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Fire, Explosion, Compatibility, and Safety Hazards of Hypergols - Hydrazine

Special Project Report

Fire, Explosion, Compatibility, and Safety Hazards of Hypergols - Hydrazine

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Approved

Abstract

This Special Project report presents information that designers, builders, and users of hydrazine systems can use to avoid or resolve hydrazine hazards. Pertinent research is summarized, and the data are presented in a quick-reference form. Further information can be found in the extensive bibliography.

Contents

Foreword

Hydrazine is a colorless, corrosive, strongly reducing liquid compound. Current aerospace applications include its use in the Space Transportation System as a fuel for the auxiliary power units, in satellites as a monopropellant for thrusters, and in jet aircraft as fuel for auxiliary power sources. Although hydrazine is immensely useful in these applications, there are also drawbacks. For example, hydrazine vapor is flammable and detonable; both liquid and vapor hydrazine are corrosive, react with many materials, and are susceptible to catalytic decomposition; and hydrazine is highly toxic. The users and designers of hydrazine systems must be aware of these hazards and safeguard against them.

This AIAA Special Report preserves the text of NASA document RD-WSTF-0002 Rev A, December 17, 1998, "Fire, Explosion, Compatibility, and Safety Hazards of Hydrazine," developed by the NASA White Sands Test Facility for the Propulsion and Power Division of the Lyndon B. Johnson Space Center and the Air Force Space Division. In the interests of technology transfer, custody of the material was assigned to AIAA through of Memorandum of Understanding dated February 1999. One of the purposes of this Memorandum is to provide broader distribution of the valuable information developed and published in the original manual.

The authors of the NASA Revision A manual, dated December 16, 1998 are: Stephen S. Woods, Donald B. Wilson, Dennis D. Davis, Michelle Barragan, Walter Stewart, Radel L. Bunker, and David L. Baker. Authors to the earlier 1990 edition are: Michael D. Pedley, David L. Baker, Harold D. Beeson, Richard C. Wedlich, Frank J. Benz, Radel L. Bunker, and Nathalie B. Martin.

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Acronyms

A, E_a	Arrhenius parameters
ACGIH	American Conference of Governmental and Industrial Hygienists
AHJ	Authority Having Jurisdiction
APU	Auxiliary power unit
ARC	Accelerating rate calorimeter
ASME	American Society of Mechanical Engineers
CERCLA	Comprehensive Environmental response, Compensation, and Liability Act
C-J	Chapman-Jouguet
CPIA	Chemical Propulsion Information Agency
DDT	Deflagration to detonation transition
DOT	Department of Transportation
DOT	Department of Transportation
EIS	Electrochemical Impedance Spectroscopy
EPA	Environmental Protection Agency
FDCA	Food, Drug, and Cosmetics Act
GI	Gastrointestinal
HAZMAT	Hazardous Materials
HZ	Hydrazine
IDLH	Immediately Dangerous To Life or Health
IRFNA	Inhibited Red Fuming Nitric Acid
JANAF	Joint-Army-Navy-Air Force
JANNAF	Joint-Army-Navy-NASA-Air Force
LEPC	Local Emergency Planning Committee
LFL and UFL	Lower and Upper Flammability Limit
MIE	Minimum Ignition Energy
MMH	Monomethylhydrazine
MSDS	Material Safety Data Sheet
NIOSH	National Institute of Occupational Safety and Health
NPDES	National Pollutant Discharge Elimination System
OSHA	Occupational Safety and Health Administration
PEL	Permissible Exposure Limits
RCRA	Resource Conservation and Recovery Act
REL	Recommended Exposure Limit
RQ	Reportable Quantity
SARA	Superfund Amendments and Reauthorization Act
SERC	State Emergency Response Commission
SI	International System units
SMAC	Spacecraft Maximum Acceptable Concentration
STEL	Short Term Exposure Limit
STS	Space Transportation System
TLD-1	Toxic Level Detector 1
TLV	Threshold Limit Value
TLV-TWA	Threshold Limit Value - Time Weighted Average
TOMES	Toxicology, Occupational Medicine, and Environmental Series
TPQ	Threshold Planning Quantity
TRI	Toxic Release Inventory
TSCA	Toxic Substances Control Act

Glossary

Activation Energy (or Apparent Activation Energy): In absolute-rate theory, the energy associated with the formation of an activated complex intermediate between the reactant(s) and product(s) of an elementary reaction. An "apparent" activation energy is used as the parameter E_a in an Arrhenius function when the exact kinetic mechanism is unknown.

Adiabatic: A process in which the system changes state without thermal energy exchange between the system and the surroundings.

Adiabatic Compression: Mechanical work transferred to a system under conditions where there is an increase in the internal energy of the material for a static system or an increase in the enthalpy for a dynamic system. If the process is also reversible (in the thermodynamic definition), this change is also isentropic.

Adiabatic Factor: The temperature change that occurs when all the limiting reactant is completely consumed (normalized extent of reaction equals 1 when the reaction system is operated adiabatically). This factor is useful for comparing exothermicity or endothermicity of several reactions.

Adiabatic Flame Temperature: The temperature of thermodynamic equilibrium in a reaction or in a set of reactions that occurs in a process operating adiabatically.

