

## Alfred University CHEMICAL HYGIENE PLAN

### Appendix J - Peroxide Forming Chemicals

#### Time Limits for Safe Storage and Removal of Peroxide forming chemicals

This list is not all-inclusive; there are numerous other chemicals that can form peroxides. Be sure to read SDSs, chemical container labels and other chemical references to determine potential to form peroxides.

<b>SAFE STORAGE TIME LIMITS FOR PEROXIDE FORMERS</b> dispose of chemicals at time specified in this table	
Unopened chemicals from manufacturer	18 months or (expiration date)
Opened containers:	
Chemicals in Table A	3 months
Chemicals in Tables B and D	12 months
Uninhibited chemicals in Table C	Discard in 24 hours
Inhibited chemicals in Table C (Do not store under inert atmosphere)	12 months

<b>A. Chemicals that form explosive levels of peroxides without concentration</b>		
Butadiene <sup>a</sup>	Isopropyl ether	Sodium amide (sodamide)
Chloroprene <sup>a</sup>	Potassium metal	Tetrafluoroethylene <sup>a</sup>
Divinylacetylene	Potassium amide	Vinylidene chloride

<b>B. Chemicals that form explosive levels of peroxides on concentration</b>		
Acetal	Diethyl ether	4-Methyl-2-pentanol
Acetaldehyde	Diethylene glycol dimethyl ether (diglyme)	2-Pentanol
Benzyl alcohol	Dioxanes	4-Penten-1-ol
2-Butanol	Ethylene glycol dimethyl ether (glyme)	1-Phenylethanol
Cumene	4-Heptanol	2-Phenylethanol
2-Cyclohexen-1-ol	2-Hexanol	2-Propanol
Cyclohexene	Methylacetylene	Tetrahydrofuran
Decahydronaphthalene	3-Methyl-1-butanol	Tetrahydronaphthalene
Diacetylene	Methylcyclopentane	Vinyl ethers
Dicyclopentadiene	Methyl isobutyl ketone	Other secondary alcohols

<b>C. Chemicals that may autopolymerize as a result of peroxide accumulation</b>		
Acrylic acid <sup>b</sup>	Methyl methacrylate <sup>b</sup>	Vinyl chloride
Acrylonitrile <sup>b</sup>	Styrene	Vinylpyridine
Butadiene <sup>c</sup>	Tetrafluoroethylene <sup>c</sup>	Vinyladiene chloride
Chloroprene <sup>c</sup>		Vinyl acetate
Chlorotrifluoroethylene		Vinylacetylene

<b>D. Chemicals that may form peroxides but cannot clearly be placed in sections A,B or C</b>		
Acrolein	p-Chlorophenetole	4,5-Hexadien-2-yn-1-ol
Allyl ether <sup>d</sup>	Cyclooctene <sup>d</sup>	n-Hexyl ether
Allyl ethyl ether	Cyclopropyl methyl ether	o,p-Iodophenetole
Allyl phenyl ether	Diallyl ether <sup>d</sup>	Isoamyl benzyl ether <sup>d</sup>
p-(n-Amyloxy)benzoyl chloride	p-Di-n-butoxybenzene	Isoamyl ether <sup>d</sup>
n-Amyl ether	1,2-Dibenzoyloxyethane <sup>d</sup>	Isobutyl vinyl ether
Benzyl n-butyl ether <sup>d</sup>	p-Dibenzoyloxybenzene <sup>d</sup>	Isophorone <sup>d</sup>
Benzyl ether <sup>d</sup>	1,2-Dichloroethyl ethyl ether	B-Isopropoxypropionitrile <sup>d</sup>
Benzyl ethyl ether <sup>d</sup>	2,4-Dichlorophenetole	Isopropyl 2,4,5-trichlorophenoxy- acetate
Benzyl methyl ether	Diethoxymethane <sup>d</sup>	Limonene
Benzyl 1-naphthyl ether <sup>d</sup>	2,2-Diethoxypropane	1,5-p-Methadiene
1,2-Bis(2-chloroethoxy) Ethane	Diethyl ethoxymethylene-Malonate	Methyl p-(n-amlyoxy)-benzoate
Bis(2 ethoxyethyl)ether	Diethyl fumarate <sup>d</sup>	4-Methyl-2-pentanone
Bis(2-(methoxyethoxy)-ethyl) ether	Diethyl acetal <sup>d</sup>	n-Methylphenetole
Bis(2-chloroethyl)ether	Diethyketene <sup>f</sup>	2-Methyltetrahydrofuran
Bis(2-ethoxyethyl)adipate	m,o,p-diethoxybenzene	3-Methoxy-1-butyl acetate
Bis(2-ethoxyethyl)phthalate	1,2-Diethoxyethane	2-Methoxyethanol
Bis(2-methoxyethyl)-Carbonate	Dimethoxymethane <sup>d</sup>	3-Methoxyethyl acetate
Bis(2-methoxyethyl) ether	1,1-Dimethoxyethane <sup>d</sup>	2-Methoxyethyl vinyl ether
Bis(2-methoxyethyl) Phthalate	Dimethylketene <sup>f</sup>	Methoxy-1,3,5,7-cyclo-octa-tetraene
<b>A. Continued next page</b>		

