

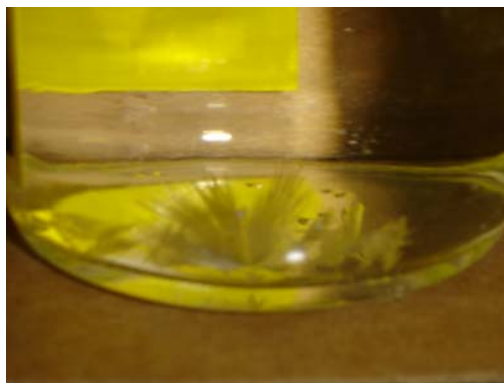
Chemical Safety Training

Peroxide-Forming Chemicals

Overview

Peroxide-forming chemicals are a class of compounds that have the ability to form shock-sensitive explosive peroxide crystals. A peroxide is a chemical that contains a peroxy (O-O) unit, one that has the chemical formula of O_2^{-2} . Many organic solvents found in laboratories have the potential to form explosive peroxide crystals. Diethyl ether and tetrahydrofuran are two of the more common peroxide-forming chemicals used at UIC. It is extremely important that these steps be followed regarding the identification, handling, storage, and disposal of peroxide-forming chemicals.

Under normal storage conditions, the materials listed in this document have the potential to generate and accumulate peroxide crystal formations which may violently detonate when subjected to thermal or mechanical shock. Peroxide-forming chemicals react with oxygen to form peroxy compounds, even at low concentrations. The risk associated with peroxide formation increases if the peroxide crystallizes or becomes concentrated by evaporation or distillation. Factors that affect the rate of peroxide formation include exposure to air, light, heat, moisture and contamination from metals.



PeroxideFormation

IMPORTANT NOTE: Peroxide crystals may form on the container plug or the threads of the lid and detonate when the lid is twisted. Do not open a liquid organic peroxide or peroxide-forming chemical if crystals or a precipitate are present.

Purchasing Considerations

- When possible, purchase only peroxide-forming chemicals which contain a peroxide formation inhibitor (e.g., tetrahydrofuran or diethyl ether inhibited with butylated hydroxytoluene (BHT)) or metal can with inner coating .
- Only purchase quantities of peroxide-forming chemicals that you expect to use within expiration and disposal timeframes.

Labeling Requirements

- All bottles of peroxide-forming chemicals must have the **date received** marked on the container.
- When the bottle is first opened, the container must be marked with the **date opened**.

Sample Label

Peroxide-Forming Chemical	
Date Received:	_____
Date Opened:	_____

Storage and Use Requirements

- Do not store peroxide-forming chemicals in direct sunlight as light can accelerate the chemical reactions that form peroxides.
- Unused chemicals should not be returned to original container. Store in inert plastic or brown glass containers), free of any other contaminants.
- Store peroxidizable substances at the lowest feasible temperature. If the peroxide-forming chemical is flammable and requires refrigeration, then an explosion-proof refrigerator must be used.
- Do not distill, evaporate or concentrate a peroxide-forming chemical until you have first tested it for the presence of peroxides. (Peroxides are usually less volatile than their parent material and will tend to concentrate in the hot distillation pot).
- Test peroxidizable chemicals at least annually and before use involving heat or evaporation. Either a 10% ethanolic KI solution may be used for a colorimetric test or ready-to-use peroxide strips are available from distributors, e.g. Grainger or Fisher.
- **NEVER, UNDER ANY CIRCUMSTANCES, touch or attempt to open container of a peroxide-forming liquid if there are whitish crystals around the cap and/or in the bottle. The friction of screwing the cap may detonate the bottle. If you encounter such a bottle, contact EHSO for assistance. DO NOT TOUCH OR MOVE THE SUSPECT BOTTLE BY YOURSELF FOR ANY REASON.**

Disposal Requirements

- There are four classes of peroxide-forming chemicals based upon the peroxide formation hazard:
Class A – Severe Peroxide Hazard **Class C** – Shock and Heat Sensitive
Class B – Concentration Hazard **Class D** – Potential Peroxide-Forming Chemicals
- Peroxide-forming chemicals must be disposed within the timeframes specified in the table below regardless if the container is unopened, unless they have been tested and found free of peroxides (see above). Disposal with EHS must occur within the timeframe allowed once the container is received or opened, which ever is the earlier of the two dates.

	Class A	Class B	Class C	Class D
Date Opened	3 months	6 months	6 months	Only if peroxide crystals are present
Date Received	1 year	1 year	1 year	

- Submit a chemical removal request to EHSO to request the disposal of a peroxide-forming chemical. The form is available on EHSO website at: www.uic.edu/depts/envh
- EHSO has contractors available to test and, if necessary, stabilize peroxide-forming

chemicals.

