



6. Handling and Removing Peroxides

BACKGROUND

This document is to be used when handling and removing peroxides. Its purpose is to minimize the occurrence and impact of accidents that could occur when using peroxides. Special precaution must be used when handling peroxide forming compounds, 'peroxide formers'. The information from the document was sourced from Sigma Aldrich (see resources).

PEROXIDE FORMERS

A significant number of laboratory solvents can undergo autoxidation under normal storage conditions to form unstable and potentially dangerous peroxide by-products. This process is catalyzed by light and heat and occurs when susceptible materials are exposed to atmospheric oxygen. Molecular structure is the primary factor relating to a material's potential for hazardous peroxide formation.

Most overviews of potential peroxide-forming chemicals classify various materials into three categories, on the basis of peroxide formation susceptibility, each with general handling and use guidelines.¹ The two categories relevant to solvents are defined as solvents that pose a peroxide related safety risk without having to be pre-concentration (see Group A, next section) and solvents that necessitate pre-concentration in order to form peroxides (see Group B, next section). Storage time guidelines for previously opened containers is provided in the following section. Please note that the storage time indicated below are based on these solvents continually being stored in opaque containers and under inert atmospheric gases.

PEROXIDE TESTING SCHEDULE

Note: this list may not be comprehensive.

Testing Schedule

There are four classes of peroxide-forming chemicals based upon the peroxide formation hazard:

- Class A – Severe Peroxide Hazard
- Class B – Concentration Hazard
- Class C – Shock and Heat Sensitive
- Class D – Potential Peroxide-Forming Chemicals

	Class A	Class B	Class C	Class D
Date Opened	3 months	6 months	6 months	1 year



Class A – Severe Peroxide Hazard

Spontaneously decompose and become explosive with exposure to air without concentration.

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

Class B – Concentration Hazard

Require external energy for spontaneous decomposition.
peroxides when distilled, evaporated or otherwise concentrated.

Form explosive

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

Class C – Shock and Heat Sensitive

Highly reactive and can auto-polymerize as a result of internal peroxide accumulation. The peroxides formed in these reactions are extremely shock and heat sensitive.

Acrylic acid	Chlorotrifluoroethylene	Vinyl acetate
Acrylonitrile	Methyl methacrylate	Vinylacetylene (gas)
Butadiene (gas)	Styrene Vinylpyridine	Vinylidene chloride
Chloroprene	Tetrafluoroethylene (gas)	Vinyl chloride (gas)



Class D – Potential Peroxide Forming Chemicals

May form peroxides but cannot be clearly categorized in Class A, B, or C.

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-Isopropoxypropionitrile
Benzyl ethyl ether	2,4-Dichlorophenetole	Isopropyl-2,4,5-trichlorophenoxy acetate
Benzyl methyl ether	Diethoxymethane	n-Methylphenetole
Benzyl-1-naphthyl ether	2,2-Diethoxypropane	2-Methyltetrahydrofuran
1,2-Bis(2-chloroethoxy)ethane	Diethyl ethoxymethylenemalonate	3-Methoxy-1-butyl acetate
Bis(2-ethoxyethyl)ether	Diethyl fumarate	2-Methoxyethanol
Bis(2-(methoxyethoxy)ethyl) ether	Diethyl acetal	3-Methoxyethyl acetate
Bis(2-chloroethyl) ether	Diethylketene	2-Methoxyethyl vinyl ether
Bis(2-ethoxyethyl) adipate	Diethoxybenzene (m-,o-,p-)	Methoxy-1,3,5,7-cyclooctatetraene
Bis(2-methoxyethyl) carbonate	1,2-Diethoxyethane	b-Methoxypropionitrile
Bis(2-methoxyethyl) ether	Dimethoxymethane	m-Nitrophenetole
Bis(2-methoxyethyl) phthalate	1,1-Dimethoxyethane	1-Octene
Bis(2-methoxymethyl) adipate	Di(1-propynyl) ether	Oxybis(2-ethyl acetate)
Bis(2-n-butoxyethyl) phthalate	Di(2-propynyl) ether	Oxybis(2-ethyl benzoate)
Bis(2-phenoxyethyl) ether	Di-n-propoxymethane	b,b-Oxydipropionitrile
Bis(4-chlorobutyl) ether	1,2-Epoxy-3-isopropoxypropane	1-Pentene
Bis(chloromethyl) ether	1,2-Epoxy-3-phenoxypropane	Phenoxyacetyl chloride
2-Bromomethyl ethyl ether	p-Ethoxyacetophenone	a-Phenoxypropionyl chloride
beta-Bromophenetole	1-(2-Ethoxyethoxy)ethyl acetate	Phenyl-o-propyl ether
o-Bromophenetole	2-Ethoxyethyl acetate	p-Phenylphenetone
p-Bromophenetole	(2-Ethoxyethyl)-a-benzoyl benzoate	n-Propyl ether
3-Bromopropyl phenyl ether	1-Ethoxynaphthalene	n-Propyl isopropyl ether
tert-Butyl methyl ether	o,p-Ethoxyphenyl isocyanate	Sodium 8-11-14-eicosatetraenoate