Arrhenius Function: A mathematical model for defining the temperature dependency of an observed macroscopic kinetic reaction rate.   The rate is equal to $A\exp(-E_a/RT)$, where A is the preexponential factor, E_a is the apparent activation energy, R is the ideal gas law constant, and T is the absolute temperature.

Authority Having Jurisdiction (AHJ): Organization, office, or individual responsible for "approving" equipment, an installation, or a procedure. The designation is used in a broad manner because jurisdiction and "approval" agencies vary, as do their responsibilities. Where public safety is primary, the AHJ may be a federal, state, local, or other regional department or individual such as a fire chief, fire marshal, chief of a fire prevention bureau, labor department, health department, building official, electrical inspector, or others having statutory authority. In many circumstances, the AHJ is the property owner or his designated departmental official. At government installations, the AHJ may be the commanding officer or a designated department official. Approved is herein defined as being authorized by, or acceptable, to the AHJ.

Autoignition Temperature: The lowest temperature at which a material will spontaneously ignite. No additional ignition energy (ignition source) is required.

Burning Rate: The rate of liquid mass consumption per unit area ($kg/(m^2 \cdot s)$).

Burning Velocity: The velocity at which the liquid level decreases. It is the burning rate/density of the liquid (m/s).

Catalyst: A chemical compound or chemical species that alters the rate of a chemical reaction. The catalyst is not altered by the reaction.

Cell Size: Refers to the width of the characteristic fish scale-shaped cell pattern etched on a smoked foil during a gas-phase detonation. The cell pattern is produced by the path of the triple-point, i.e. intersection of a primary shock wave, a transverse shock wave, and a Mach stem wave. The cell width is used as a parameter for characterizing detonations.

Chapman-Jouguet Detonation: Describes a stable detonation state that is consistent with most experimental measurement. The steady-state solution of the conservation equations at which the Rankin line is tangent to the Hugoniot curve.

Critical Diameter: The tube diameter necessary for a gaseous detonation to propagate from the tube to an unconfined environment (Equation 3.6, $d_c = 13\lambda$).

Critical Energy: The minimum energy required to initiate an unconfined detonation in a specified mixture.

Deflagration: A flame moving through a flammable mixture in the form of a subsonic wave (with respect to the unburned mixture).

Dermal Exposure: The penetration of a toxic chemical through skin and into the blood stream. Such exposure can be rapid and difficult for the body to eliminate.

Detonable Mixture: The state of a specified mixture that, upon application of the critical energy for the mixture, will initiate and sustain a detonation. This mixture is also flammable.

Detonation: Exothermic chemical reaction coupled to a shock wave that propagates through a detonable mixture. The velocity of the shock wave is supersonic with respect to the unburned gases. After initiation, the thermal energy of the reaction sustains the shock wave, and the shock wave compresses the unreacted material to sustain the reaction. Initiation of a detonation can occur with a deflagration to detonation transition (DDT).

Diluent: In a mixture, an inert material that reduces the concentration of the remaining materials.

Dynamic Parameters: Four parameters (detonability limits, initiation energy, cell size, and critical tube diameter) used to describe the dynamic characteristics of a detonation. They are in contrast to the static C-J detonation parameters; velocity, detonation temperature, detonation pressure, and detonation density.

Equivalence Ratio: The ratio of the actual fuel-oxidizer ratio to the stoichiometric fuel-oxidizer ratio.

Exothermic: The production of thermal energy by a chemical reaction.

Explosion: The rapid equilibration of pressure between the system and the surroundings, such that a shockwave is produced. Explosions may occur through mechanical failure of vessels containing high-pressure fluids or through rapid chemical reactions producing large volumes of hot gases.

Explosion Potential: A parameter that is useful for comparing an unknown system (reaction) to well-known reactions. It is the product of system volume (constant), adiabatic flame temperature, total moles per unit of mass in the system at equilibrium, and the ideal gas law constant.

Fire: Sustained burning, as manifested by any or all of the following: light, flame, heat, and smoke (ASTM E 176-97b).[*]

Fire Point: The lowest temperature at which a flame continuously exists over a liquid surface upon ignition by an open flame.

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[*]ASTM Fire Test Standards, 3rd Ed. 1990, ASTM, 1916 Race St., Philadelphia, PA 19103.

Flame: A hot, usually luminous zone of gas, or particulate matter in gaseous suspension, or both, that is undergoing exothermic chemical reaction. A flame may be stationary with the flammable mixture fed into the reaction zone, or a flame may propagate through the flammable mixture, as in a deflagration.

Flame Speed: Refers to the velocity of propagation of the reaction zone through the flammable mixture, as measured by a stationary observer. Usually measured at the front of the flame.

Flame Velocity: When coordinates are centered in the flame front it is the velocity at which unburned gases move through the combustion zone in the direction normal to the flame front.

Flammability Limits: The lower (LFL) and upper (UFL) vapor concentrations (usually reported as volume percent) of fuel in a flammable mixture that will ignite and propagate a flame. These limits are functions of temperature, pressure, diluents, and ignition energy.

Flash Point: The lowest temperature, corrected to 101.3 kPa (14.7 psia) of pressure, of a material at which application of an ignition source causes the vapor of the material to ignite momentarily under specified conditions.

