

Standard Operating Procedure for Peroxide-forming Chemicals



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SOP Title: Peroxide-forming Chemicals	Reviewed by:
Location(s): Science Center	

1. Purpose/Background:

Peroxide-formers are a class of chemical compounds with unusual stability problems and are one of the most hazardous classes of chemicals routinely handled in the laboratory. Peroxides can be formed via intentional chemical reactions (i.e., ozonolysis), but just as hazardous is the inadvertent peroxide formation during storage of certain compounds. To varying degrees, shock, heat or friction may cause unexpected explosion of peroxidized organic chemicals.

2. Scope :

Chemical selection:

- Be aware of the use of peroxide-forming chemicals during experiment design.
- If possible, purchase peroxide forming chemicals containing an inhibitor such as butylated hydroxytoluene (BHT).

Hazard Control:

- Date peroxide-forming chemicals when received, opened, and tested.
- Dispose of peroxide-forming chemicals according to Appendix A.
- Never open a container of peroxide-forming chemical if it is expired or the liquid appears cloudy.

3. Procedures:

Storage and Handling Steps for Peroxide-forming Chemicals

- Restrict quantities to the minimum amount needed.
- Store in airtight bottles, away from light and heat. Avoid using containers with loose-fitting lids and ground-glass stoppers.
- Certain chemicals should be stored under nitrogen, if possible (App A, List A).
- Evaluate for peroxide formation regularly and always prior to distillation. Some materials may need evaluation as often as every 3 months.
- Crystallization, discoloration, and stratification are signs a peroxide-former may have become shock sensitive– Do not move the container. Call EH&S promptly at x3882 or 2762.
- If evaporation or distillation is necessary, do not distill to a dry residue. Always leave at least 10-20% residual bottoms.

Labeling Information

Dates when chemicals are received, opened and tested should be written directly on the container label in permanent marker or labels are available from EH&S upon request. Common

peroxide formers, guidance on recommended shelf life and time interval for peroxide evaluation is provided in Appendix A.

Part 1. Initial Screening—Verify:

- Identity of chemical.
- Date last opened (or if unopened, date received) is known and is within the recommended safe storage period per guidance in Appendix A.
- Evaporation of the chemical is known or estimated to be less than 10%
- Container shows no visible discoloration, liquid stratification, or crystallization (around the cap or in solution).

CAUTION: Never try to force open a rusted or stuck cap on a container of a peroxide-forming chemical.

If any items above cannot be verified, the container should be considered unsafe and should not be disturbed, promptly contact EH&S at x3882 or 2762 for assistance with safe disposal.

Part 2. Peroxide Testing

Dip strips provide the highest sensitivity and the most accurate quantification of peroxide concentration for routine testing. They are easier, faster and safer to use than other methods and detect a wider range of peroxides. However, dip strips are inconvenient to use for testing nonvolatile solvents and have a limited shelf life. Contact EH&S at x. 3882 or 2762 for details.

A common test used is the EMQuant® Peroxide Test Strip (0-100 ppm range). Available through VWR, Part Number EM 100-81-1.

Assessing Peroxide Levels

1-3 ppm peroxide	Considered safe for use
3-10 ppm peroxide	Procure new material if distilling
10 – 30 ppm	Treat as Hazardous Waste and dispose
>30 ppm	Avoid handling and contact EHS for proper disposal

Management of Hazards

Task	Potential Hazard	Precautions or Action to be taken
Screening	Chemical Exposure	Use appropriate PPE if handling chemicals
Distillation	Concentrating peroxides	Ensure proper testing before distillation/ Use appropriate PPE/ maintain 10% residual bottoms
Testing	Chemical exposure	Use appropriate PPE if handling chemicals
	Emergency situation arises	Call Campus Police at x5555

Repeat Issues or Issues that are not Resolved

If safety issues are not appropriately managed, a meeting will be set with the responsible person for the lab, the Science Center Director and the Director of Environmental Health and Safety.

4. References:

- National Research Council, Prudent Practices in the Laboratory, National Academy Press: Washington, DC, 1995.
- Kelly , R.J. "Review of Safety Guidelines for Peroxidizable Organic Chemicals," Chemical Health & Safety- American Chemical Society–, 1996, 4(5), 28-36.

APPENDIX A: Lists of Common Peroxide Forming Chemicals

(NOTE: The lists below cover many commonly known peroxide formers, but are not all-inclusive)

List A: Chemicals known to form explosive levels of peroxides without concentration

Suggested safe storage period: If unopened from manufacturer, up to 18 months or stamped expiration date, whichever comes first. After opening, materials should be discarded or evaluated for peroxides within 3 months. Store under nitrogen if possible.

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

a When stored as a liquid monomer

List B: Chemicals known to present peroxide hazards upon concentration (distillation/evaporation)

Suggested safe storage period: If unopened from manufacturer, up to 18 months or stamped expiration date, whichever comes first. After opening, materials should be discarded or evaluated for peroxides within 12 months.

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

List C: Chemical that may autopolymerize as a result of peroxide accumulation

Suggested safe storage period: If unopened from manufacturer, up to 18 months or stamped expiration date, whichever comes first.

- After opening, materials without inhibitors should not be stored for longer than 24 hours.
- After opening, materials with inhibitors should be discarded or evaluated for peroxides within 12 months.

Acrylic acid ^a	Tetrafluoroethylene ^b
Acrylonitrile ^a	Vinyl acetate
Butadiene ^b	Vinylacetylene
Chloroprene ^b	Vinyl chloride
Chlorotrifluoroethylene	Vinylpyridine
Methyl methacrylate ^a	Vinylidene chloride
Styrene	

a Although these chemicals form peroxides, no explosions involving these monomers have been reported.

b When stored in liquid form, these chemicals form explosive levels of peroxides without concentration. They may also be stored as a gas in gas cylinders. When stored as a gas, these chemicals may autopolymerize as a result of peroxide accumulation