Introduction

Peroxide forming compounds (PFCs) are useful in laboratory research because of their reactivity and oxidative capacity, however those properties also make them dangerous. PFCs have been the cause of many laboratory explosions and deaths as they are prone to explosion when subjected to heat, light, friction, and mechanical shock. It is important for all researchers using peroxide forming compounds to be able to recognize hazardous peroxide accumulation and be aware of how to safely use and dispose of their chemicals.

The rate of peroxide formation depends on the compound and storage conditions. Some peroxides quickly become explosive and some are only reactive after long periods of concentration. Compounds that form peroxides can be divided into four groups. Group A compounds form explosive peroxides even without concentration. Group B compounds are hazardous only when peroxide levels are concentrated, which can occur through evaporation or distillation. Group C compounds can autopolymerize due to peroxide formation. Group D compounds can form peroxides but are not easily placed in Groups A-C. The compounds listed in Tables II-IV are not exhaustive but represent many of the peroxide forming compounds used in research laboratories.

Always consult the SDS/MSDS for appropriate storage and handling instructions for specific compounds.

Potential Hazards

- **Explosion:** Peroxide Forming Compounds may produce unstable products over time. These products can result in violent explosions.

Personal Protective Equipment

- Use chemical splash goggles for eye protection, in combination with a full-length face shield for operations that are not behind a fume hood sash or blast shield.
- Wear appropriate gloves at all times while handling PFCs. Make sure the glove works with the PFC in question as many PFCs penetrate common lab gloves rapidly.
    - Change gloves immediately if contaminated.
- Wear fire/flame resistant lab coat (100% cotton based), cotton based clothing, long pants, and closed-toe shoes.

Special Handling Procedures

- Purchase the smallest possible container appropriate for your needs.
- Carefully review the SDS before working with these compounds.
- Avoid contact between PFCs and metal sources, such as spatulas. In some circumstances metal can promote explosive decomposition. Use wood or ceramic instead.
- Ignition sources should be kept away from peroxide forming compounds.
- Carefully store the container after each use; wipe the neck, cap and threads with a cloth, apply inert gas if necessary, make sure the container is completely sealed.
- Avoid friction and grinding, this includes the use of glass stoppers and is why bottle necks and caps should be wiped down before storing.
- All spills must be cleaned up immediately
- Never return unused materials back to the original container.
- Do not evaporate containers that held PFCs or distill to dryness, this can cause peroxide concentration and increases the potential for explosion.
    - Leave at least 20% of the liquid in the bottles.
    - When possible, add non-volitile organic compounds (like mineral oil) to dilute any peroxides remaining after distillation.

- If solids or crystals are observed in the liquid or around the cap, leave the container and contact EH&S for disposal.

Peroxide Storage

Table I: Peroxidizable Chemicals Storage Lengths

Unopened Chemicals from manufacturer	18 months
Open Containers	
Chemicals in Table **III**	3 months
Chemicals in Table IV and Table VI	12 months
Uninhibited chemicals in Table V	**24 hours**
Inhibited chemicals in Table V	12 months

- Label containers with: date received; date opened; and if applicable, date of the last peroxide test.
  - Some companies put expiration dates on peroxide formers, any expired bottles must be checked for peroxide formation or disposed of.
- Store peroxide formers in sealed, air-impermeable containers (such as dark amber glass with a tight fitting lid).
- Iron inhibits peroxide formation in some compounds, keep the metal cans they come in and continue to use them for storage.
- Containers of peroxide formers should be stored away from heat and light, and protected from physical damage and ignition sources.
- Peroxide forming compounds should not be stored at temperatures that cause the peroxide to freeze or precipitate. Such storage will make the compounds very sensitive to shock.
- Store peroxide formers, especially those in Group A, under nitrogen or inert gas.
  - Some inhibitors require small amounts of oxygen to function so inhibited chemicals should not be stored under inert gas unless instructed to do so by the SDS.
- Check the containers frequently for signs of peroxide formation, see evaluation procedure below.
  - Peroxide formation indicates the possibility of a shock sensitive container, do not move the container and contact EH&S for disposal as soon as possible.
- Make sure peroxide formers are stored away from incompatible chemicals to reduce the likelihood of violent chemical reactions.