Froth: The froth is a medium in which gas bubbles are surrounded by a thin film of liquid hydrazine, maximizing the surface area between the ullage gas and the liquid hydrazine.

Halocarbons: Organic compounds containing one or more of the elements fluorine, chlorine, bromine, and iodine.

Hazard: A situation (or potential event) that may result in death or injury to personnel, or damage to equipment. Includes the effect of fire, flash, explosion, shock, concussion, fragmentation, corrosion, or toxicity.

Heat Generation Potential: The product of the temperature sensitivity and the adiabatic factor. A useful dimensionless group for characterizing and comparing reactions.

Heat of Reaction: For a given temperature and pressure, the enthalpy of the products of a reaction minus the enthalpy of the reactants.

Hypergolic: Spontaneous ignition of two materials upon contact (no additional ignition energy is required).

Ignition: Introduction of sufficient energy into a flammable mixture or material to produce a flame.

Ingestion: The introduction of a toxic material into the body through the mouth or by breathing.

Material Compatibility: Materials are considered compatible with each other if their rate of degradation when in contact is insignificant for the application.

Minimum Ignition Energy: The minimum energy required to ignite a flammable mixture under given conditions (temperature, pressure, diluents).

Monopropellant: A liquid propellant that decomposes exothermically to produce hot gases; e.g., hydrogen peroxide, hydrazine.

Order of Reaction: A parameter used to define the concentration (or pressure) dependency of the kinetic rate of reaction. For elementary reactions, the order coincides with the molecularity (for

$H_2 + I_2 \rightarrow 2HI$ the forward reaction rate is second order, the $R_{forward} \propto \{Conc.\ H_2\}^m \times \{Conc.\ I_2\}^k$ where m=1 and k=1. The overall order of reaction n = m + k = 2 for this example.

Oxidizer: Primarily air, oxygen, halogens, the hypergolics (N_2O_4 or fuming nitric acid) or any material that undergoes a reduction in chemical terms (will readily accept electrons from the fuel).

Permissible Exposure Limit (PEL): The degree of exposure of workers to hazardous gases and vapors is regulated by the Occupational Safety and Health Administration (OSHA). The regulation specifies permissible exposure limits (PELs) that for hydrazine includes a ceiling limit (employee exposure not to be exceeded during any part of the work day) of 1.0 ppm (1.3 mg/m^3) and a skin designation that requires the use of protective clothing and equipment. For more information, see Section 5.1.2.

Pool Fire: Used to describe the sustained burning of a pool of liquid fuel. The rate of burning, called burn rate, is measured in terms of depth change/time or mass consumed/time.

Shock: A violent collision or impact and the subsequent transmission of energy through the system. The energy moves as a wave at velocities greater than the speed of sound relative to the undisturbed material.

Spacecraft Maximum Acceptable Concentration (SMAC): The maximum allowable concentration for spacecraft applications, typically based on standards and requirements for ground applications. For specific SMACs see Section 5.3.5.

Temperature Sensitivity: A measure of the response of reaction rate to temperature, E_a/RT^2 (E_a = activation energy; R = gas constant; T = temperature).

Thermal Runaway: Operation of a system that contains material which reacts exothermically, in a manner that the rate of thermal energy generation exceeds the rate at which thermal energy is transferred to the surroundings. The system temperature increase can lead to an increase in this imbalance and then lead to autoignition of the reaction.

Threshold Limiting Value: The average concentration of toxic gas to which most workers can be exposed during working hours (8 hours per day, 5 days per week) for prolonged periods without adversely affecting their health.

Total Mass Burning Rate: The rate of total mass of reactant consumed (kg/s) in a burning system.

Toxic: Poisonous. A material that causes physiological damage to the body.

Ullage: The vapor space above the liquid surface within the system.

Vapor: A component in the gas phase that is in equilibrium with its corresponding liquid phase. The temperature of the system must be below the critical temperature of the component so it can exist as a liquid phase.

Trademarks

The following commercial products that require trademark designation are mentioned in this document. This information is given for the convenience of users of this Special Report and does not constitute an endorsement. Equivalent products may be used if they can be shown to lead to the same results.

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Inconel
Interscan
Kalrez
Kel-F
Koropon
Krytox

Kynar
MACOR
Microseal
Mobil Jet Oil II
Monitox
Mykroy/Mycalex
Mylar
Permendur
Pyromet
Ryton
SCAPE
SCAN Kit
Splash uit
Stoody 6
Stycast
Teflon
Tefzel
Waspaloy

1   Introduction to hazard assessment

Hydrazine (HZ), N_2H_4, is used as an aerospace fuel, an antioxidant in industrial processes, and in the production of pesticides and pharmaceuticals, to name just a few applications. The hazards associated with the use of vapor and liquid hydrazine in aerospace systems are the focus of this special report.

1.1   About this special report

This special report presents information that designers, builders, and users of hydrazine systems can use to avoid or resolve hydrazine hazards. Pertinent research is summarized, and the data is presented herein as for concise quick-reference resource. Additional information can be found in the sources cited throughout the special report. An example of a hazard analysis is provided in Annex A. The chemical, physical, and thermodynamic properties of hydrazine are provided in Annex B.

Readers are cautioned that, although every reasonable effort has been made to present accurate information, the authors and publisher make no warranty nor do they assume legal responsibility for its validity. Readers are urged to assess each situation carefully and to choose data that appear most appropriate.