<b>D. Con't Chemicals that may form peroxides but cannot clearly be placed in sections A,B or C</b>		
Bis(2-methoxymethyl) Adipate	3,3-Dimethoxypropene	B-Methoxypropionitrile
Bis(2-n-butoxyethyl) Phthalate	2,4-Dinitrophenetole	m-Nitrophenetole
Bis(2-phenoxyethyl) ether	1,3-Dioxepane <sup>d</sup>	1-Octene
Bis(4-chlorobutyl) ether	Di(1-propynyl)ether <sup>f</sup>	Oxybis(2-ethyl acetate)
Bis(chloromethyl) ether <sup>e</sup>	Di(2-propynyl)ether	Oxybis(2-ethyl benzoate)
2-Bromomethyl ethyl ether	Di-n-propoxymethane <sup>d</sup>	B,B-oxydipropionitrile
B-Bromophenetole	1,2-Epoxy-3-isopropoxy-propene <sup>d</sup>	1-Pentene
o-Bromophenetole	1,2-Epoxy-3-phenoxy-propene	Phenoxyacetyl chloride
p-Bromophenetole	p-Ethoxyacetophenone	a-Phenoxypropionyl chlorid
3-Bromopropyl phenyl ethe	2-Ethoxyethyl acetate	Phenyl o-propyl ether
1,3-Butadiyne	(2-Ethoxyethyl)-o-benzoyl benzoate	p-Phenylphenetone
Buten-3-yne	1-(2-Ethoxyethoxy)ethyl acetate	n-Propyl ether
tert-Butyl ethyl ether	1-Ethoxynaphthalene	n-Propyl isopropyl ether
tert-Butyl methyl ether	o,p-Ethoxyphenyl isocyanate	Sodium 8,11,14-eicosa-tetraenoate
n-Butyl phenyl ether	1-Ethoxy-2-propyne	Sodium ethoxyacetylde <sup>f</sup>
n-Butyl vinyl ether	3-Ethoxypropionitrile	Tetrahydropyran
Chloroacetaldehyde diethylacetal <sup>d</sup>	2-Ethylacrylaldehyde oxim	Triethylene glycol diacetate
2-Chlorobutadiene	2-Ethylbutanol	Triethylene glycol dipropionate
1-(2-Chloroethoxy)-2-phen-oxyethane	Ethyl B-ethoxypropionate	1,3,3-Trimethoxypropene <sup>d</sup>
Chloroethylene	2-Ethylhexanal	1,1,2,3-Tetrachloro-1,3-butadiene
Chloromethyl methyl ether <sup>e</sup>	Ethyl vinyl ether	4-Vinyl cyclohexene
B-Chlorophenetole	Furan	Vinylene carbonate
o-Chlorophenetole	2,5-Hexadiyn-1-ol	Vinylidene chloride <sup>d</sup>

**Notes:**

<sup>a</sup> When stored as a liquid monomer.

<sup>b</sup> Although these chemicals form peroxides, no explosions involving these monomers have been reported.

<sup>c</sup> 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.

<sup>d</sup> These chemicals easily form peroxides and should probably be considered under Part B.

<sup>e</sup> OSHA - regulated carcinogen.

<sup>f</sup> Extremely reactive and unstable compound.

## Removing Peroxides

Peroxides are particularly dangerous. These procedures should be carried out only by knowledgeable laboratory personnel.

