

USE AND STORAGE OF PEROXIDE-FORMING CHEMICALS

Background

Much of the information in this SOP is adapted from the publication, *Prudent Practices in the Laboratory, Handling and Management of Chemical Hazards, Updated Edition*, from the National Research Council. Some common laboratory chemicals can form peroxides. Once peroxides are formed, these chemicals can become extremely sensitive to thermal or mechanical shock and may explode violently. Peroxides are formed through a spontaneous reaction with oxygen. Simply opening the container can initiate peroxide formation, while light and heat act to accelerate the process.

Manufacturers may add an inhibitor to peroxide forming chemicals to counter peroxide formation. For many peroxide-forming solvents, butylated hydroxy toluene (BHT) is commonly added. BHT 'scavenges' oxygen in the solvent and prevents it from reacting with the solvent to form peroxides. Over time, BHT or other inhibitors in the solvent can become exhausted allowing peroxides to form. Distilling the solvent can completely remove the BHT and make the solvent immediately susceptible to peroxide formation.

Examples of chemicals that are prone to forming peroxides are found in the tables at the end of this SOP.

Safe Handling and Usage

- Store all peroxidizable compounds in tightly closed, air-impermeable, light-resistant containers, away from light, heat, direct sunlight, sources of ignition, oxidizers, and oxidizing agents. Consult the Safety Data Sheet (SDS), storage under Nitrogen may be advisable.
- Make sure caps are replaced promptly after use. Store in the original manufacturer's container whenever possible. Protect containers from shock, friction, and do not shake.
- Keep a record for all peroxidizable compounds to indicate the date of receipt, the date the container was first opened, and disposal date according to peroxide lists provided or information from the SDS. At the time of receipt, the container should be permanently marked or label affixed (see sample label below) indicating the date of receipt, date of opening, test date(s), and disposal date. Including a notice such as **Warning-Peroxide Former** can also be helpful.
- If a peroxide-forming chemical or container is of unknown age or history, if crystals or solid masses are visibly present on or in the container or lid, or if the chemical shows

discoloration, string-like formations, or liquid stratification, do not open the container. Contact EHS for assistance.

- Most peroxides are not volatile. Loss of solvent via an ill-fitting lid can concentrate any peroxides that are present. A nearly empty container, for which the solvent cannot be accounted, may be a hazard. Contact EHS for assistance.
- Immediately rinse empty containers that once held peroxide-forming solvents. Do not allow residues to evaporate. Do not attempt to open or rinse a container of unknown age and history. Contact EHS for assistance.

Testing

The following test procedures may be used on most organic solvents.

Iodide Test

- Add 1-3 ml of the liquid to be tested to an equal volume of acetic acid, add a few drops of 5% aqueous potassium iodide solution, and mix. The appearance of a yellow to brown color indicates the presence of peroxides. Alternatively, addition of 1 ml of a freshly prepared 10% solution of potassium iodide to 10 ml of an organic liquid in a 25 ml glass cylinder should produce a yellow color if peroxides are present.
- Add 0.5 ml of the liquid to be tested to a mixture of 1 ml of 10% aqueous potassium iodide solution and 0.5 ml of dilute hydrochloric acid to which has been added a few drops of starch solution just prior to the test. The appearance of a blue or blue-black color within a minute indicates the presence of peroxides.

Ferrous Thiocyanate Test

A drop of the solvent to be tested is mixed with a drop of sodium ferrothiocyanate reagent, which is prepared by dissolving 9 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in 50 ml of 18% hydrochloric acid. Add 0.5-1.0 g granulated zinc followed by 5 g sodium thiocyanate. When the transient red color fades, add 12 g more of sodium thiocyanate and decant the liquid from the unused zinc into a clean-stoppered bottle. Pink or red coloration indicates the presence of peroxides.

Peroxide Test Strips

Peroxide detection test strips are commercially available from most laboratory equipment supply vendors. Follow the manufacturer's instructions for storing and using the product. Observe any product expiration dates to ensure adequate detection.

Treatment

If peroxides are detected, the solvent must be treated prior to use. All solvents containing peroxides must be treated, if safe to do so, prior to requesting collection by EHS to ensure safety in handling, transport, and disposal. Any of the following procedures may be used to remove peroxides. One of the above test procedures should be employed following treatment to ensure that peroxides have been removed.