Throughout this special report, the following conventions are used:

- ambient pressure and temperature refer to a pressure of 101.3 kPa (14.7 psia) and temperature of 298 K (77 °F),

- neat hydrazine is hydrazine that is free from adulteration,

- high-purity hydrazine contains a minimum of 99.0 percent by weight hydrazine and less than or equal to 0.005 percent by weight aniline,

- monopropellant-grade hydrazine contains a minimum of 98.5 percent by weight hydrazine, and

- data are given in SI (International System) units with US customary units in parentheses.

1.2   Approach to performing a hazard assessment

Section 1.2 presents guidelines for determining if a particular hazard exists, using the information presented in this special report. A diagram depicting the overall hazards associated with hydrazine is presented in Figure 1.

As shown in Figure 1, four categories of potential hazards are discussed in this special report, and considered in assessing the overall hazards of hydrazine: fire, explosion, material compatibility, and safety/exposure. For clarity, two of the potential hazards, explosion and material compatibility, have been subdivided. Explosion has been divided into the three major processes that generate the pressure that can lead to explosions in hydrazine systems. These processes are deflagration, detonation, and thermal-chemical processes. Material Compatibility has been divided into two sections entitled "Effect of Hydrazine" and "Effect of Material." The "Effect of Hydrazine" section describes how hydrazine degrades materials by altering their physical properties. The "Effect of Material" section describes how materials can accelerate the rate of hydrazine decomposition. Listed under each category of potential hazard in Figure 1 are criteria that define when the potential hazard exists, and the effects produced by that potential hazard.

The criteria for, and the effects produced, by each potential hazard are presented in more detail in Sections 1.2.1 through 1.2.4. These sections should be read carefully to gain familiarity with the four categories of potential hazards and the terminology that is used in assessing these hazards.

Sections 1.2.1 through 1.2.4 also specify information about the system or environment that is needed to assess each potential hazard. With this information, the following approach can be utilized to establish the overall hazard that exists when hydrazine is used.

- Consider each of the four categories of potential hazards independently, using the "Criteria" and the "Effects Produced" information contained in Sections 1.2.1 through 1.2.4.

- Determine if the system state, environmental conditions, or both meet criteria resulting in a hazardous situation.

The conditions that lead to a potential hazard are given under each Criteria. Further information on the criteria of a potential hazard is listed under a corresponding section of this special report.
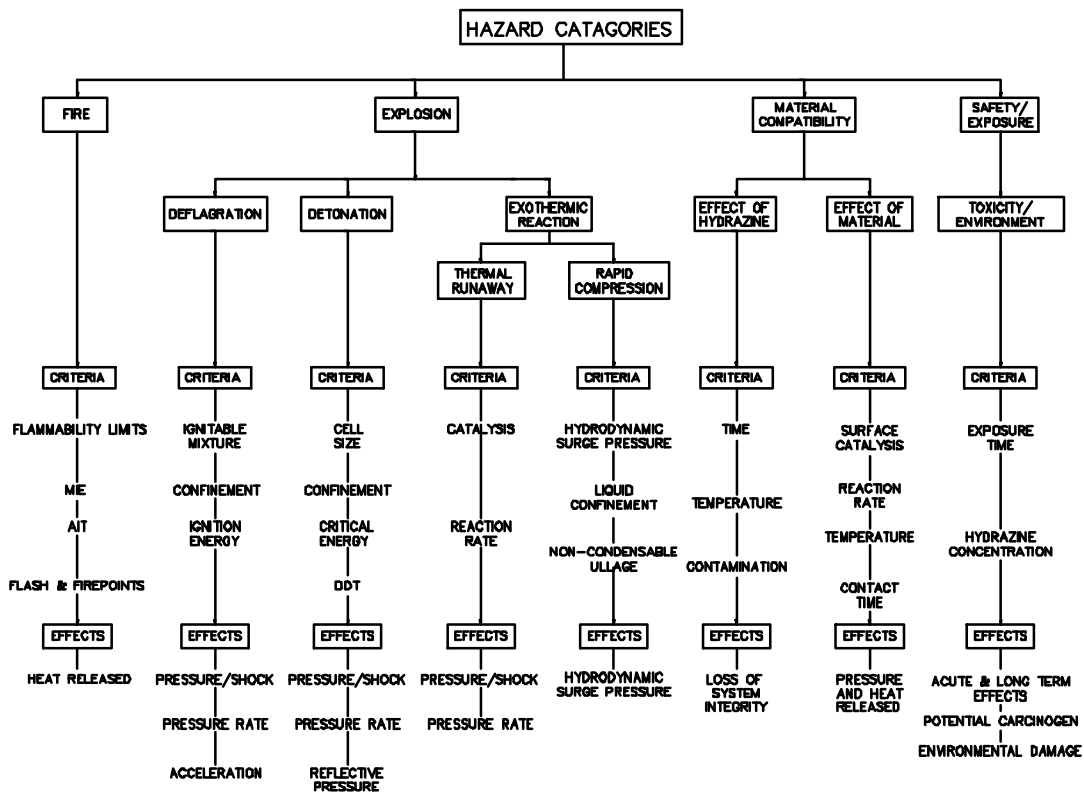

Figure 1 — Overall hazards diagram

For example, a flammable mixture is one criterion of a fire. When assessing a potential fire hazard, it is necessary to refer to the detailed information on flammability in Section 2.1.1 so that the existence of a flammable mixture can be determined. Because a flammable mixture exists does not necessarily signify that a hazardous condition, i.e. a fire will be produced.