### Properly dispose of remaining materials as hazardous waste.

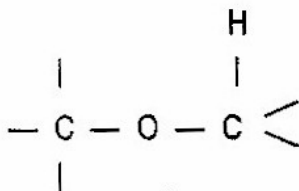
- Removal of peroxides with alumina:  
A 2 X 33 cm column filled with 80 g of 80 – mesh basic activated alumina is usually sufficient to remove all peroxides from 100 to 400 ml of solvent, whether water-soluble or water-insoluble. After passage through the column, the solvent should be tested for peroxide content. Peroxides formed by air oxidation are usually decomposed by the alumina, not merely absorbed on it. However, for safety it is best to slurry the wet alumina with dilute acidic solution of ferrous sulfate before disposal as hazardous waste.
- Removal of peroxides with Molecular Sieves®:  
Reflux 100 ml of the solvent with 5 g of 4- to 8- mesh indicating activated 4A Molecular Sieves® for several hours under nitrogen. The sieves are separated from the solvent and require no further treatment because the peroxides are destroyed during their interaction with the sieves.
- Removal of peroxides with ferrous sulfate:  
A solution of 6 g of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , 6 ml of concentrated sulfuric acid, and 11 ml of water is stirred with 1 L of water-insoluble solvent until the solvent no longer gives a positive test for peroxides. Usually only a few minutes are required.  
Diacyl peroxides can be destroyed by this reagent as well as by aqueous sodium hydrogen sulfite, sodium hydroxide, or ammonia. However, diacyl peroxides with low solubility in water, such as dibenzoyl peroxide, react very slowly. A better reagent is a solution of sodium iodide or potassium iodide in glacial acetic acid.
- Procedure for destruction of diacyl peroxides:  
For 0.01 mol of diacyl peroxide, 0.022 mol (10% excess) of sodium or potassium iodide is dissolved in 70 ml of glacial acetic acid, and the peroxide added gradually with stirring at room temperature. The solution is rapidly darkened by the formation of iodine. Let stand a minimum of 30 minutes before disposal as hazardous waste. Most dialkyl peroxides do not react readily at room temperature with ferrous sulfate, iodide, ammonia, or the other reagents mentioned above. However, these peroxides can be destroyed by a modification of the iodide procedure.
- Procedure for destruction of dialkyl peroxides:  
1 ml of 36% (w/v) hydrochloric acid is added to the above acetic acid/ potassium iodide solution as an accelerator, followed by 0.01 mol of the dialkyl peroxide. The solution is heated to 90 to 100° C on a steam bath over the course of 30 minutes and held at that temperature for 5 hours.

References: Prudent Practices in the Laboratory, National Research Council, 1995.

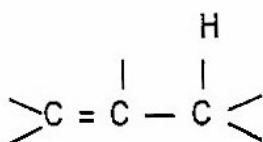
“Review of Safety Guidelines for Peroxidizable Organic Chemicals,” Chemical Health and Safety, September/October 1996.

Below are diagrams of moieties that can form organic peroxides. These moieties are ranked from highest (1) to lowest (14) risk of forming potentially dangerous peroxide concentrations.

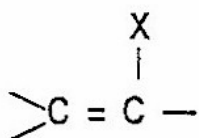
1. Ethers and acetals with  $\alpha$ -hydrogen



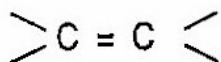
2. Alkenes with allylic hydrogen



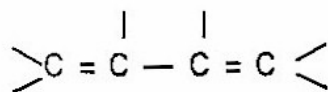
3. Chloroalkenes, fluoroalkenes



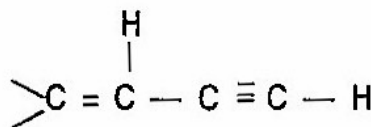
4. Vinyl halides, esters, ethers



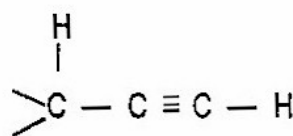
5. Dienes



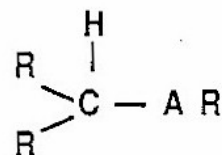
6. Vinylalkynes with  $\alpha$ -hydrogen



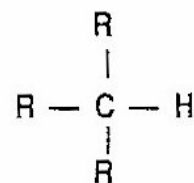
7. Alkylalkynes with  $\alpha$ -hydrogen



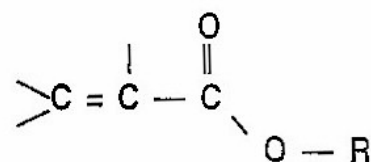
8. Alkylalkynes with tertiary  $\alpha$ -hydrogen



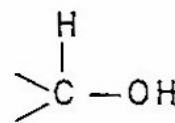
9. Alkanes and cycloalkanes with tertiary hydrogen



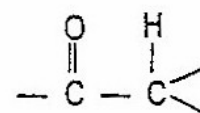
10. Acrylates, methacrylates



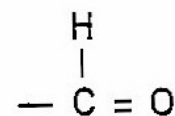
11. Secondary alcohols



12. Ketones with  $\alpha$ -hydrogen



13. Aldehydes



14. Ureas, amides, and lactams with  $\alpha$ -hydrogen atom on a carbon attached to nitrogen

