Value (TLV) is 10 ppb
  - IDLH is 15 to 50 ppm
  - Odor threshold is 1 - 8 ppm
- ◆ **NTO**
  - NIOSH Recommended Exposure Level (REL) is 1 ppm
  - IDLH is 20 ppm
  - Odor threshold is 1 - 3 ppm

## 13.1 Uses of Monitors

- ◆ Monitoring for personnel protection
  - 10 to 100 ppb - **Hydrazines**
  - 1 to 10 ppm - **NTO**
- ◆ Monitoring for residual propellant / contamination
  - 100 to 1000 ppb
- ◆ Leak detection
  - 0.1 to 10 ppm



# Aside

- ◆ Concentrations in the Gas Phase
  - Units of ppm and ppb are volume / volume
    - ppm  $\rightarrow 10^{-6}$  (microliters / liter)
    - ppb  $\rightarrow 10^{-9}$  (nanoliters / liter)
  - Use Ideal Gas Law to calculate mass from volume

# Example

- ◆ Room 20 x 30 x 10 foot at 10 ppb MMH
  - $1.7 \times 10^5$  liters total room volume
  - Volume of MMH
    - $(1.7 \times 10^5 \text{ liters}) \times (10 \times 10^{-9}) = 1.7 \times 10^{-3} \text{ liters}$
    - $(1.7 \times 10^{-3} \text{ liters} \times 1 \text{ atm}) / (0.08205 \times 298 \text{ K}) = 6.9 \times 10^{-5} \text{ moles}$
    - $6.9 \times 10^{-5} \text{ moles} \times 46 \text{ grams/mole} = 3.2 \times 10^{-3} \text{ g}$
    - 3.2 mg

## 13.2 Classify Monitors by Method of Detection

- ◆ **Colorometric**
  - Chemical reaction produces color change
- ◆ **Electrochemical**
  - Measure oxidation or reduction in solution
- ◆ **Thermal**
  - Measure heat from a chemical reaction

## 13.2.1 Colorimetric Monitors

- ◆ Dosimeter Badges
  - Usually passive
  - Watch for color change with time
  - Estimate dose by comparison with color standard
  - May be read with optical instrument

## 13.2.1.1 Dosimeter Badges



## 13.2.2 Colorimetric Monitors

- ◆ Paper Tape Monitor
  - Active sampling using air pump
  - Sample pumped through a paper tape treated with an indicator
  - Color change read by optical reflectance or transmittance
  - Tape advances to fresh spot following reading