- Evaluate the potential effects in each appropriate hazard category. The effects of each hazard are listed under the corresponding "Effects Produced" heading.

  For example, once it has been shown that a potential fire hazard exists, the effect (heat, in this case) produced by the fire must be evaluated. Section 2 presents information on flame velocities and heats of reactions, which can be used to determine the rate and duration of heat release.

- Perform the overall assessment of all potential hazards by considering individual system hazards and the hazards that occur through interaction between systems.

  An example of a detailed hazard assessment is given in Annex A.

1.2.1   Fire hazards

To assess a possible fire hazard, the following information about the system and environment must be known:

- phase(s), pressure, and temperature of hydrazine,

- environment (e.g., hydrazine, diluents, and oxidizers) and corresponding concentrations, and

- ignition sources and amount of energy that can be released by each.

1.2.1.1 Criteria for a potential fire hazard

The criteria used to determine if there is a potential fire hazard from hydrazine vapor are: flammability limits, minimum ignition energy, and autoignition temperature. The lower and upper flammability limits (LFL and UFL) specify the minimum and maximum hydrazine vapor concentrations that will ignite and propagate a flame. The flammability limits are a function of temperature, pressure, and other factors (Section 2.1.1). The minimum ignition energy (MIE), the energy required to initiate a fire (Section 2.1.1), is a function of temperature, pressure, and oxidizer content. The autoignition temperature (AIT) is the temperature in a system at which the entire volume of gases or vapors spontaneously ignites (Section 2.1.2). The AIT data for hydrazine is highly variable, system specific, and should be used with caution. When the concentration of hydrazine vapor is within the flammability limits and the MIE is present or when the temperature of the hydrazine vapor is at the AIT, a potential fire hazard exists.

When oxidizer vapors or diluent gases are present, the potential fire hazard from hydrazine liquid is generally evaluated by using flash and fire points and MIE. The flash point of liquid hydrazine is the temperature at which the vapor above the liquid forms an ignitable mixture with air. The fire point is the temperature at which the vapor above the liquid can continuously support a flame. The fire point normally occurs at a higher temperature than the flash point. Flash and fire points can change, depending on the nature of the vapor above the liquid (e.g., the presence of diluents and oxidizers). If the temperature of the liquid hydrazine is at or above the flash or fire point, and the MIE is present, a potential fire hazard exists.

1.2.1.2 Effects produced by fire

The hazards from a fire are determined by assessing the effects produced by the fire on the system or environment.

For the purposes of this special report, the primary effect of a fire is heat. A fire is characterized by the rate and duration of the heat release. In the vapor phase, the rate and duration of the heat release can be calculated using the flame velocity, the amount of hydrazine present, and the heat of reaction (Section 2.1.3.4). In the liquid phase, the rate and duration can be calculated using the surface area of the liquid pool, the heat of reaction, and the burning rate.

A fire hazard exists when an evaluation of the specific system or its environment shows the heat release is sufficient to cause dangerous or undesirable conditions.

1.2.2 Explosion hazards

In this special report, it is assumed that an explosive event (see glossary) is produced either directly or indirectly by the release of chemical energy. Explosions can arise from three processes that hydrazine can undergo, and in some cases, generate high pressures. These are: deflagration, detonation, and thermal-chemical processes.

1.2.2.1 Deflagration

A deflagration is a flame moving through a flammable mixture in the form of a subsonic wave (with respect to the unburned mixture).

To assess an explosion hazard due to deflagration, the following information about the system and environment must be known:

- phase(s), pressure, and temperature of hydrazine,

- environment (e.g., hydrazine, diluents, and oxidizers) and corresponding concentrations,

- ignition sources and amount of energy released by the source,

- mechanical properties of a confining system, and

- presence of obstacles that can accelerate the deflagration.

1.2.2.1.1 Criteria for a potential explosion hazard from a deflagration

The flammability criteria for fire also apply to deflagrations. An explosion hazard exists when hydrazine vapor is within the flammability limits, the MIE is present, and obstacles, turbulence, or confinement necessary to accelerate the deflagration are present or when the deflagration is confined in a system and the pressure due to the deflagration can exceed the burst pressure of the system.

When hydrazine liquid is present, a potential explosion hazard from a deflagration exists when the temperature of the liquid hydrazine is at or above the fire point and the MIE is present.

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1.2.2.1.2 Effects produced by a deflagration

The primary effects of a deflagration are fire and if the deflagration is confined, pressure. Calculation of deflagration pressures in partially confined systems is very difficult. In a confined system the pressure generated by the hydrazine (calculated from Equation 5) is compared to the burst pressure of the system. If the maximum pressure which can be generated exceeds the burst pressure, an explosion hazard exists. The venting rate of relief valves or burst disks must be great enough to prevent the burst pressure of a system from being reached. The pressure increase rate can be calculated with Equations 9 and 10.

