

Peroxide-Forming Chemicals



Overview

Peroxide-forming chemicals are a class of compounds that have the ability to form shock-sensitive explosive peroxide crystals. Many of the organic solvents commonly used in laboratories at Weill Cornell Medicine (WCM) are peroxide formers.

Typical classes of compounds that form peroxides include:

- Ethers, acetals, and ketals, especially cyclic ethers and those with primary and/or secondary alkyl groups;
- Aldehydes, including acetaldehyde and benzaldehyde;
- Compounds containing benzylic hydrogens; and
- Compounds containing allylic hydrogens, including most alkenes; vinyl and vinylidene compounds, and dienes.

Ethers are the most commonly used peroxide formers at WCM such as tetrahydrofuran, dioxane, diethyl ether, isopropyl ether.

Refer to Appendix A for a list of typical peroxide formers found at WCM and guidance on safe storage and testing frequency.

PLEASE NOTE: Peroxide crystals may form on the container plug or the threads of the lid, and detonate when the lid is twisted. Do not open a liquid organic peroxide or peroxide-forming chemical if crystals or a precipitate are present.

Applicability

This Update applies to all WCM personnel who are involved with the ordering, storage, or use of laboratory chemicals and reagents with a peroxide-forming hazard.

Definitions

A peroxide is a chemical that contains a peroxy (O-O) unit, one that has the chemical formula of O_2^{2-} .

Responsibilities

Environmental Health and Safety (EHS) inspects and tests peroxide formers periodically. EHS also provides technical assistance to lab personnel about the safe handling, storage, and disposal of peroxide-forming chemicals as well as training as needed.

Lab personnel ensures that peroxide-forming chemicals are appropriately managed, labeled, and disposed of in accordance with this update.

Procedure

1. Purchasing Considerations

- When possible, obtain peroxide-forming chemicals which contain a peroxide formation inhibitor or stabilizer (e.g., butylated hydroxytoluene or BHT), especially when purchasing materials that are known to auto polymerize such as methyl methacrylate.).

- Only purchase quantities of peroxide-forming chemicals that you expect to use within safe storage timeframes.

2. Inventory Requirements

- Confirm that peroxide-forming chemicals are included in the [Salute](#) chemical inventory upon receipt, and removed from the inventory when discarded.

3. Labeling Requirements

- All containers of peroxide-forming chemicals must be labeled with the date received and the date of opening. EHS can provide labels similar to the example below.

WARNING MAY FORM EXPLOSIVE PEROXIDE			
Date Received: _____		Date Opened: _____	
Use and store according to EHS guidance: http://ehs.weill.cornell.edu			
TEST RECORD (Dispose if peroxide concentration > 100 ppm)			
Test Date	Peroxides (ppm)	Test Date	Peroxides (ppm)

4. Storage and Use Requirements

- Always consult the manufacturer's Safety Data Sheet.
- Follow Appendix A safe storage and testing guidelines.
- Store peroxide formers in original, airtight bottles, away from light and heat. Do not use containers with loose-fitting lids and ground glass stoppers.
- Crystallization, discoloration, and stratification are signs that a peroxide former may have become shock-sensitive so do not use or move such containers and contact EHS immediately at 646-962-7233.

5. Testing Peroxide Forming Chemicals

- **High Hazard Substances (HHS)** such as pyrophoric, unstable, water reactive, acutely toxic chemicals will not be tested for peroxide formation. Discard at the manufacturer's expiration date or one year from receiving, whichever comes first. For details on HHS, refer to the EHS Update on [High Hazard Operating Procedures](#).
- When testing for peroxide, use the guidelines below to interpret results and determine action to take.
- **Prior to distillation or evaporation:** confirm that peroxide-forming solvents have been tested for peroxide formation.

<25 ppm	Considered safe for general use
25-100 ppm	Not recommended for distilling or concentrating
>100 ppm	Avoid handling and contact EHS for safe disposal immediately



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Environmental Health and Safety

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Appendix A: Storage, Disposal & Testing Guidelines for Common Peroxide-Forming Chemicals

The lists below are not all-inclusive. Always consult the manufacturer's Safety Data Sheet or contact EHS for more guidance.

CLASS A PEROXIDE FORMERS – SEVERE PEROXIDE HAZARD

These compounds spontaneously decompose and become explosive with exposure to air without concentration.

Safe Storage Guideline:

Unopened container: discard or test for peroxide formation at 12 months from receiving or at manufacturer's expiration date whichever comes first.

Opened container: test for peroxide formation quarterly.



Example of peroxide crystals

Butadiene (liquid monomer)	Isopropyl ether	Sodium amide (sodamide)
Chloroprene (liquid monomer)	Potassium amide	Tetrafluoroethylene (liquid monomer)
Divinyl acetylene	Potassium metal	Vinylidene chloride

CLASSES B AND C PEROXIDE FORMERS – CONCENTRATION AND AUTOPOLYMERIZATION HAZARDS

Class B: peroxide hazards on concentration (e.g., evaporation or distillation).

Class C: peroxides accumulation may result in violent polymerization of monomers.

Safe Storage Guideline:

Unopened container: discard or test for peroxide formation at 12 months from receiving date or at manufacturer's expiration date whichever comes first.

Opened container: test for peroxide formation every 6 months.

Opened container used for distillation or evaporation: test for peroxide formation immediately before distillation.

Class B

Acetal	Cumene	Diacetylene	Methylacetylene	1-Phenylethanol
Acetaldehyde	Cyclohexanol	Diethyl ether	Methylcyclopentane	2-Phenylethanol
Benzyl alcohol	2-Cyclohexen-1-ol	Dioxanes	MIBK	2-Propanol *
Benzaldehyde	Cyclohexene	Ethylene glycol dimethyl ether (glyme)	2-Pentanol	Tetrahydrofuran
2-Butanol	Decahydronaphthalene	Furan	4-Penten-1-ol	

* Tested prior to concentration or distillation only.

Class C

Acrylic acid	Chloroprene	Styrene	Vinyl acetylene	Vinylidene chloride
Acrylonitrile	Chlorotrifluoroethylene	Tetrafluoroethylene	Vinyl chloride	
Butadiene	Methyl methacrylate	Vinyl acetate	Vinyl pyridine	

GENERAL HANDLING CONSIDERATIONS FOR PEROXIDE-FORMING CHEMICALS

- **Prior to distillation or evaporation:** confirm that peroxide-forming solvents have been tested for peroxide formation.
- **Secondary alcohols** used for distillation or evaporation must be managed and stored as peroxide formers. Secondary alcohols are compounds in which the hydroxyl group, -OH, is attached to a saturated carbon atom which has two carbon atoms attached to it such as 2-pentanol, 2-butanol and 2-propanol.

References

National Fire Protection Association.

Robert J. Alaimo, Handbook of Chemical Health and Safety, American Chemical Society, Chapters 52 and 59.

[Sigma-Aldrich, Peroxides Forming Solvents.](#)

[WCM Chemical Hygiene Plan](#)



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