

Guidelines for the use of Peroxide-Forming Chemicals

Overview

Some common organic chemicals can react with air to form unstable and dangerous peroxide compounds. Peroxides are a class of chemical compounds with unusual stability issues 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. Some compounds form explosive peroxides and others are polymerizable unsaturated compounds that can initiate a runaway, explosive polymerization reaction. To varying degrees, shock, heat or friction may cause unexpected explosions of peroxidized organic chemicals.

Peroxide formation is accelerated by exposure to air, light, heat, moisture and contamination from metals. Peroxides may form in containers that have not been opened as they may have been packaged while exposed to air.

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

Recommended Work Practices

1. Chemical Selection

- Consider elimination or substitution of the peroxide-forming chemical in the process.
- Purchase minimum quantities to ensure use within the recommended storage durations.
- Purchase peroxide-forming chemicals which contain a peroxide inhibitor, if possible, or add a peroxide inhibitor in the laboratory. Be aware that such inhibitors become depleted over time.

2. Labeling

- In addition to having the chemical name on the container label
 - Date received
 - Date the container is first opened
 - Name of the owner (e.g. PI, researcher, teaching staff)
- Example label:

Warning Peroxide-Forming Chemical Test Before Using
Date Received: _____
Date Opened: _____
Name of Owner: _____

3. Storage and Handling

- The quantity of peroxide-forming chemicals should be limited to the minimum amount needed.
- Store in airtight bottles, away from light and heat. Avoid using containers with loose-fitting lids or ground glass stoppers. It is preferable to use containers that enable the contents to be viewed without having to be moved or opened.
- Refrigerators used for storage must be explosion-proof. Note that refrigeration does not prevent and may not inhibit peroxide formation.
- Certain peroxide formers, including those in Appendix A – List A, should be stored under nitrogen if possible.
- Rotate all stock to prevent aging. Use on a FIFO (first-in first-out) basis.
- Evaluate for peroxide formation regularly. Some materials may need evaluation as often as every 3 months.
- Test all peroxide-forming chemicals prior to distillation, evaporation or concentration. Do not distill to a dry residue; always leave at least 10-20% residual bottoms.
- Chemicals whose identity or age is unknown should not be disturbed. Contact your supervisor and EH&S to arrange for removal. Properly dispose of chemicals that are past their maximum retention times.
- Crystallization, discoloration, and/or stratification are signs a peroxide former may have become shock sensitive. Dangerous levels of peroxides are evident when:
 - A bottle that has whitish crystals around the cap and/or a viscous liquid or precipitate within
 - Solid chemicals (such as potassium metal, potassium amide and sodium amide) show discoloration and/or formation of a surface crust
 - Never try to force open a rusted or stuck cap on a container of peroxide-forming chemicals
 - **Do not move the container. Secure the area around the chemical so that it is protected from movement and can't be disturbed. Contact your laboratory supervisor and EH&S promptly.**

4. Evaluating Peroxide Forming Chemicals

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

- Initial Screening – verify
 - Identity of the 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 the solution

If the items in the initial screening cannot be verified, the container should be considered unsafe and should not be disturbed. Promptly notify the laboratory supervisor and contact EH&S for assistance with safe disposal.

- Peroxide Testing

Containers passing the initial screening may be tested for peroxide content. Four peroxide detection methods are commonly used. These 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. These strips are easier, faster and safer to use than other methods and detect a wider range of peroxides. Commercially available dip strips may be purchased from most laboratory suppliers. Two common peroxide dip strips available are:

- EM Quant peroxide test strips – range 1-100 ppm, from Fisher Scientific
- Quantofix peroxide test strips – application range 1-100mg/L, from Sigma Aldrich

- Assessing Peroxide Levels

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

5. Disposal

- At Expiration

When peroxide-forming chemicals reach their expiration date, it is recommended that you process the chemicals for collection. If peroxide concentrations are at or near the 100 ppm level, notify EH&S prior to requesting collection.