## 13.2.2.1 Example of a Paper Tape Monitor



## 13.2.2.2 Second Example of a Paper Tape Monitor



Scott/Bacharach

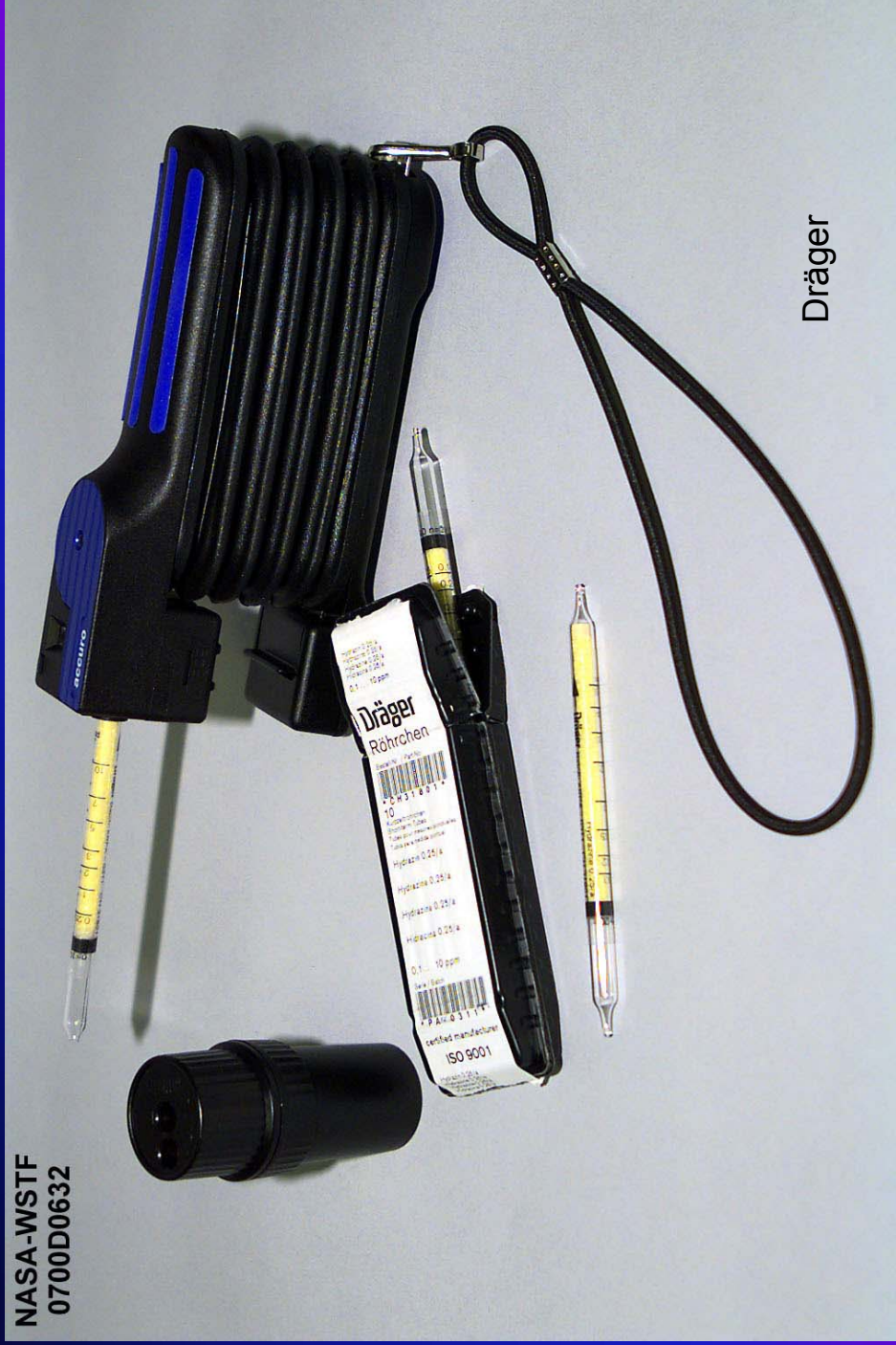


## 13.2.3 Colorimetric Monitors

- ◆ Indicator tubes
  - Active sampling using air pump
  - Length of color change in tube correlates to concentration

