

Guidelines for Use of Peroxide Forming Chemicals

Many laboratory chemicals are prone to the formation of explosive peroxides under normal usage. Opinions vary regarding the level at which peroxide formation poses a risk: while a maximum concentration of 100 ppm is widely accepted among industrial hygienists, OSHA has no published guidelines for the storage, use, and disposal of peroxidizable chemicals. To ensure the safety of Gettysburg College employees, the following guidelines have been established with regards to peroxide forming chemicals.

Purchase

Peroxidizable compounds should be purchased in quantities, which can be exhausted within the time indicated in Table A. Container sizes should be selected according to use requirements so that exposure to air is minimized through reduced container openings.

Table A: Safe Storage Period for Peroxide Forming Chemicals

Description	Safe Storage Period
Unopened chemicals from Manufacturer	18 months
Opened Containers	
Chemicals in List A	3 months
Chemicals in List B and D	12 months
Uninhibited Chemicals in List C	24 hours
Inhibited Chemicals in List C	12 months

Labeling

All peroxidizable materials in Lists A—D must have a label containing the date received from the manufacturer and the date opened. Additionally, labels must state, “PEROXIDIZABLE COMPOUND: DISCARD OR TEST WITHIN XX MONTHS AFTER OPENING,” where XX is the safe storage period from Table A. Labels should be in red print on a white background.

Storage

All peroxidizable compounds should be stored away from heat and light. All containers must have tight closures to prevent air exposure, evaporation and concentration of peroxides.

Safe Handling

Test for peroxides before distilling or evaporating any List A or B material. (See Appendix H in Gettysburg College Chemical Hygiene Plan for test methods) Before distilling any List C material, a suitable polymerization inhibitor must be added. During

distillation, addition of a high molecular weight inerting solvent, such as mineral oil or a phthalate ester will dilute residual peroxides when distillation is complete. Should such a diluent be undesirable, distill to not less than 10%. NEVER distill to a dry residue.

Safety glasses and a face shield should be used when evaporating or distilling mixtures that contain peroxidizable compounds.

Disposal

All peroxidizable compounds from Lists A—D will be removed from laboratories for disposal after the safe storage period expires. This includes unopened chemicals after 18 months of storage.

All peroxidizable compounds suspected of having high peroxide levels, because of visual observation of unusual viscosity or crystal formation, or because of age, should be considered extremely dangerous. DO NOT attempt to open these containers as peroxide crystals around the container cap could detonate. Contact the Environmental Health & Safety Office at 337-6813 for assistance.

References

1. Recognition and Handling of Peroxidizable Compounds; Data Sheet 655; National Safety Council: Chicago, IL, 1987
2. Kelly, Richard J., Review of Safety Guidelines for Peroxidizable Organic Chemicals, Chemical Health & Safety, American Chemical Society, Sept/Oct. 1996.
3. Furr, Keith Handbook of Lab Safety, 4th ed., CRC Press, 1995.

Classes of Peroxidizable Chemicals

List A: Chemicals that form explosive peroxides without concentration

Butadiene (liquid monomer)	Isopropyl ether
Chloroprene (liquid monomer)	Tetrafluoroethylene (liquid monomer)
Divinylacetylene	Vinylidene chloride

List B: Chemicals that form explosive peroxides on concentration

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-Penten-1-ol
Cyclohexene	4-Penten-1-ol
Decahydronaphthalene	1-Phenylethanol
Diacetylene	2-Phenylethanol
Dicyclopentadiene	Tetrahydrofuran
Diethyl ether	Tetrahydronaphthalene
Diethylene glycol dimethyl ether (diglyme)	Vinyl ethers
Dioxanes	Other Secondary Alcohols
Ethylene glycol dimethyl ether (glyme)	
4-Heptanol	

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

Acrylic acid ¹	Tetrafluoroethylene
Acrylonitrile ¹	Vinyl acetate
Butadiene	Vinylacetylene
Chloroprene	Vinyl chloride
Chlorotrifluoroethylene	Vinylpyridine
Methyl methacrylate ¹	Vinyladiene chloride
Styrene	

1 Although these chemicals form peroxides, there are no reported explosions.

List D: Chemicals that may form peroxides but cannot clearly be placed in List A—C.