The hazard associated with the heat generated by a deflagration is covered in Section 1.2.1. The hazard resulting from a deflagration transition to a detonation is covered in Section 1.2.2.2.

1.2.2.2 Detonation

To assess hazards due to detonation (see Glossary), the following information about the system and environment must be known:

- pressure and temperature of hydrazine vapor,*

- environment (e.g., hydrazine, diluents, and oxidizers) and the corresponding concentrations,

- ignition sources and amount of energy released by the source, and

- type of confinement.

1.2.2.2.1 Criteria for a potential explosion hazard from a detonation

The general criteria for detonation is that the combination of the system and the dynamics of the deflagration (flame movement) lead to a deflagration to detonation transition (DDT) (Section 3.2). The criteria that must be met for a detonation to occur are related to the composition and state of the flammable material in the system, the size and shape of the vessel or enclosure, and the energy source that initiates the detonation. The dynamic parameters, critical tube diameter, critical transition diameter, and initiation energy are based on cell size which is determined from experiment or empirical correlation. For a detonation to occur, there must be a sufficient volume for a detonation cell to form and sufficient initiation energy or a flow path that will support a DDT (Equations 11 through 16). To use these equations, the cell size, which varies with the composition, initial temperature, and initial pressure of the hydrazine mixture, must be known.

1.2.2.2.2 Effects produced by a detonation

To determine if a detonation hazard exists, the resulting effects produced by the detonation must be assessed.

The pressure produced by a detonation is described by the Chapman-Jouguet (C-J) condition (Section 3.2) and is a characteristic of the reactant mixture. Computer programs have been developed to calculate the C-J condition.

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*Hydrazine vapor is readily detonated. Hydrazine liquid has not been detonated in cylindrical vessels of diameters up to 10.2 cm (4 in.). The ignition energy was provided by approximately 887 g (1.96 lb) of C4 initiated by a #8 blaster's cap.

When a DDT occurs, the final detonation pressure (C-J pressure) is dependent on the extent of the deflagration before transition. For example, consider neat hydrazine vapor contained in a system at 50 kPa (7.3 psia) and 300 K (80 °F). If the vapor undergoes a DDT immediately after ignition, then the detonation pressure (C-J pressure) will be approximately 28 times the initial pressure. If the DDT is delayed, and the pressure in the system increases due to the deflagration, then the C-J pressure will be 28 times the pressure at the time of the DDT. A worst-case detonation hazard occurs when the deflagration has proceeded almost to completion before the transition takes place. This case can be estimated by using the adiabatic pressure (see Section 3.1.1) produced by the deflagration as the initial system pressure in C-J calculations. Pressures produced when a detonation wave is reflected at locations such as elbows and tees can be two to three times the incident pressure (i.e., the C-J pressure).

1.2.2.3 Thermal-chemical processes

Any thermal-chemical reaction system is a potential explosion hazard if the reaction produces a net increase in moles of gas or vapor (Section 3.1) when the system volume is confined, if the system operates adiabatically (or nearly adiabatically), or when the rate of heat generated exceeds the rate of heat exchange with the environment leading to a thermal runaway. Hydrazine is thermodynamically unstable and while its degradation is slow under ambient conditions increasing temperature accelerates this decomposition. In addition many materials act as catalysts for hydrazine decomposition and careful selection of system materials must occur (Section 4).

Three cases that may cause explosion hazards when operating hydrazine systems are considered: near-isothermal decomposition in a closed system; thermal runaway in an isolated system; rapid compression in an open system.

To assess hazards due to a thermal-chemical reaction, the following information about the system and environment must be known:

- phase(s), pressure, and temperature of the hydrazine,

- environment (e.g., hydrazine, diluents, and oxidizers) and corresponding concentrations,

- materials in contact with hydrazine and corresponding surface areas,

- system thermal capacity and heat transfer properties, and

- pressure limitations of the system.

1.2.2.3.1 Near-isothermal hydrazine decomposition

If the enthalpy of reaction of hydrazine decomposition (Annex B) is dissipated to the environment as it is generated, the system operates to maintain the temperature constant.

1.2.2.3.1.1 Criteria for hazard from near-isothermal hydrazine decomposition

If the system is a rigid volume and closed to addition or removal of mass, the pressure will increase as the reaction proceeds to completion.

1.2.2.3.1.2 Effects produced by near-isothermal hydrazine decomposition

Pressure increases as the moles of decomposition product gases increase. For isothermal processes, the pressure increase can be approximately calculated using the following:

- Ideal Gas Law,

- quantity of hydrazine and diluents,

- kinetic parameters given in Table 17 or the figures of Section 4,

- surface area of the material on which the hydrazine is decomposing if catalysis is occurring,

- volume of system, and

- initial conditions.

Assessment examples are given in Section 4.3.

1.2.2.3.2 Thermal runaway

If the system operates non-isothermally the temperature can reach a condition where heat is generated faster than it can be dissipated to the environment and the system undergoes a thermal runaway.

1.2.2.3.2.1 Criteria for thermal runaway hazards

The system temperature increases continuously (unless limited by quantity of hydrazine) as long as the rate of energy generation exceeds the rate of heat exchanged with the environment. If the system is closed and a constant volume the pressure increases.

