

# Management of Time Sensitive Reactive and Unstable Chemicals

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# Management of Time Sensitive Reactive and Unstable Chemicals

## OBJECTIVES

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

# Management of Time Sensitive Reactive and Unstable Chemicals

## 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
- ▶ Evacuation After Chemical Explosion At Bedford Park – Australia – 07/30/12
- ▶ Army Team Makes Safe Unstable Chemicals at Dundalk IT – Ireland – 10/07/12
- ▶ 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 chemicals with emphasis on time sensitive chemicals
  - Identify chemicals and products that present a time sensitive hazard
  - Control procurement of these chemicals
  - Procedures for storage of these chemicals
  - Have a defined disposal process for these chemicals prior to procurement
  - Training users on the management of these chemicals

## Management of Time Sensitive Chemicals

- 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 removes inhibitors

# Management of Time Sensitive Reactive and Unstable Chemicals

## 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 chemicals to see if peroxides are present

- ◆ Potassium iodide – not as accurate as strips

- ◆ Ferrous thiocyanate – complex

# Management of Time Sensitive Reactive and Unstable Chemicals

## 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 when unstabilized
- ▶ Types of chemicals
  - Acrolein
  - Vinylic monomers such as styrene, divinylbenzene, methyl methacrylate, vinyl acetate
  - 1,3-Butadiene – gas

## 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



# Management of Time Sensitive Reactive and Unstable Chemicals

## 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 and 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

# Management of Time Sensitive Reactive and Unstable Chemicals

## Chemicals That Are Explosive When Dry

- ▶ Chemicals are usually wetted with a solvent or water
- ▶ Wetted with 25% or more liquid
- ▶ 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

# Management of Time Sensitive Reactive and Unstable 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 that 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

# Management of Time Sensitive Reactive and Unstable Chemicals

## Corrosive Gas Cylinder Hazard



Damage in lab



- Old Hydrogen Fluoride  
Cylinder

## 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 the 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; chloroform
  - Alkali metals – can form superoxides
  - Others – see references and resources



## References and Resources

- ▶ CRC Handbook of Laboratory Safety – 5<sup>th</sup> 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](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](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](http://www.hss.energy.gov/HealthSafety/WSHP/Chem_Safety/Self_Assess/Time_mgmt3_rev_2af.pdf)

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## QUESTIONS?