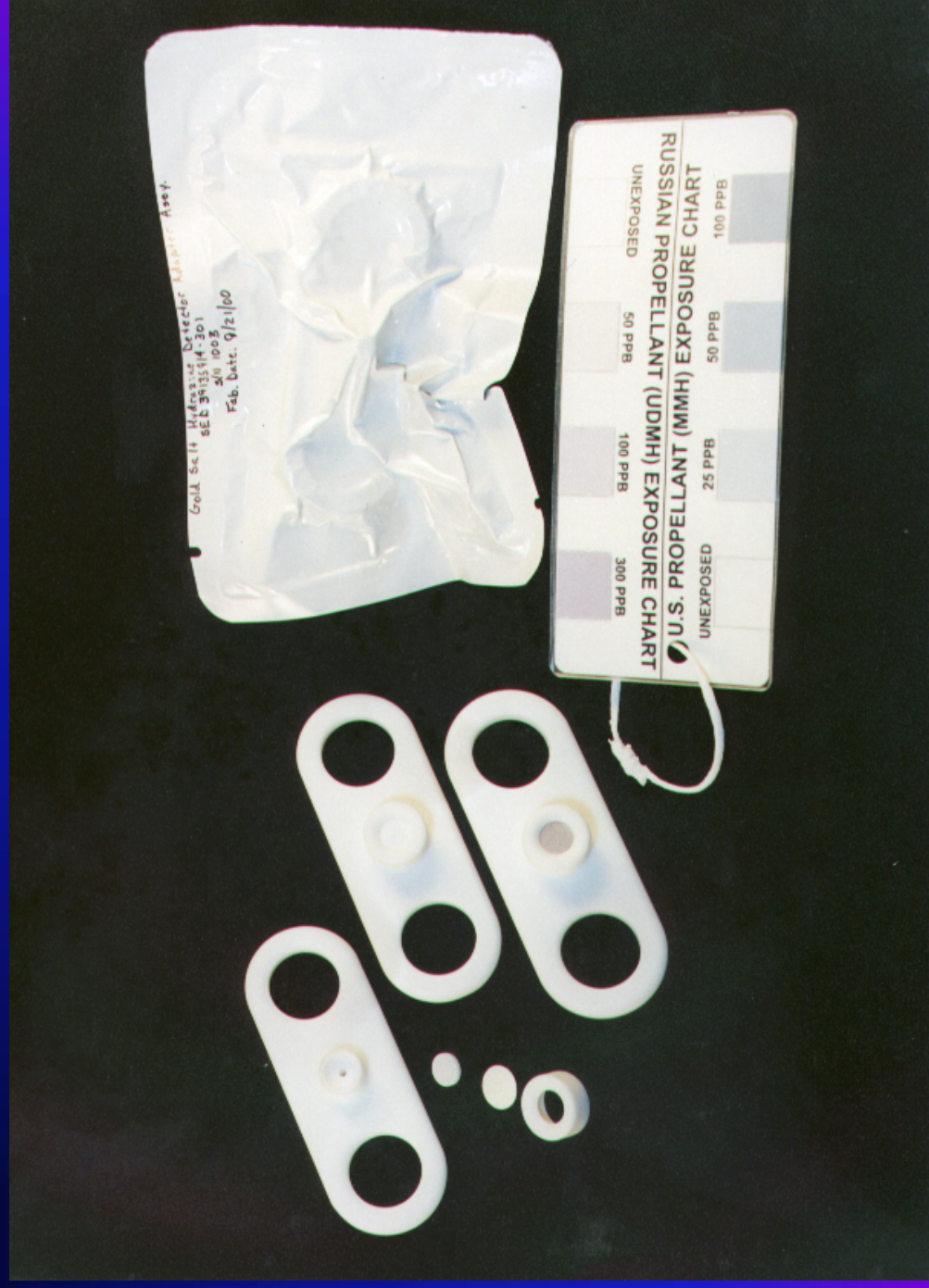
# 13.2.3.1 Example of Indicator Tubes

NASA-WSTF  
0700D0632



Dräger

## 13.2.3.2 Shuttle Airlock MMH/UDMH Detector



## 13.2.4 Electrochemical Monitors

- ◆ Measure an electrochemical reaction by flow of current (coulometry)
  - Active sampling
  - Diffusion of propellant into electrolyte
  - Measure flow of current between electrodes at an applied potential
  - Current is proportional to concentration

