INFORMATION ON PEROXIDE-FORMING COMPOUNDS

Peroxides 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 inadvertent peroxide formation during storage of certain compounds. Some compounds form explosive peroxides. Others are polymerizable unsaturated compounds that can participate a runaway, explosive polymerization reaction catalyzed by peroxides. To varying degrees, shock, heat, or friction may cause unexpected explosion of peroxidized organic chemicals.

Common classes of compounds that form peroxides include:

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

Refer to Appendix A for a list of common peroxide forming chemicals and recommendations on safe storage durations.

STORAGE AND HANDLING

- The quantity of peroxide-forming chemicals kept should be restricted to the minimum amount needed.
- Store peroxide-formers in airtight bottles, away from light and heat. Avoid using containers with loose-fitting lids and ground glass stoppers.
- Certain peroxide formers, including those in Appendix A-List A, should be stored under nitrogen if possible.
- Evaluate chemicals for peroxide formation regularly and always prior to distillation (see "Evaluating Peroxide Formers"). 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, and call EH&S promptly at 725-9999.
- If evaporation or distillation is necessary, do not distill to a dry residue. Always leave at least 10-20% residual bottoms.

LABELING

WARNING

MAY FORM EXPLOSIVE PEROXIDE

Store, handle, and dispose with caution. Store in tightly closed original container. Avoid exposure to light, air and heat. If crystals, discoloration, or layering are visible, do not open.
Contact EH&S for assistance (725-9999).

Date Received: Date Opened::

Peroxide Test Results

Discard or test every ___ months
If > 100 ppm, avoid use & contact EH&S.

Date: ☐ < 100 ppm ☐ > 100 ppm
Date: ☐ < 100 ppm ☐ > 100 ppm
Date: ☐ < 100 ppm ☐ > 100 ppm

All peroxide-forming compounds should be labeled as shown to the left, with the date received and the date opened. For common peroxide formers, guidance on recommended shelf life and time interval for peroxide evaluation is provided in App. A.

Contact EH&S at 723-0448 for labels.

GENERAL PRECAUTIONS

Chemical selection:

- If possible, use a material that does not form peroxides.
- If possible, purchase peroxide forming chemicals containing an inhibitor such as butylated hydroxytoluene (BHT).

Hazard Control:

- Use fume hood or other appropriate exhaust ventilation if inhalation hazard is anticipated.
- Wear appropriate lab attire and personal protective equipment (PPE).
- Utilize shields, barricades, and additional PPE (such as face shields with throat protectors and heavy gloves) where there is a possibility of explosion or vigorous chemical reaction.

EVALUATING PEROXIDE FORMERS

Prior to using peroxide formers and as needed (see App. A), conduct the two-part evaluation for peroxide content:

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 725-9999 for assistance with safe disposal).

Part 2. Peroxide Testing

Containers passing the initial screening (Part 1) may be tested for peroxide content. Four peroxide detection methods are commonly used. They include two qualitative variations on the iodine detection method, the qualitative ferrous thiocyanate method, and the use of semi-quantitative redox dip strips.

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.

- ➢ A common test used is the MQuant™ Peroxide Test Strip (0-100 ppm range). Available through Fisher Scientific, Catalog # M1100810001.

Assessing Peroxide Levels:

< 25 ppm	Considered safe for general use
25-100 ppm	Not recommended for distilling or otherwise concentrating
>100 ppm	Avoid handling and contact EH&S for assistance with safe disposal

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 (1,1-diethoxyethane)	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 dimethyl ether (diglyme)	Tetrahydronaphthalene
	Vinyl ethers
Dioxanes	Other secondary alcohols
Ethylene glycol dimethyl ether (glyme)	
4-Heptanol	

List C: Chemicals 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]	
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.

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.

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