Method 1 - Activated Alumina

Peroxides can be removed by passing the solvent through a short column of activated alumina. This method is effective for both water-insoluble and water-soluble solvents (except low molecular weight alcohols). Since this method does not destroy peroxides, the alumina should be flushed with a dilute acid solution of potassium iodide or ferrous sulfate following treatment to remove peroxides from the alumina.

Method 2 - Ferrous Salt

Peroxide impurities in water-soluble solvents are easily removed by gently shaking with a concentrated solution of a ferrous salt. A frequently used ferrous salt solution can be prepared either from 60 g of ferrous sulfate + 6 ml concentrated sulfuric acid + 110 ml water; or from 100 g of ferrous sulfate + 42 ml of concentrated hydrochloric acid + 85 ml of water.

Common Peroxidizable Compounds

As stated in Prudent Practices, “Essentially all compounds containing C-H bonds pose risk of peroxide formation if contaminated with various radical initiators, photosensitizers, or catalysts. For instance, secondary alcohols such as isopropanol form peroxides when exposed to normal fluorescent lighting and contaminated with photosensitizers, such as benzophenone. It is prudent to dispose old samples of organic compounds of unknown origin or history, or those prone to peroxidation if contaminated; secondary alcohols are a specific example.”

Although not completely inclusive, following are common chemicals that are known to form peroxides (Prudent Practices).

Peroxide Hazard on Storage, without Concentration			
Butadiene	Chlorobutadiene (Chloroprene)	Divinyl acetylene	Isopropylether
Methacrylate	Potassium amide	Potassium metal	Sodium amide
Tetrafluoroethylene	Vinylidene chloride		
Hazard Due to Peroxide Concentration			
Acetal	Acetaldehyde	Benzyl alcohol	Cumene (Isopropylbenzene)
Cyclohexene	2-Cyclohexen-1-ol	Cyclohexanol	Cyclooctene



