Fact Sheet

OSU ENVIRONMENTAL HEALTH & SAFETY

Safety Instruction

Peroxide Forming Materials

Overview

Peroxides are a class of chemical compounds with unusual stability problems and are potentially 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. Some compounds form unstable peroxides and others are unsaturated compounds that can participate in a runaway polymerization reaction. To varying degrees, shock, heat or friction may cause unexpected reaction of peroxidized organic chemicals. With this in mind special precautions must be taken when handling peroxide formers in a laboratory setting or disposing of peroxide formers as hazardous waste.

Common classes of peroxide forming compounds 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.
- Compounds containing allylic hydrogens, including most alkenes: vinyl and vinylidene compounds and dienes.

Refer to the section below for a list of common peroxide forming chemicals and recommendations on safe storage durations.

Note: Unopened, factory sealed containers which are not expired or greater than 18 months old are generally not considered as a significant peroxide forming risk due to exposure to air.

General Precautions

- When possible, use a material that does not form peroxides.
- Whenever possible, purchase peroxide forming materials containing an inhibitor such as butylated hydroxytoluene (BHT).
- Use fume hood or other appropriate exhaust ventilation when handling peroxide formers.
- Utilize shields, barricades, and additional PPE (face shields with throat protectors and heavy gloves) where there is the possibility of a vigorous chemical reaction.

Storage & 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 the list below, should be stored under nitrogen whenever 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 three months.
- Crystallization (pictured left), discoloration, and stratification are signs a peroxide former may have become shock sensitive – Do not move the container, contact EH&S promptly.
- If evaporation or distillation is necessary, do not distill to a dry residue. Always leave a minimum of 10-20% liquid.

Contact EHS:
ehs@oregonstate.edu
ehs.oregonstate.edu/
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Labeling

All peroxide forming compounds should be labeled with the warning 'may form explosive peroxide' or similar verbiage, as well as the date received and date last opened. This is in addition to standard chemical labeling procedures.

Evaluating Peroxide Formers

Prior to using peroxide formers and as needed conduct the two-part evaluation for peroxide content.

Initial Screening – Verify:

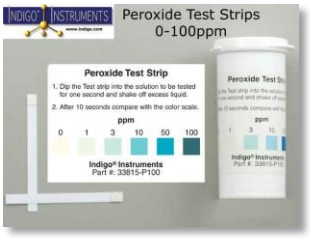
- Identity of chemical
- Date last opened (or if unopened, date received) is known and is within the recommended safe storage period per guidance below.
- Evaporation of the chemical is known or estimated to be less than 10%.
- Container shows no visible discoloration, liquid stratification, or crystallization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

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

Peroxide Testing: Containers passing the initial screening 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.

While any of these methods may be used 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 dip strip test used is the MQuant™ Peroxide Test Strip (0-100 ppm range). Available from EMD Millipore, or VWR catalog # EM1.10081.0001



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 disposal.

Lists of Common Peroxide Forming Chemicals

Note: The lists below cover many commonly known peroxide formers, but are not intended to be all-inclusive.

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

Divinyl acetylene	Divinyl ether	Isopropyl ether
Vinylidene chloride	Potassium metal	Potassium amide
Sodium amide (sodamide)	Butadiene[1]	Chloroprene[1]
Tetrafluoroethylene[1]		

[1] When stored as a liquid monomer

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 when possible.*

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

Acetal(1,1-diethoxyethane)	Acetaldehyde	Benzyl alcohol
2-Butanol	Cumene	Cyclohexanol
Decahydronaphthalene	Diacetylene	Diethyl ether
Diethylene glycol dimethyl ether (diglyme)	Ethylene glocol dimethyl ether (glyme)	4-Heptanol

2-Hexanol	Methylacetylene	3-Methyl-1-butanol
Methylcyclopentane	Methyl isobutyl ketone	4-Methyl-2-pentanol
2-Pentanol	4-Penten-1-ol	1-Phenylethanol
2-Phenylethanol	2-Proponal	Tetrahydrafuran
Tetrahydronaphthalene	Vinyl ethers	Other secondary alcohols

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.

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

Acrylic acid[1]	Acrylonitrile[1]	Butadiene[2]
Chloroprene[2]	Chlorotrifluoroethylene	Methyl methacrylate[1]
Styrene	Tetrafluoroethylene[2]	Vinyl acetate
Vinylacetylene	Vinyl chloride	Vinylpryidine

[1] Although these chemicals form peroxides, no explosions involving these monomers have been reported.

[2] 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 auto-polymerize 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.

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.