- Post Expiration

When a peroxide forming chemical is older than its expiration date or is stored longer than the recommended periods in Appendix A:

- If crystals are visible in the solution or if crystals are on or in the container do not open or move the container

- Notify the laboratory supervisor and EH&S immediately for assistance with safe disposal procedures.

Appendix A

Peroxide-forming chemicals can be divided into 4 groups (based on the peroxide formation hazard). Note the lists below cover many commonly known peroxide formers, but are not all-inclusive – check the Safety Data Sheet for the chemical before use to determine if there is the possibility of peroxide formation.

The tables below show the generally accepted test and disposal timeframes for these groups. Refer to the Safety Data Sheet for each chemical to determine the supplier's recommendations.

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

^aWhen 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
dimenthyl ether (diglyme)	Vinyl ethers
Dioxanes	Other secondary alcohols
Ethylene glycol dimethyl ether (glyme)	
4-Heptanol	

Appendix A (continued)

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.

List D:

Potential Peroxide-Forming Chemicals

These chemicals may form peroxides but cannot clearly be categorized as any of the above.

Acrolein	p-Chlorophenetole	4,5-Hexadien-2-yn-1-ol
Allyl ether	Cyclooctene	n-Hexyl ether
Allyl ethyl ether	Cyclopropyl methyl ether	o,p-Iodophenetole
Allyl phenyl ether	Diallyl ether	Isoamyl benzyl ether
p-(n-Amyloxy)benzoyl chloride	p-Di-n-butoxybenzene	Isoamyl ether
n-Amyl ether	1,2-Dibenzoyloxyethane	Isobutyl vinyl ether
Benzyl n-butyl ether	p-Dibenzoyloxybenzene	Isophorone
Benzyl ether	1,2-Dichloroethyl ethyl ether	B-Isopropoxy-propionitrile
Benzyl ethyl ether	2,4-Dichlorophenetole	Isopropyl
Benzyl methyl ether	Diethoxymethane	Limonene
Benzyl 1-naphthyl ether	2,2-Diethoxypropane	1,5-p-Methadiene
1,2-Bis(2-chloroethoxy)- ethane	Diethyl ethoxymethylene-malonate	Methyl p-(n-amyloxy)benzoate
Bis(2 ethoxyethyl)ether	Diethyl fumarate	4-Methyl-2-pentanone
Bis(2(methoxyethoxy)-ethyl) ether	Diethyl acetal	n-Methylphenetole
Bis(2-chloroethyl) ether	Diethyketene	2-Methyltetra-hydrofuran
Bis(2-ethoxyethyl) adipate	m,o,p-Diethoxybenzene	3-Methoxy-1-butyl acetate
Bis(2-ethoxyethyl) phthalate	1,2-Diethoxyethane	2-Methoxy-ethanol
Bis(2-methoxyethyl) carbonate	Dimethoxymethane	Methoxy-1,3,5,7-cyclooctatetraene
Bis(2-methoxyethyl) ether	1,1-Dimethoxyethane	B-Methoxy-propionitrile
Bis(2-methoxyethyl) phthalate	Dimethylketene	m-Nitro-phenetole
Bis(2-methoxymethyl) adipate	3,3-Dimethoxypropene	1-Octene
Bis(2-n-butoxyethyl) phthalate	2,4-Dinitrophenetole	Oxybis(2-ethyl acetate)
Bis(2-phenoxyethyl) ether	1,3-Dioxepane	Oxybis(2-ethyl benzoate)
Bis(4-chlorobutyl) ether	Di(1-propynyl)ether	B,B-oxydi-propionitrile
Bis(chloromethyl) ether	Di(2-propynyl)ether	1-Pentene
2-Bromomethyl ethyl ether	DI-n-propoxymethane	Phenoxyacetyl chloride
B-Bromophenetole	1,2-Epoxy-3-isopropoxypropane	a-Phenoxy-propionyl chloride
o-Bromophenetole	1,2-Epoxy-3-phenoxypropane	Phenyl o-propyl ether
p-Bromophenetole	p-Ethoxyacetho-phenone	p-Phenylphenetone
3-Bromopropyl phenyl ether	1-(2-Ethoxyethoxy)-ethyl acetate	n-Propyl ether

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