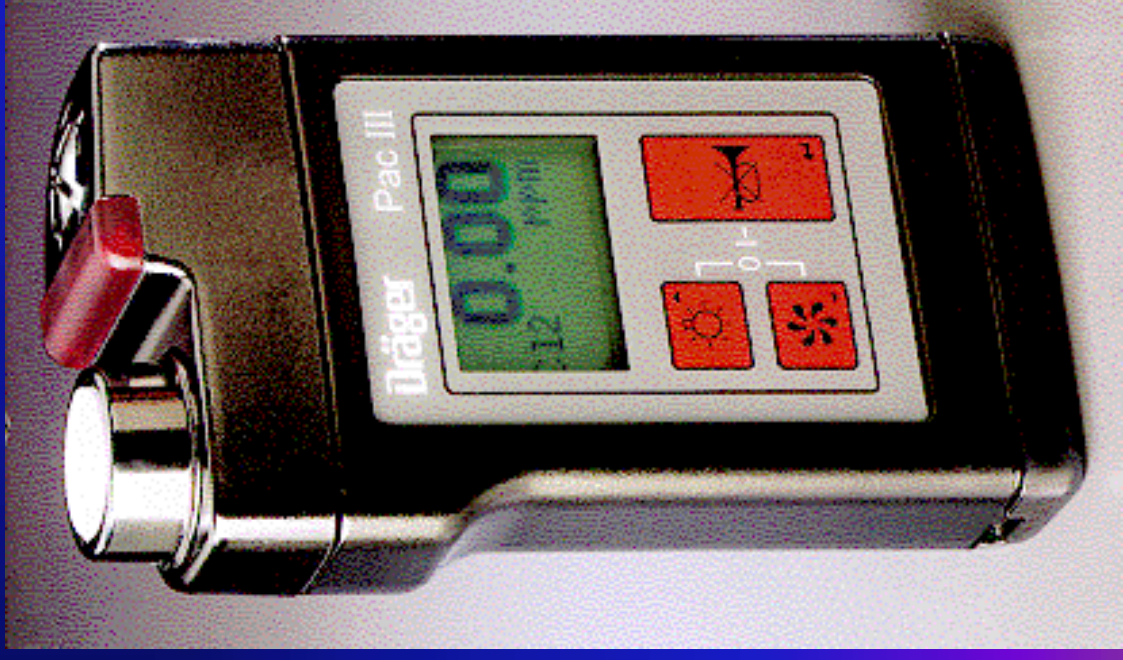
# 13.2.4.1 Example of Electrochemical Monitor

