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Management of Time Sensitive Reactive and Unstable Chemicals

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NATIONAL FIRE PROTECTION ASSOCIATION
2013 CONFERENCE & EXPOSITION
McCORMICK PLACE CONVENTION CENTER
CHICAGO, ILLINOIS
JUNE 10, 2013

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OBJECTIVES

- Define categories of time sensitive reactive and unstable chemicals
- Understand how these chemicals become reactive or unstable over time and to know what has happened when these chemicals are not properly managed
- Learn how to store and effectively manage these chemicals to prevent emergency situations

Headlines from Recent Events

- 'Overpressurized' container bursts in Wetherill, sends students to hospital – 02/22/11
- School Evacuated As Bomb Squad Deals With Unstable Chemical – 07/09/11

Unstable Chemical

- Evacuation After Chemical Explosion At Bedford Park – Australia – 07/30/12
- Army Team Makes Safe Unstable Chemicals at Dundalk IT – Ireland – 10/07/12

Celloidin wool

- Unstable Chemical Forces UC San Diego Evacuation – 11/09/12

Time Sensitive Chemicals

- Time sensitive chemicals have the special ability to become significantly more hazardous during storage
- Peroxide forming chemicals
- Chemicals that become unstable reactive upon depletion of inhibitor
- Chemicals that are explosive when dry
- Gases that are corrosive to their cylinders

Hazards Associated with Time Sensitive Chemicals

- Peroxide forming chemicals may explode when moved; heated; or exposed to light, shock or friction
- Auto-polymerization may occur in unstable chemicals with rapid heat release and pressure buildup resulting in violent container rupture or explosion
- Fire and/or explosion when chemicals dry out
- Gas cylinder rupture with release of corrosive gas

Management of Time Sensitive Chemicals

- Establish procedures for management of all chemicals with an emphasis on time sensitive chemicals
  - Identify chemicals and products that present a time sensitive hazard
  - Control procurement of these chemicals
  - Establish procedures for storage of these chemicals
  - Have a defined disposal process for these chemicals prior to procurement
  - Train users on the management of these chemicals

Management of Time Sensitive Chemicals

- Establish a process for tracking these chemicals
  - Know where they are located
  - Date containers when received
  - Dates when the chemicals have been inspected
  - Discard chemicals prior to their expiration date
- Appropriate storage conditions for each chemical
- Plans to address chemicals that may be hazardous or unsafe
  - Testing for hazards (when possible)
  - Establish action levels for treatment
  - Always test liquids for peroxides before distillation

Peroxide Forming Chemicals

- Four categories of peroxide formers
  - Chemicals that form explosive levels without concentration (most dangerous)
  - Chemicals that form explosive levels upon concentration
  - Chemicals that may autopolymerize as a result of peroxide accumulation
  - Chemicals that form peroxides but don't fit in the other categories

Source: Kelly, Richard J., *Review of Safety Guidelines for Peroxidizable Organic Chemicals*, Chemical Health & Safety, September/October 1996 Volume 3 Number 5

Peroxide Forming Chemicals

- Form light, heat and/or shock sensitive peroxides and peroxide compounds
- Controls to prevent peroxide formation
  - Dark colored glass bottles or steel cans
  - Inert cover gas over liquid to minimize availability of oxygen to form peroxides
  - Inhibitor added to stabilize chemical and prevent peroxide formation
  - Storage time since opening of the container

Peroxide Forming Chemicals

- Examples
  - Acrolein
  - Ethers – ethyl ether, isopropyl ether, others
  - Tetrahydrofuran (THF)
  - Vinyl acetate
  - Secondary alcohols – 2-propanol (isopropyl alcohol), 2-butanol (butyl alcohol)
  - 1,3-Butadiene – gas

Peroxide Forming Chemicals

- Identification
  - MSDS statements
    - May form explosive peroxides upon prolonged storage
    - Avoid contact with light
    - May contain peroxide inhibitors
    - Do not evaporate or distill to dryness
    - Store in a tightly closed container
    - Stabilized with hydroquinone

Peroxide Forming Chemicals

- Key Management Controls
  - Understanding proper storage requirements
  - Understanding rate of peroxide formation and how the inhibitors control the rate of formation
  - Define the inspection frequency for each chemical and track in a database
  - Visually inspect container before handling for signs of peroxide formation
  - Test before distillation; distillation concentrates peroxides, if present, and removes inhibitors

Peroxide Forming Chemicals

- Key Management Controls
  - Know how to test for peroxide level
  - No test method is 100% accurate
    - Dip test strips – available in several ranges from most lab supply companies, fastest test method
      - Limitations – may not detect poly-peroxides, may not work with non-solvent liquids, shelf life
    - Solution tests – add solutions to sample of chemicals to see if peroxides are present
      - Potassium iodide – not as accurate as strips
      - Ferrous thiocyanate – complex test

