

Peroxide Formers

Organic peroxides are a dangerous fire hazard if allowed to react with reducing agents. They are potent oxidizers and are a severe explosion hazard when shocked when/if exposed to heat, or if they undergo a spontaneous chemical reaction. Upon contact with some reducing agents, explosions can occur. Many peroxides commonly handled in laboratories are far more sensitive to shock than most primary explosives (e.g., TNT). Many laboratory chemicals can form peroxides, particularly when exposed to air. The following are those chemicals with the ability to develop peroxides and have the potential to cause explosions.

- Ethers, Acetals, and Ketals, especially Cyclic Ethers and those with primary and Secondary Alkyl Groups
- Aldehydes, including Acetaldehyde and Benzaldehyde
- Compounds containing Benzylic Hydrogens
- Compounds containing Allylic Hydrogens, including most Alkenes; Vinyl and Vinylidene Compounds, and Dienes

Labeling

Label all peroxide formers upon receipt with the words “peroxide former” The date of arrival and date of the opening must be prominently displayed on all containers

Storage and Handling

- Keep the quantity of peroxide-forming chemicals to the minimum amount needed.
- Store peroxide-formers in airtight bottles, away from light and heat.
- Avoid using glass ground stoppers.
- Store specific peroxide formers, including those in List A, under nitrogen, if possible.

Working with Peroxide Formers

- Keep the quantity of peroxide-forming chemicals at the minimum amount needed.
- Store peroxide-formers in airtight bottles, away from light and heat. Avoid using glass ground stoppers.
- Specific peroxide formers, including those in List A, should be stored under nitrogen if possible.
- Evaluate for peroxide formation regularly.
- Crystallization, discoloration, and stratification are signs peroxide former may have become shocked sensitive. Do not move the container; call EHS promptly at (204) 934-2487

Evaluate for peroxide formation regularly. Look for signs of crystallization, discoloration, and stratification. These are signs that the peroxide former may have become shocked sensitive. **Do not move the container!** Call EHS promptly at (204) 934-2487.

Disposal

Older containers of peroxide-forming chemicals, or containers of unknown age or history, must be handled very carefully and should never be opened by researchers. Treat any peroxide-forming chemical with visible discoloration, crystallization, or liquid stratification should as potentially explosive. Older steel containers that have visible rust may also be hazardous.

If any of these conditions are observed on a peroxide forming a chemical container or if the origin and age are unknown, **do not attempt to move or open the container**. Contact EHS at (205) 934-2487 to get the container inspected and disposed of properly.

Types

Class A: Peroxide Hazard on Storage – Without Concentration

- Can form peroxides that are difficult to detect and eliminate
- Label these items with a date of receipt and date of opening
- Dispose of these items six months after opening or 18 months if unopened

Working with Peroxide Formers

Examples

- Butadiene
- Chloroprene
- Divinylacetylene
- Isopropyl Ether
- Potassium Amide
- Potassium Metal
- Sodium Amide
- Tetrafluoroethylene
- Vinylidene Chloride

Class B: Hazard Due to Peroxide on Concentration

- Can undergo explosive polymerization initiated by dissolved oxygen.
- Label these items with a date of receipt and date of opening
- Dispose of these items 12 months after opening or 2 years if unopened

For Class B: When alcohols listed are used for purposes that do not involve heating, chemical reaction, bulk evaporation or other activities that may stress the peroxidizable material, it is not necessary to test these containers for peroxidation and may be allowed to keep for a longer duration.

Examples

- 1-Phenylethanol
- 2-Butanol
- 2-Cyclohexene-1-ol
- 2-Hexanol
- 2-Pentanol
- 2-Phenylethanol
- 2-Propanol
- 3-Methyl-1-butanol
- 4-Heptanol
- 4-Penten-1-ol
- Acetal
- Acetaldehyde
- Benzyl alcohol
- Cumene
- Cyclohexanol
- Cyclohexene
- Decahydronaphthalene
- Diacetylene
- Dicyclopentadiene
- Diethyl ether
- Diethylene glycol dimethyl ether (diglyme)
- Diethylene glycol dimethyl ether (glyme)
- Methyl isobutyl ketone
- Methylacetylene
- Methylcyclopentane
- Tetrahydrofuran
- Diethylene glycol dimethyl ether (diglyme)
- Dioxanes
- Ethylene glycol dimethyl ether (glyme)
- Methyl isobutyl ketone
- Methylacetylene
- Methylcyclopentane
- Tetrahydrofuran

Working with Peroxide Formers

Class C: Auto Polymerize as a Result of Peroxide Accumulation

- May explode when relatively small quantities of peroxides are formed
- Normally have an inhibitor added to the substance by the manufacturer to prevent peroxides from forming
- Label these items with a date of receipt and date of opening
- Dispose of inhibited items after two years and uninhibited items within 24 hours of use/opening

Examples

- Acrylic acid
- Acrylonitrile
- Butadiene
- Chloroprene
- Chlorotrifluoroethylene
- Methylmethacrylate
- Styrene
- Tetrafluoroethylene
- Vinyl acetate
- Vinyl acetylene
- Vinyl chloride
- Vinyl pyridine
- Vinylidene chloride

Evaluating and Testing

Evaluating

- All opened containers of peroxide formers should be tested every three months for peroxides.
 - Examine chemical for visible crystals.
 - Peroxide crystals tend to form on the inner surfaces of the container.
 - If you do not see crystals, or if the container is metal or opaque, proceed to the next step.
 - If you do see viscous liquid or crystalline solids, do not handle the chemical any further.
 - The crystals may cause an explosion if subjected to impact or friction.
 - Immediately contact EHS at (205) 934-2487.

Working with Peroxide Formers

- Determine whether it is safe to test for peroxides.
- If the contents of the container have evaporated to less than 10% of the original volume, you may not test for peroxides.
- If you know the history of the chemical, you can test its contents if it is one of the following:
 - o For chemicals with a low peroxide hazard, the container is opened and <2 years old or unopened and <3 years old.
- For chemicals with a medium peroxide hazard, the container opened and <1 year old or unopened and <2 years old.
- For chemicals with a high peroxide hazard, the container is opened and <6 months old or unopened and <1 year old.
- Containers used for storage of peroxidizable compounds or retention of materials that become hazardous upon prolonged storage shall be limited to a maximum of six months after opening.
- Containers must then be disposed of safely.
- All opened containers of such materials should be tested every three months for peroxides.

Testing

- Use peroxide test strips to demonstrate the presence or absence of peroxides. These are available from most distributors of general chemical supplies.
- If no peroxides are detected, the container label should be marked to indicate the absence of peroxides and the date of the test.
- The material can then be retained for an additional three months.
- If peroxides are detected by the Department of Occupational Health & Safety should be notified immediately!

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- The material can then be retained for an additional three months. If peroxides are detected by the Department of Environmental Health & Safety (EHS) should be notified immediately!