NASA-WSTF  
0700D0628



Interscan

## 13.2.4.2 Example of Electrochemical Monitor

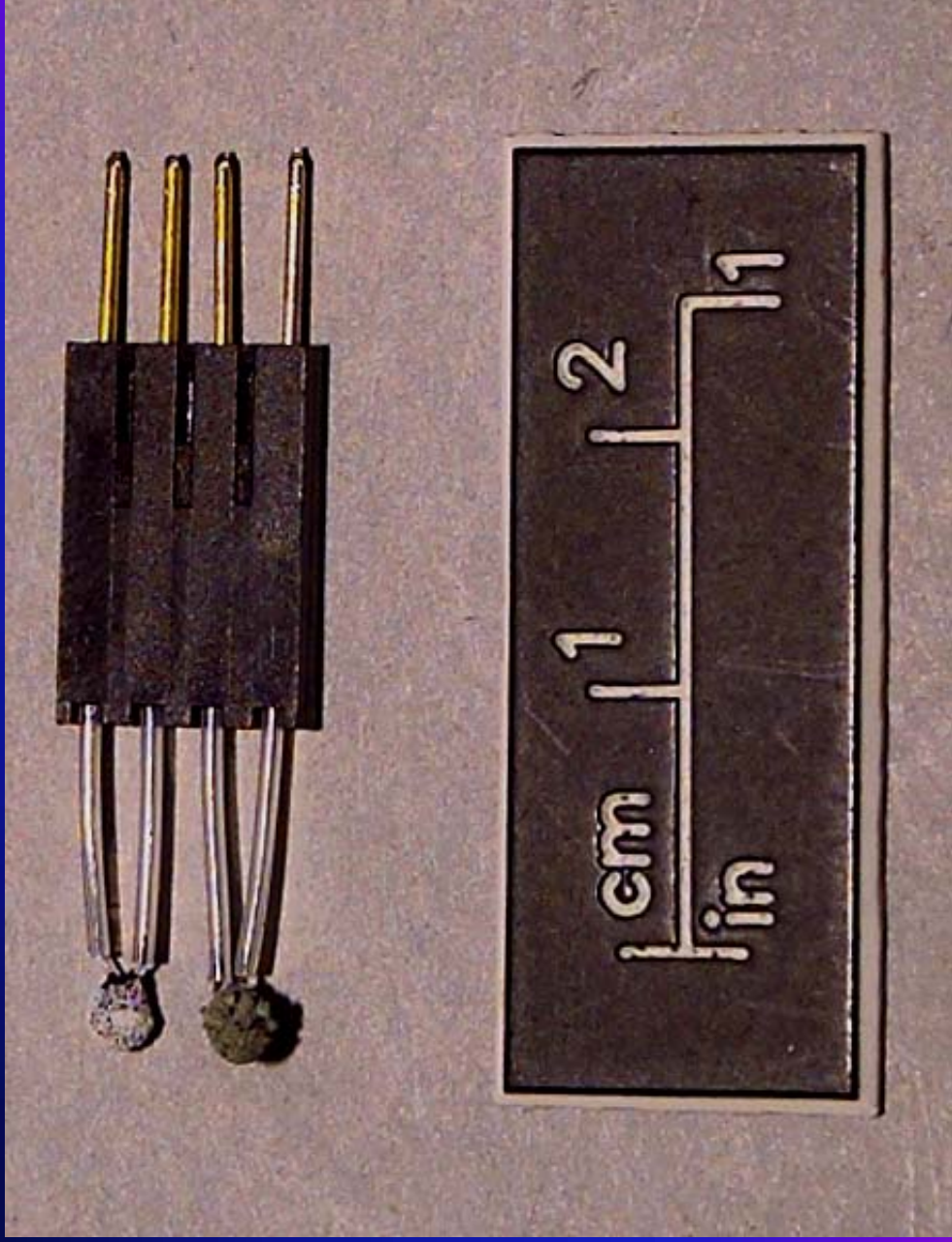


Dräger

## 13.2.5 Thermal Monitors

- ◆ Measure temperature rise from a chemical reaction
  - Reactive chemical on temperature sensor
  - Simple
  - Use for high levels of contaminants

## 13.2.5.1 Example of Thermal Monitor





## 13.3 Common Interferants

### ◆ Hydrazines Monitors

- Ammonia
- Isopropyl alcohol
- Hydrogen

### ◆ NTO Monitors

- Chlorine
- Ozone

## 13.4 Ideal Specifications

- Sensitivity 10 ppb
- Free from interferences
- Response time one minute or less for 90% of actual concentration
- Capable of re-use after exposure to "high" concentrations

## 13.4 Ideal Specifications

- Portable
- Single hand operation, capable of being operated by personnel wearing PPE
- Rugged - Not affected by expected bumping or swinging
- Long calibration cycle

## 13.4 Ideal Specifications

- Chemical and physical interference characterized
- Self diagnostics capability (battery check, zero, etc.)
- Capable of operating with a charger when possible to minimize battery depletion
- Performance specifications established and consistent between different units

# Operation

- ◆ Check calibration, operation, battery
- ◆ Equilibrate in measurement environment
- ◆ Zero in measurement environment (without propellant)
- ◆ Sample for appropriate length of time
  - May depend on concentration
- ◆ Recovery time

# Importance of Stable Zero

- ◆ Response of monitor may drift with:
  - Temperature
  - Humidity
  - Background gases

# Sampling Time

- ◆ Response time may depend on concentration

## 13.5 “Calibration” of Monitors

- ◆ Produce stable streams of known concentration
  - Difficult with reactive species
- ◆ Verify concentration with analytical techniques
- ◆ Expose monitors in suitable configuration



## 13.5.1 Producing Gas Streams

- ◆ Trace gas standards
  - NO<sub>2</sub> in nitrogen
- ◆ Permeation system for hydrazines
  - Teflon tubes containing hydrazines
  - Constant temperature glass container
  - Flush container with nitrogen
  - Combine with an air stream for dilution

## 13.5.1.1 Permeation System



## 13.5.1.2 Permeation System



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## 13.5.2 Analysis of Gas Streams

- ◆ Quantitative trapping of known gas volume
  - Sulfuric acid on firebrick
- ◆ Desorption into solution
- ◆ Analysis
  - Electrochemical measurement (coulometry)
  - HPLC with electrochemical detection