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Cyclopentene	Decahydronaphthalene	Diacetylene	Dicyclopentadiene
Diethyl ether	Diethylene glycol dimethyl ether	Dioxanes	Ethylene glycol dimethyl ether
Furan	4-Heptanol	Isopropyl ether	Methyl acetylene
3-Methyl-1-butanol	Methyl cyclopentane	Methyl isobutyl ketone	2-Pentanol
4-Penten-1-ol	1-Phenylethanol	2-Phenylethanol	2-Propanol ²
Tetrahydrofuran	Tetrahydronaphthalene	Vinyl ethers	Other secondary alcohols ²
Auto-Polymerize as a Result of Peroxide Accumulation			
Acrylic acid	Acrylonitrile	Butadiene	2-Butanol
Chlorotrifluoroethylene	Ethyl acrylate	Methyl methacrylate	Tetrafluoroethylene
Styrene	Vinyl acetate	Vinyl acetylene	Vinyl chloride
Vinyl pyridine			
Chemical that Form Peroxides but Cannot be Clearly Placed in One of the Above Categories¹			
Acrolein	Allyl ether	Allyl ethyl ether	Allyl phenyl ether
p-(n-Amyloxy)benzoyl chloride	n-Amyl ether	Benzyl n-butyl ether	Benzyl ether
Benzyl ethyl ether	Benzyl methyl ether	Benzyl-1-naphthyl ether	1,2-Bis(2-chloroethoxy)ethane
Bis(2-ethoxyethyl)ether	Bis(2-(methoxyethoxy)ethyl)ether	Bis(2-chloroethyl)ether	Bis(2-ethoxyethyl)adipate
Bis(2-2-methoxyethyl) carbonate	Bis(2-methoxyethyl) ether	Bis(2-methoxyethyl) phthalate	Bis(2-methoxymethyl) adipate
Bis(2-n-butoxyethyl) phthalate	Bis(2-phenoxyethyl)ether	Bis(4-chlorobutyl)ether	Bis(chloromethyl)ether
2-Bromomethyl ethyl ether	Beta-Bromophenetole	o-Bromophenetole	p-Bromophenetole
3-Bromopropyl phenyl ether	t-Butyl methyl ether	n-Butyl phenyl ether	n-Butyl vinyl ether
Chloroacetaldehyde diethylacetal	2-Chlorobutadiene	1-(2-Chloroethoxy)-2-phenoxyethane	Chloroethylene
Chloromethyl methyl ether	b-Chlorophenetole	o-Chlorophenetole	p-Chlorophenetole
Cyclooctene	Chloropropyl methyl ether	Diallyl ether	p-Di-n-butoxybenzene
1,2-Dibenzoyloxyethane	p-Dibenzoyloxybenzene	1,2-Dichloroethyl ethyl ether	2,4-Dichlorophenetole
Diethoxymethane	2,2-Diethoxypropane	Diethyl ethoxymethylenemalonate	Diethyl fumarate
Diethyl acetal	Diethylketene	m,o,p-Diethoxybenzene	1,2-Diethoxyethane
Dimethoxymethane	1,1-Dimethoxyethane	Di(1-propynyl)ether	Di(2-propynyl)ether
Di-n-propoxymethane	1,2-Epoxy-3-isopropoxypropane	1,2-Epoxy-3-phenoxypropane	p-Ethoxyacetophenone
1-(2-Ethoxyethoxy)ethyl acetate	(2-Ethoxyethyl)-a-benzoyl benzoate	1-Ethoxynaphthalene	o,p-Ethoxyphenyl isocyanate
1-Ethoxy-2-propyne	3-Ethoxypropionitrile	2-Ethylacrylaldehyde oxime	2-Ethylbutanol
Ethyl-b-ethoxypropionate	2-Ethylhexanal	Ethyl vinyl ether	2,5-Hexadiyn-1-ol
4,5-Hexadien-2-yn-1-ol	n-Hexyl ether	o,p-Iodophenetole	Isoamyl benzyl ether
Isoamyl ether	Isobutyl vinyl ether	Isophorone	b-Isopropoxypropionitrile
Isopropyl-2,4,5-trichlorophenoxy acetate	n-Methylphenetole	2-Methyltetrahydrofuran	3-Methoxy-1-butyl acetate
2-Methoxyethanol	3-Methoxyethyl acetate	2-Methoxyethyl vinyl ether	Methoxy-1,3,5,7-cyclooctatetraene
b-Methoxypropionitrile	m-Nitrophenetole	1-Octene	Oxybis(2-ethyl acetate)
Oxybis(2-ethyl benzoate)	b,b-Oxydipropionitrile	1-Pentene	Phenoxyacetyl chloride
a-Phenoxypropionyl chloride	Phenyl-o-propyl ether	p-Phenylphenetone	n-Propyl ether
n-Propyl isopropyl ether	Sodium 8-11-14-eicosatetraenoate	Sodium ethoxyacetylde	Tetrahydropyran



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Triethylene glycol diacetate	Triethylene glycol dipropionate	1,3,3-Trimethoxypropene	1,1,2,3-Tetrachloro-1,3-butadiene
4-Vinyl cyclohexene	Vinylene carbonate		

¹ R.J. Kelly, "Review of Safety Guidelines for Peroxide-Forming Organic Chemicals", Chemical Health & Safety, September/October 1996

² Reagent grade purity secondary alcohols including 2-propanol can form explosive peroxides. Data suggest that the formation does not occur as readily as it does for chemicals such as diethyl ether and tetrahydrofuran. Testing and dating for peroxides is recommended. Labeling containers as having the potential to form peroxides is an alternative. At the minimum, personnel using secondary alcohols need to know that age and exposure to air along with evaporation or distillation can create a serious peroxide issue.

Sample Label

WARNING: MAY FORM EXPLOSIVE PEROXIDES

Store, handle and dispose of per EHS SOP, ***Use and Storage of Peroxide-Forming Chemicals***. Keep in tightly-closed, original container. Avoid exposure to light, air, and heat. If crystals, discoloration, or layering are visible, do not open. Contact EHS for guidance.

THIS CHEMICAL HAS A LIMITED SHELF LIFE

Date received: _____ Date opened: _____ Disposal Date: _____

PEROXIDE TEST RESULTS

(If within the concentration range from 25-100 ppm, material can be used but don't evaporate or concentrate)

Date/Test Results _____
Date/Test Results _____
Date/Test Results _____
Date/Test Results _____
Date/Test Results _____