n-Butyl phenyl ether	1-Ethoxy-2-propyne	Sodium ethoxyacetylide
n-Butyl vinyl ether	3-Ethoxypropionitrile	Tetrahydropyran
Chloroacetaldehyde diethylacetal	2-Ethylacrylaldehyde oxime	Triethylene glycol diacetate
2-Chlorobutadiene	2-Ethylbutanol	Triethylene glycol dipropionate
1-(2-Chloroethoxy)-2-phenoxyethane	Ethyl-b-ethoxypropionate	1,3,3-Trimethoxypropene
Chloroethylene	Ethylene glycol monomethyl ether	1,1,2,3-Tetrachloro-1,3-butadiene
Chloromethyl methyl ether	2-Ethylhexanal	4-Vinyl cyclohexene
beta-Chlorophenetole	Ethyl vinyl ether	Vinylene carbonate
o-Chlorophenol	2,5-Hexadiyn-1-ol	

TESTING FOR PEROXIDE FORMATION

Peroxide Content and Uses

Peroxide formers must be tested for peroxide content before using, especially where there is a potential for exposure to heat or shock during the process. The following are general guidelines concerning the degree of hazard associated with peroxide contamination at the levels indicated.

< 3 ppm	Reasonably safe for most laboratory procedures involving moderate quantities
3 – 30 ppm	Possible moderate hazard depending on type of use. Avoid concentration of the peroxides. Disposal recommended if ether is not to be used
> 30 ppm	Unacceptable; may pose a serious hazard. Dispose of ether or remove peroxides using a suitable procedure.

If the container shows any evidence of crystal formation in solution or around the cap, or of oil formation, should be treated as extremely hazardous and should not be handled. Treat ether as a bomb!

PROCEDURE FOR REMOVING PEROXIDES

Either of the following procedures may be used to remove the peroxides:

1. **Activated Alumina Method:** peroxides can be conveniently 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 dilute acid solution of potassium iodide or ferrous sulfate following treatment to remove peroxides
2. **Ferrous Salt Method:** Peroxide impurities in water-soluble solvents are easily removed by shaking with a concentrated solution of ferrous salt. A frequently used ferrous salt solution can be prepared either from 60 gm of ferrous sulfate + 6 mL concentrated sulfuric acid + 100 mL of water, or from 100 gm of ferrous sulfate + 42 mL concentrated hydrochloric acid + 85 mL of water.



RELATIONSHIP OF HAZARD TO TYPE OF USE

The degree of hazard associated with peroxide contamination is dependent on the way the material is used. Concentration of the peroxides will increase the hazard. The following are general guidelines for a variety of common uses.

Distillation: Only material containing 0 ppm of peroxides should be used for distillations or refluxes, and care must be taken to ensure that the distillation container does not go dry. Leave at least 10% residue or “bottoms” when distilling peroxidizable compounds. Peroxide forming materials must be tested prior to use in a distillation, and must be peroxide free. Safety glasses are essential at all times and a shield should be used during the distillation or evaporation process. If it is necessary to remove peroxides, it can be accomplished by washing with a 5% solution of sodium metabisulphite or ferrous sulphate.

Evaporation: Evaporation (e.g. in a rotary evaporator) concentrates the peroxides and poses a hazard. When the volume is small and the evaporation is carried out near room temperature, ethers with low levels of peroxides may be reasonably safe. When high volumes and/or high temperatures are used, the ether must be peroxide free. Personal protective equipment is required, as noted in previous paragraph.

Chromatography: Peroxides formers with moderate levels of peroxides are probably suitable for a variety of forms of chromatography, provided that the ether is not going to be subsequently evaporated. Note, however, that peroxides bind to alumina and to some other adsorbents. This may concentrate peroxides at the top of a column, resulting in a hazard if the column is not washed with a suitable solvent and is then allowed to dry out.

Users should be aware of potential problems associated with peroxides, and dispose of solvents containing 30 ppm peroxides and more immediately.

RESOURCES

Sigma Aldrich <https://www.sigmaaldrich.com/CA/en/technical-documents/technical-article/chemistry-and-synthesis/reaction-design-and-optimization/peroxide-formation>