## 13.5.2.1 Firebrick Sampling for Hydrazines

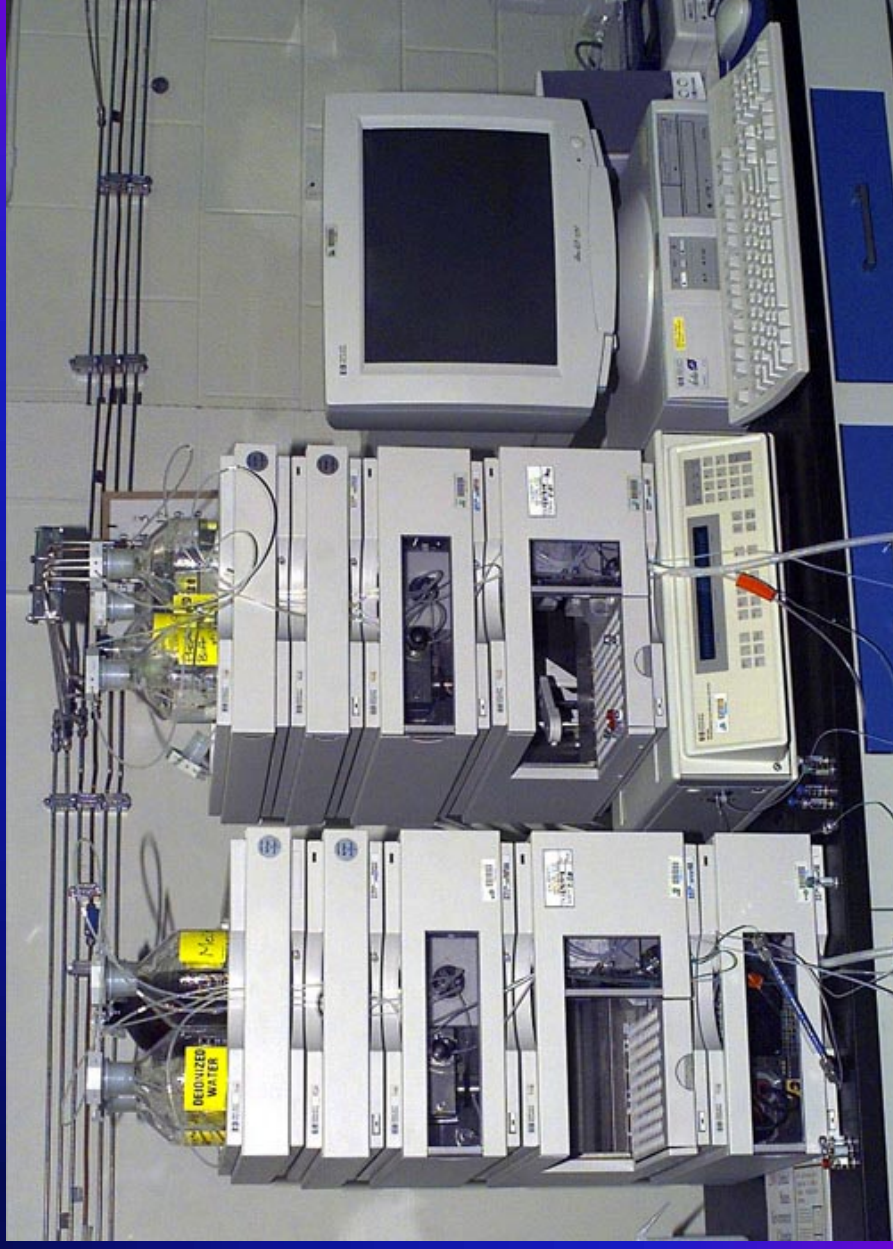


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## 13.5.2.2 HPLC for Analysis



# Course Outline

- ✓ Introduction
- ✓ Accidents
  - ✓ Examples of the “problems”
- ✓ Step 1 - Identify the Hazards
  - ✓ Toxicity Hazard
  - ✓ Reactivity Hazard
  - ✓ Fire Hazard
  - ✓ Explosion Hazard
  - ✓ Hypergol Properties, References & Other Information
- ◆ Step 4 - Manage the Risks
  - Primary Controls
    - ✓ Design
      - ✓ Material Compatibility
    - ✓ Build Up
    - ✓ Operation
  - Secondary Controls
    - ✓ PPE
    - ✓ Detectors/Monitors
- ◆ Course Evaluations