Acrolein	1,2-Epoxy-3-isopropoxypropane ²
Allyl ether ²	1,2-Epoxy-3-phenoxypropane
Allyl ethyl ether	Ethoxyacetophenone
Allyl phenyl ether	1-(2-Ethoxyethoxy)ethyl acetate
p-(n-Amyloxy)benzoyl chloride	2-Ethoxyethyl acetate
n-Amyl ether	(2-ethoxyethyl)-o-benzoylbenzoate
Benzyl n-butyl ether	1-Ethoxynaphthalene
Benzyl ether	Ethoxyphenyl isocyanate
Benzyl ethyl ether	1-ethoxy-2-propyne

Benzyl methyl ether	3-ethoxypropionitrile
Benzyl 1-naphthyl ether ²	2-ethylacrylaldehyde oxime
1,2-Bis(2-chloroethoxy)ethane	2-ethylbutanol
Bis(2-ethoxyethyl) ether	Ethyl ethoxypropionate
Bis(2-methoxyethoxy)ethyl ether	2-ethyl hexanal
Bis(2-chloroethyl) ether	Ethyl vinyl ether
Bis(2-ethoxyethyl) adipate	Furan p-phenylphenetone
Bis(2-ethoxyethyl) phthalate	2,5-hexadiyn-1-ol
Bis(2-methoxyethyl) carbonate	4,5-hexadien-2-yn-1-ol
Bis(2-methoxyethyl) ether	n-hexyl ether
Bis(2-methoxyethyl) phthalate	Iodophenetole
Bis(2-methoxymethyl) adipate	Isoamyl ether ²
Bis(2-n-butoxyethyl) phthalate	Isobutyl vinyl ether
Bis(2-phenoxyethyl) ether	Isophorone ²
Bis(4-chlorobutyl) ether	p-isopropoxypropionitrile ²
Bis(chloromethyl) ether	Isopropyl 2,4,5-trichlorophenoxyacetate
2-bromomethyl ethyl ether	Limonene
Bromophenetole	1,5-p-methadiene
3-bromopropyl phenyl ether	Methyl p-(n-amylloxy)benzoate
1,3-butadiyne	4-methyl-2-pentanone
Buten-3-yne	n-methylphenetole
Tert-butyl ethyl ether	2-methyltetrahydrofuran
Tert-butyl methyl ether	3-methoxy-1-butyl acetate
n-butyl phenyl ether	2-methoxyethanol
n-butyl vinyl ether	3-methoxyethyl acetate
Chloroacetaldehyde diethylacetal ²	2-methoxyethyl vinyl ether
2-chlorobutadiene	Methoxy-1,3,5,7-cyclooctatetraene
1-(2-chloroethoxy)-2-phenoxyethane	Methoxypropionitrile
Chloroethylene	m-Nitrophenetole
Chloromethyl methyl ether	1-Octene
Chlorophenetole	Oxybis(2-ethyl acetate)
Cyclooctene ²	Oxybis(2-ethyl benzoate)
Cylcopropyl methyl ether	Oxydipropionitrile
Diallyl ether ²	1-Pentene
p-Di-n-butoxybenzene	Phenoxyacetyl chloride
1,2-dibenzoyloxyethane ²	Phenoxypropionyl chloride
p-Dibenzoyloxybenze ²	Phenyl o-propyl ether
1,2-dichloroethyl ethyl ether	n-propyl ether
2,4-dichlorophenetole	n-propyl isopropyl ether
Diethoxymethane ²	Sodium 8,11,14-eicosatetraenoate
2,2-Diethoxypropane	Sodium ethoxyacetylde
Diethylethoxymethylenemalonate	Tetrahydropyran
Diethyl fumarate	Triethylene glycol diacetate
Diethyl acetal ²	Triethylene glycol dipropionate
Diethylketene	1,3,3-trimethoxypropene ²

Diethoxybenzene	1,1,2,3-tetrachloro-1,3-butadiene
1,2-Diethoxyethane	4-vinyl cyclohexene
Dimethoxymethane ²	Vinylencarbonate
1,1-Dimethoxyethane ²	Vinylidene chloride ²
Dimethylketene	
3,3-Dimethoxypropene	
2,4-Dinitrophenetole	
1,3-Dioxepane ²	
Di(1-propynyl) ether	
Di(2-propynyl) ether	
Di-n-propoxymethane ²	

² These chemicals easily form peroxides and should probably be considered under List B