Chemicals That Become Unstable Reactive Upon Depletion Of Inhibitor

- May polymerize when the inhibitor is depleted
- Most are also peroxide formers
- Classified as “unstable reactive” Class 2 chemical when stabilized – Class 4 without a stabilizer
- Types of chemicals
  - Acrolein
  - Vinylic monomers such as styrene, divinylbenzene, methyl methacrylate, vinyl acetate
  - 1,3-Butadiene – gas

Polymerization Event Involving Unstable Reactive Chemicals

- Styrene Release in Cincinnati in 2005 Styrene Event
  - Railroad tank car was on the tracks for several months and was left on rail siding for more than a month
  - The styrene had stabilizer for 2-4 months
  - There were high temperatures in August
  - Evacuation for ½ mile
  - Closed nearby airport – in flight path
  - PRV vented gas safely
  - Tank car cooled by fire department hose streams

Chemicals That Become Unstable Reactive Upon Depletion Of Inhibitor

- Identification
  - MSDS statements
    - Avoid loss of dissolved air, loss of inhibitor, and contamination with incompatible materials
    - Explosive polymerization will only occur if material does not contain an inhibitor (stabilizer)
    - Shelf life is dependent on storage temperature and inhibitor level
    - Recommended storage temperature: 2 - 8 °C
    - Container may rupture from polymerization

Chemicals That Become Unstable Reactive Upon Depletion Of Inhibitor

- Key Management Controls
  - Understanding storage requirements
    - Storage temperatures critical to consumption of inhibitor
    - Shelf life – follow manufacturers recommendations
    - Know what chemical is used to inhibit polymerization – add as needed to store safely
    - Most require oxygen for inhibitor to work – may require stirring to keep oxygen dissolved in product
    - Dispose of chemicals when outdated or no longer needed

Chemicals That Are Explosive When Dry

- Chemicals are usually wetted with a solvent or water
- Wetted with 25% or more liquid
  - Some explosives are shipped as flammable liquids if they are wetted with 25% or more in a solvent
- Types of chemicals
  - Acetyl peroxide in dimethyl phthalate
  - Flexible collodion (nitrocellulose)
  - Picric acid
  - Urea nitrate

Chemicals That Are Explosive When Dry

- Identification
  - MSDS statements
    - Do not allow this material to dry out
    - Maintain at least 20% water content to minimize explosive potential
    - May explode spontaneously in storage
    - Very unstable if allowed to dry completely
- Storage
  - Keep containers tightly closed
  - Segregate from incompatible chemicals

Chemicals That Are Explosive When Dry

- Key Management Controls
  - Establish an inspection frequency to verify wetting of chemical
  - Add additional wetting agent to keep minimum wetted concentration
  - Dispose of chemical when not longer needed or prior to expiration date

Gases That Are Corrosive To Their Cylinders

- Gases the chemically react with the metal walls of the cylinders that they are stored in
- Lecture bottle size cylinders are the biggest hazard
- Types of chemical gases
  - Hydrogen bromide
  - Hydrogen chloride
  - Hydrogen fluoride
  - Tungsten hexafluoride

Corrosive Gas Cylinder Hazard

- Old Hydrogen Fluoride Cylinder

Damage in lab

Gases That Are Corrosive To Their Cylinders

- Key Management Controls
  - Buy gas cylinders that can be returned to the manufacturer
  - Return the gas cylinders to the manufacturer before the date when they will no longer accept them
    - NFPA 45 A.11.1.2 Cylinders of hydrogen fluoride and hydrogen bromide should be returned to the supplier within 2 years of the shipping date.

Time Sensitive Chemicals

- Key Management Controls
  - If one of these types of chemicals becomes hazardous, get professional help.
  - If your company/organization uses these types of chemicals, know who to contact for help before you need assistance.
- Other Types of Time Sensitive Chemicals
  - Gas forming – calcium carbide forms acetylene; chloroform forms phosgene
  - Alkali metals – can form superoxides
  - Others – see references and resources

References and Resources

- CRC Handbook of Laboratory Safety – 5th Ed.
- Handbook of Chemical Health and Safety
- National Research Council - Prudent Practices in the Laboratory (2011 edition)
- Richard J. Kelly *Review of Safety Guidelines for Peroxidizable Organic Chemicals*, Chemical Health & Safety, September/October 1996 Volume 3 Number 5
- NFPA 45 Standard on Fire Protection for Laboratories Using Chemicals
- Peroxides: http://www.ilpi.com/msds/ref/peroxide.html#further

References and Resources

- Management of time sensitive chemicals (I): Misconceptions leading to incidents: http://www.hss.energy.gov/healthsafety/wshp/chem_safety/Self_Assess/manuscript1.pdf
- Management of time-sensitive chemicals (II): Their identification, chemistry and management: http://www.hss.energy.gov/HealthSafety/WSHP/chem_safety/Self_Assess/manuscript2.pdf
- Management of time-sensitive chemicals (III): Stabilization and treatment: http://www.hss.energy.gov/HealthSafety/WSHP/Chem_Safety/Self_Assess/Time_mgmt3_rev_2af.pdf

QUESTIONS?

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