1.2.2.3.2.2 Effects produced by a thermal runaway

For a non-isothermal process, the pressure increase rate can be determined by solving a series of nonlinear, differential equations. See Section 4.3 for examples. Under non-isothermal conditions, the system will fail if sufficient hydrazine is present to decompose and produce pressures that exceed the system burst pressure.

1.2.2.3.3 Rapid compression

Rapid compression occurs in a system when accelerating liquid compresses ullage gases or vapors in a confined volume. The rapid temperature rise of the compressed material acts as a possible ignition source for the hydrazine. If a froth is created at the liquid hydrazine ullage gas or vapor interface the rate of thermal energy transfer into the hydrazine can increase producing a greater potential hazard. Pressure increases as a result of compression, temperature rise and hydrazine decomposition product gases. If system pressure exceeds design burst pressure, a failure resulting in potential hazard can occur.

To assess an explosion hazard due to rapid compression, the following information about the system or environment must be known:

- initial temperatures of flowing hydrazine liquid and ullage gas,

- pressure and volume of the ullage gas,

- location of system dead-ends,

- hydrodynamic surge pressure at the system dead-ends, and

- burst pressure of the system.

1.2.2.3.3.1 Criteria for a hazard from rapid compression

The criteria for a hazard from rapid compression are the presence of liquid hydrazine, a dynamic system,* a non-condensable gas ullage, a froth (see Section 3.3.3.1), and liquid confinement. The initiation mechanism of this process is the enthalpy change of the ullage material during adiabatic compression. The condition (i.e. temperature and pressure) of the froth is a function of the dynamic surge pressure created when the moving liquid hydrazine impacts a dead-end. When the ullage temperature starts at ambient and the fluid dynamic surge pressure is greater than 17.2 MPa (2500 psia), sufficient enthalpy is created to initiate exothermic decomposition of the hydrazine contained in the froth. The froth and fluid dynamic surge pressure are both dependent upon the initial pressure and volume of the ullage. The fluid dynamic surge pressure is also strongly dependent on the velocity of the hydrazine liquid. Rapid compression which meets the above criteria will generate pressure, and thus a potential explosion hazard will exist.

1.2.2.3.3.2 Effects produced by rapid compression

A hazard from rapid compression exists when the generated pressure exceeds the strength of the confining system.

If the fluid dynamic surge pressure is known, the final generated pressure can be estimated from Figure 21 and Tables 20 and 21. The fluid dynamic surge pressure can be estimated by applying Equations 18 through 22, or by substituting water for hydrazine and performing experiments with the system.

It should be noted that a hazard can also exist when the fluid dynamic surge pressure alone exceeds the strength of the system.

1.2.3   Material compatibility

Hydrazine affects materials by degrading them and altering their physical and chemical properties. Materials affect hydrazine by accelerating its decomposition. Section 4 of this special report provides additional information on compatibility.

1.2.3.1 Effect of hydrazine

To assess a material compatibility hazard due to hydrazine contacting a material, the following information about the system and environment must be known:

- phase(s) and temperature of hydrazine,

- exposure time,

- surface condition and area exposed to hydrazine, and

- contamination present.

1.2.3.1.1 Criteria for a potential material compatibility hazard from materials exposed to hydrazine

The criteria for hydrazine's ability to affect a material (Section 4.1) are the length of time the material will

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*Explosive events caused by rapid compression have only been observed when the liquid hydrazine was flowing.

be exposed to hydrazine, the temperature of the hydrazine in contact with the material, the surface condition and area exposed to hydrazine, and the contamination present. Tables 14 and 15 for metals and nonmetals, respectively, indicate the amount of corrosion and changes observed for various materials exposed to hydrazine at a specified temperature. These corrosion rates may increase when operating temperatures higher than those listed in the tables are used.

1.2.3.1.2 Effects produced on materials exposed to hydrazine

The physical and chemical properties of materials can be changed by exposure to hydrazine leading to corrosion (loss of material), stress corrosion cracking (fracture), and embrittlement. A material compatibility hazard exists when degradation of the material can lead to loss of system integrity or component function.

1.2.3.2 Effect of material

Materials can act as a catalyst and accelerate the decomposition rate of hydrazine and thus the pressure increase rate. Therefore, to assess the presence of a material compatibility hazard, the following information about the system and environment must be known:

- phase(s), quantity, and temperature of hydrazine,

- environment (e.g., hydrazine, diluents, contaminants, and oxidizers) and corresponding concentrations,

- surface condition and area of the material,

- system thermal capacity and heat transfer properties, and

- pressure limitations of the system.

1.2.3.2.1 Criteria for a potential material compatibility hazard from hydrazine exposed to catalytic materials

A potential material compatibility hazard exists when the material catalytically decomposes hydrazine. Material compatibility data are presented in Section 4.

1.2.3.2.2 Effects produced in hydrazine exposed to catalytic materials

A material compatibility hazard exists when the hydrazine decomposition reaction is accelerated to the point that pressures generated affect the operation of or damage the system or environment. (The methods used to determine these pressures are presented in Section 1.2.2.3.) An actual material compatibility hazard can lead to an explosion hazard if the generated pressures exceed the strength of the confining system.

1.2.4   Exposure hazards

Exposure hazards can be divided into two categories: hazards to personnel (toxicity), and hazards to the environment. Unlike the previous section, the criteria listed here do not apply to a potential hazard. If these criteria are met, an actual exposure hazard exists.