Peroxide Evaluation

- Any PFC of unknown age or origin should be handled very carefully and assumed to be explosive.
- Do not open these containers, contact EH&S for disposal.
- Depending on the substance and age EH&S may have to contact the bomb squad to come and deactivate the chemical prior to disposal.

1. Visual Inspection

Start peroxide evaluations with a visual inspection of the closed container. If a container exhibits any peroxide characteristics, such as those listed below, assume there are dangerous levels of peroxides and do not disturb it. Contact EH&S to assist with further evaluation or disposal.

For liquids, look for:

- Crystallization around the cap or in the liquid
- Discoloration

- Stratification of the liquid

A flashlight can be used to increase visibility inside amber bottles

For solids, look for:

- Discoloration
- Surface crust (e.g. potassium metal forms a yellow or orange superoxide at the surface)

Evaluation of alkali metals and their amides should be based on visual inspection only. These substances react violently with water and oxygen so further peroxide tests should not be used.

Any chemicals that don't pass the visual inspection should be considered very hazardous. Contact EH&S for disposal.

2. Open Container

NEVER try to force open a rusted or stuck cap on a peroxide forming compound.

Only open the container if:

- ☐ It has passed the visual test
- ☐ The age and origin of the container/chemical are known
- ☐ Group A Chemicals
  - Previously opened chemicals not used in the last 3 months must be less than 6 months old
  - Unopened chemicals from the manufacturer must be less than 2 years old
    - If this is in question, assume the chemical has been opened.
- ☐ Group B, C, and D Chemicals
  - Previously opened chemicals not used in the last 12 months must be less than 5 years old
  - Unopened chemicals from the manufacturer must be less than 10 years old.

Repeat the visual inspection again with the container open to see if any peroxide characteristics are visible now that the lid is off.

3. Test for Peroxides

There are several tests that can be used to check for peroxide formation, their use will depend on the type of chemical you are working with.

- If you are working with PFCs make sure you know how to properly test your chemicals.

For liquids the easiest method is to use a peroxide test strip and follow the manufacturer directions to determine the peroxide levels.

Table II: Peroxide Levels and Chemical Use

Peroxide Level	Use	Recheck frequency
< 25 PPM	Safe for general use	Recheck levels every three months
25 - 100 PPM	Not recommended for distilling or otherwise concentrating	Recheck levels monthly
> 100 PPM	DO NOT USE Consider explosive Contact EH&S for disposal	N/A

Table III: Group A Chemicals *– Chemicals that form explosive levels of peroxides without concentration*

Butadine[1]	Isopropyl ether	Sodium amide (sodamide)
Chloroprene[1]	Potassium amide	Tetrafluoroethylene[1]
Divinylacetylene	Potassium metal	Vinylidene chloride

Table IV: Group B Chemicals *– Chemicals that form explosive levels of peroxides upon concentration*

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

Table V: Group C Chemicals *– Chemicals that may autopolymerize as a result of peroxide accumulation*

Acrylic acid[2]	Methyl methacrylate[2]	Vinyl chloride
Acrylonitrile[2]	Styrene	Vinylpyridine
Butadiene[3]	Tetrafluoroethylene[3]	Vinyladiene chloride
Chloroprene[3]	Vinyl acetate	
Chlorotrifluoroethylene	Vinylacetylene	

Table VI: Group D Chemicals *– Chemicals that may form peroxides but cannot be clearly placed in Groups A-C*