Peroxide Forming Chemical Lists

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. Form explosive peroxides when distilled, evaporated or otherwise concentrated.

Acetal	Diethylene glycol dimethyl ether (diglyme)	4-Methyl-2-pentanol
Acetaldehyde	Diethyl ether	2-Pentanol
Benzyl alcohol	Dioxanes	4-Penten-1-ol
2-Butanol	Ethylene glycol dimethyl ether (glyme)	1-Phenylethanol
Cumene	Furan	2-Phenylethanol
Cyclohexanol	4-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	Methyl methacrylate	Vinyladiene chloride
Acrylonitrile	Styrene Vinylpyridine	Vinylpyridine
Butadiene (gas)	Tetrafluoroethylene (gas)	Vinyl chloride (gas)
Chloroprene	Vinyl acetate	
Chlorotrifluoroethylene	Vinylacetylene (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	Diallyl ether	Isoamyl benzyl ether
Allyl phenyl ether	p-Di-n-butoxybenzene	Isoamyl ether
p-(n-Amyloxy)benzoyl chloride	1,2-Dibenzoyloxyethane	Isobutyl vinyl ether
n-Amyl ether	p-Dibenzoyloxybenzene	Isophorone
Benzyl n-butyl ether	1,2-Dichloroethyl ethyl ether	b-Isopropoxypropionitrile
Benzyl ether	2,4-Dichlorophenetole	Isopropyl-2,4,5-trichlorophenoxy acetate

Benzyl ethyl ether	Diethoxymethane	Limonene
Benzyl methyl ether	2,2-Diethoxypropane	1,5-p-Methadiene
Benzyl-1-naphthyl ether	Diethyl ethoxymethylenemalonate	Methyl-p-(n-amyloxy)benzoate
1,2-Bis(2-chloroethoxy)ethane	Diethyl fumarate	4-Methyl-2-pentanone
Bis(2-ethoxyethyl)ether	Diethyl acetal	n-Methylphenetole
Bis(2-(methoxyethoxy)ethyl) ether	Diethylketene	2-Methyltetrahydrofuran
Bis(2-chloroethyl) ether	Diethoxybenzene (m-,o-,p-)	3-Methoxy-1-butyl acetate
Bis(2-ethoxyethyl) adipate	1,2-Diethoxyethane	2-Methoxyethanol
Bis(2-methoxyethyl) carbonate	Dimethoxymethane	3-Methoxyethyl acetate
Bis(2-methoxyethyl) ether	1,1-Dimethoxyethane	2-Methoxyethyl vinyl ether
Bis(2-methoxyethyl) phthalate	Di(1-propynyl) ether	Methoxy-1,3,5,7-cyclooctatetraene
Bis(2-methoxymethyl) adipate	Di(2-propynyl) ether	b-Methoxypropionitrile
Bis(2-n-butoxyethyl) phthalate	Di-n-propoxymethane	m-Nitrophenetole
Bis(2-phenoxyethyl) ether	1,2-Epoxy-3-isopropoxypropane	1-Octene
Bis(4-chlorobutyl) ether	1,2-Epoxy-3-phenoxypropane	Oxybis(2-ethyl acetate)
Bis(chloromethyl) ether	p-Ethoxyacetophenone	Oxybis(2-ethyl benzoate)
2-Bromomethyl ethyl ether	1-(2-Ethoxyethoxy)ethyl acetate	b,b-Oxydipropionitrile
beta-Bromophenetole	2-Ethoxyethyl acetate	1-Pentene
o-Bromophenetole	(2-Ethoxyethyl)-a-benzoyl benzoate	Phenoxyacetyl chloride
p-Bromophenetole	1-Ethoxynaphthalene	a-Phenoxypropionyl chloride
3-Bromopropyl phenyl ether	Dimethylketene	Phenyl-o-propyl ether
1,3-Butadiyne	3,3-Dimethoxypropene	p-Phenylphenetone
Buten-3-yne	2,4-Dinitrophenetole	n-Propyl ether
Tert-Butyl ethyl ether	1,3-Dioxepane	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 ethoxyacetylde
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-phenoxyethar	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-Chorophenetole	2,5-Hexadiyn-1-ol	Vinylidene chloride
Cyclopropyl methyl ether	o,p-Iodophenetole	

References

National Safety Council: Data Sheet I-655 Rev. 87

NFPA: NFPA 43B, Code for the Storage of Organic Peroxide Formulations

Reactive Hazards Reduction, Inc. <http://www.rhr-inc.com/>

EHS Update, "Peroxide-Forming Chemicals", Weill Medical College of Cornell University, November 2005

Acknowledgement: Photograph courtesy of Tom Gundlach at RHR.