To assess an exposure hazard, the following information about the environment must be known:

- phase(s) of hydrazine,

- temperature of the environment,

- environment (e.g., hydrazine, diluents, and oxidizers) and corresponding concentrations, and

- time of contact.

1.2.4.1 Criteria for an actual exposure hazard

The criteria for a toxicity hazard are exposure time and concentration. Personnel exposure to hydrazine can be chronic (long-term exposure, Section 5.1.1) or acute (short-term exposure, Section 5.1.2.). A toxicity hazard is present when personnel can be exposed to hydrazine concentrations which exceed the Threshold Limit Value (TLV), Permissible Exposure Limits (PEL), or Recommended Exposure Limit (REL) for chronic exposure (Section 5.1.1.2); or, Immediately Dangerous To Life or Health (IDLH) or Spacecraft Maximum Acceptable Concentration (SMAC) for acute exposure (Section 5.1.2.2).

State and Federal regulations specify the levels of hydrazine that pose an exposure hazard to the environment. For more information, refer to Section 5.

1.2.4.2 Resulting effects from exposure to hydrazine

The effects of a toxicity hazard and an environmental exposure hazard are listed in Section 5.

1.3   Overall hazard

The overall hazard to a system and environment may be intensified by a combination of several individual events.

An example of the cumulative effect hazards can have was illustrated by an incident involving the ninth Space Transportation System (STS-9). In this particular situation, a material compatibility hazard led to stress corrosion of an injector tube constructed from Hasteloy B. The tube subsequently ruptured, leaking hydrazine into the APU area, where it quickly froze. During re-entry, the hydrazine vaporized and ignited. By itself, the heat from the burning hydrazine may have caused system damage; however, the critical effect of the fire was to overheat the onboard APU's. When this happened, the hydrazine underwent several explosive processes, damaging two of the three APU's.

Therefore, a proper hazard assessment considers not only each hazard and topic individually but the potential effects to the system if several events occurred simultaneously.

2   Fire

Introduction

Fire is a rapid chemical reaction that produces heat and light (Lapedes 1974). Fire normally requires a fuel, an ignition source, and an oxidizer, however, hydrazine is a monopropellant which decomposes exothermically and does not require the presence of an oxidizer. A hydrazine fire can also begin without the usual ignition source; hydrazine is hypergolic with oxidizing reagents and propellant oxidizers such as inhibited red fuming nitric acid (IRFNA) and dinitrogen tetroxide.

A fire can occur with either vapor or liquid hydrazine, as well as in the mist, droplet, and spray forms of the fuel. The fire hazard from the burning hydrazine is affected by system and environmental conditions, i.e. the temperature, concentration, and pressure of the hydrazine, and the type of ignition source involved. Hazard assessment varies depending on the form of hydrazine present.

In hydrazine vapor, the fire hazard can be quantified by considering the flammability limits, ignition source, flame speed or flame velocity. In liquid hydrazine, fire points and burning rate can be used to assess the degree of fire hazard. The fire hazard in hydrazine mists, droplets, or sprays can also be measured by considering flash and fire points and burning rates. These factors vary with the purity of hydrazine vapor (neat or completely free of contaminants, mixed with air, mixed with an inert diluent, or mixed with an oxidizer) or liquid (high purity, monopropellant, or mixtures).

This section presents data on hydrazine fires. Readers are cautioned that, although every reasonable effort has been made to present accurate information in this section, the authors and publisher make no warranty nor do they assume legal responsibility for its correctness. Readers are urged to assess each situation carefully and to choose data that appear most appropriate.

2.1   Hydrazine vapor

The reactants in a hydrazine fire are usually in the gaseous phase and must be present within a specific concentration range to burn. The fire hazard of hydrazine vapor can be assessed by considering flammability, ignition, flame speed and flame velocity in neat vapor, hydrazine-air mixtures, hydrazine-diluent mixtures, and hydrazine-oxidizer mixtures.

2.1.1   Flammability

Flammability is a measure of the extent to which a vapor concentration of a fuel in a mixture will ignite and propagate a flame. The limits of flammability of a gas or vapor are the minimum and maximum fuel concentrations that can support flame propagation. The upper flammability limit (UFL) is the concentration of the most concentrated mixture that is flammable; the lower flammability limit (LFL) is the concentration of the most dilute fuel-air or fuel-diluent mixture that is flammable (see Glossary).

Flammability varies for neat hydrazine, hydrazine mixed with air, hydrazine mixed with an inert diluent, and hydrazine mixed with an oxidizer. The flammability limits for each mixture are affected by pressure, temperature, and other factors. The range of flammability is the range of concentrations between the lower and upper flammability limits. In general for many flammable mixtures the flammability range is widened by increasing temperature (Burgess and Wheeler 1911). There is limited data for hydrazine. In general, decreased pressure (below ambient) narrows the flammability range by increasing the lower flammability limit and decreasing the upper flammability limit (Coward and Jones 1952). As the pressure decreases, the two limits approach each other. When the upper and lower limits are identical, the low pressure limit (the minimum pressure required for ignition) is reached. The low pressure limit is affected by ignition energy: as the ignition energy is increased, the low pressure limit decreases (Benz, Bishop, and Pedley 1988).