Acrolein	p-Chlorophenetole	4,5-Hexadien-2-yn-1-ol
Allyl ether[4]	Cyclooctene[4]	n-Hexyl ether
Allyl ethyl ether	Cyclopropyl methyl ether	o,p-Iodophenetole
Allyl phenyl ether	Diallyl ether[4]	Isoamyl benzyl ether[4]
p-(n-Amyloxy)benzoyl chloride	p-Di-n-butoxybenzene	Isoamyl ether[4]
n-Amyl ether	1,2-Dibenzyloxyethane[4]	Isobutyl vinyl ether
Benzyl n-butyl ether[4]	p-Dibenzyloxybenzene[4]	Isophorone[4]
Benxyl ether[4]	1,2-Dichloroethyl ethyl ether	B-Isopropoxy-propionitrile[4]
Benzyl ethyl ether[4]	2,4-Dichlorophenetole	Isopropyl
Benzyl methyl ether	Diethoxymethane[4]	Limonene
Benzyl 1-napthyl ether[4]	2,2-Diethoxypropane	1,5-p-Methadiene
1,2-Bis(2-chloroethoxy)-ethane	Diethyl ethoxymethylene-malonate	Methyl p-(n-amyloxy)benzoate
Bis(2 ethoxyethyl)ether	Diethyl fumarate[4]	4-Methyl-2-pentanone
Bis(2(methoxyethoxy)-ethyl) ether	Diethyl acetal[4]	n-Methylphenetole
Bis(2-chloroethyl) ether	Diethyketene[6]	2-Methyltetra-hydrofuran
Bis(2-ethoxyethyl) adipate	m,o,p-Diethoxybenzene	3-Methoxy-1-butyl acetate
Bis(2-ethoxyethyl) phthalate	1,2-Diethoxyethane	2-Methoxy-ethanol
Bis(2-methoxyethyl) carbonate	Dimethoxymethane[4]	Methonxy-1,3,5,7-cyclooctatetraene
Bis(2-methoxyethyl) ether	1,1-Dimethoxyethane[4]	B-Methoxy-propionitrile
Bis(2-methoxyethyl) phthalate	Dimethylketene[6]	m-Nitro-phenetole
Bis(2-methoxymethyl) adipate	3,3-Dimethoxypropene	1-Octene

Bis(2-n-butoxyethyl) phthalate	2,4-Dinitrophenetole	Oxybis(2-ethyl acetate)
Bis(2-phenoxyethyl) ether	1,3-Dioxepane[4]	Oxybis(2-ethyl benzoate)
Bis(4-chlorobutyl) ether	Di(1-propynyl)ether[6]	B,B-oxydi-propionitrile
Bis(chloromethyl) ether[5]	Di(2-propynyl)ether	1-Pentene
2-Bromomethyl ethyl ether	Di-n-propoxymethane[4]	Phenoxyacetyl chloride
B-Bromophenetole	1,2-Epoxy-3-isopropoxypropane[4]	a-Phenoxy-propionyl chloride
o-Bromophenetole	1,2-Epoxy-3-phenoxypropane	Phenyl o-propyl ether
p-Bromophenetole	p-Ethoxyacetho-phenone	p-Phenylphenetone
3-Bromopropyl phenyl ether	1-(2-Ethoxyethoxy)-ethyl acetate	n-Propyl ether
1,3-Butadiyne	2-Ethoxyethyl acetate	n-Propyl isopropyl ether
Buten-3-yne	(2-Ethoxyethyl)-o-benzoyl benzoate	Sodium 8,11,14-eicosa-tetraenoate
tert—Butyl ethyl ether	1-Ethoxynaphthalene	Sodium ethoxyacetylide[6]
tert-Butyl methyl ether	o,p-Ethoxyphenyl isocyanate	Tetrahydropyran
n-Butyl phenyl ether	1-Ethoxy-2-propyne	Triethylene glycol diacetate
n-Butyl vinyl ether	3-Ethoxyopropionitrile	Triethylene glycol dipropionate
Chloroacetaldehyde diethylacetal[4]	2-Ethylacrylaldehyde oxime	1,3,3-Trimethoxy-propene[4]
2-Chlorobutadiene	2-Ethylbutanol	1,1,2,3-Tetrachloro-1,3-butadiene
1-(2-Chloroethoxy)-2-phenoxyethane	Ethyl B-ethoxy-propionate	4-Vinyl cyclohexene
Chloroethylene	2-Ethylhexanal	2,4,5-tri-chlorophenoxyacetate
Chloromethyl methyl ether[5]	Ethyl vinyl ether	Vinylene carbonate
B-Chlorophenetole	Furan	Vinylidene chloride[4]
o-Chlorophenetole	2,5-Hexadiyn-1-ol	

NOTES:

1. When stored as a liquid monomer
2. Although these chemicals form peroxides, no explosions involving these monomers have been reported.
3. 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.
4. These chemicals easily form peroxides and should probably be considered under Part B.
5. OSHA - regulated carcinogen.
6. Extremely reactive and unstable compound.