WESTERN SYDNEY UNIVERSITY

GUIDELINES FOR THE USE OF PEROXIDE-FORMING CHEMICALS

OVERVIEW

Some common organic chemicals can react with air to form unstable and dangerous peroxide compounds with storage. These peroxides may detonate with extreme violence when subjected to thermal or mechanical shock. Others may cause rapid polymerisation and initiate an explosive reaction. The risk increases if the peroxide becomes concentrated by evaporation or distillation.

Peroxide formation is accelerated by exposure to air, light, heat, moisture and contamination from metals. Peroxides may form in containers that have not been opened as they may have been packaged in an atmosphere of air.

Peroxide crystals can accumulate around the cap or stopper of a container and detonate when the lid is twisted. If a precipitate or crystals are present in a peroxide-forming chemical **do not open the lid.**

RECOMMENDED WORK PRACTICES

1. *Minimise use of peroxide-forming chemicals*

   (i) Consider elimination or substitution of the peroxide-forming chemical in the process and workplace.

   (ii) Purchase minimum quantities to ensure use within the recommended expiration and disposal period.

   (iii) Share chemicals between common users.

   (iv) Purchase peroxide-forming chemicals which contain a peroxide inhibitor if possible. Be aware that such inhibitors become depleted over time.

2. *Labelling*

   (i) Label containers of peroxide-forming chemicals with:
      a) the date received
      b) the date they are first opened

   (ii) Label containers with the name of the owner (e.g. researcher, teaching staff).

   (iii) Example label:

WARNING Peroxide-Forming Chemical **TEST BEFORE USING**
Date Received: Date Opened: Name of Owner:

3. *Storage and Use*

   (i) Store in dark, transparent bottles, in a cool place and avoid sunlight. Keep containers tightly closed. It is preferable to use containers that enable the contents to be viewed without having to be moved or opened. Do not store in ground glass stoppered bottles.

   (ii) Refrigerators used for storage must be explosion-proof. Note that refrigeration does not prevent and may not inhibit peroxide formation.

(iii) Rotate all stock to prevent ageing. Use on a FIFO (First In-First Out) basis.

(iv) All peroxide-forming chemicals must be closely monitored so that they are used or disposed of **before** the expiry date as recommended in the MSDS[1] (see Appendix 1 below).

(v) Establish a routine in your laboratory for the regular inspection and testing of peroxide-forming chemicals (e.g. the first Monday of each month).

(vi) Dangerous levels of peroxides are evident when:

- a bottle has whitish crystals around the cap and/or a viscous liquid or precipitate within,
- solid chemicals (such as potassium metal, potassium amide and sodium amide) show discolouration and/or formation of a surface crust.

In such cases, contact your supervisor immediately. **Secure and label the area around the chemical so that it is protected from movement and can't be disturbed. Arrange removal by a licensed waste disposal contractor.**

(vii) Test all peroxide-formers **prior** to distillation, evaporation or concentration regardless of age.

(iix) Evaporation or distillation of peroxide-forming chemicals will result in concentration of peroxides. Even if the solvent has been treated to destroy peroxides, distillation should cease when about 15-20% remains in the flask.

(ix) Laboratory work with ethers should be confined to fume cupboards.

(x) Do not use metal spatulas or magnetic stirring bars with peroxide-forming chemicals. Any iron leached out may lead to an explosion. Ceramic, telfon or wooden equipment should be safe to use.

(xi) Glassware or containers that have an oily or crusty residue after being used with peroxide-forming chemicals should never be scraped or scrubbed.

(xii) Properly dispose of chemicals that are past their maximum retention times using a licensed waste disposal contractor.

(xiii) Chemicals whose identity or age is unknown should not be disturbed. Contact your supervisor to arrange removal by a licensed waste disposal contractor.

(xiv) Purified solvents should be used directly and not stored for later use as any inhibitor originally present will have been removed.

4. *Detection of Peroxides*

(i) Examine peroxide-forming liquids for visible crystals or viscous liquids, and solids for discolouration or a surface crust – this indicates the presence of peroxides. Be aware that peroxide crystals tend to form on the inner surface of a container.

(ii) **If a precipitate or crystals are present in a peroxide-forming chemical do not open the lid. Contact your supervisor to arrange removal by a licensed waste disposal contractor. Secure and label the area around the chemical so that it is protected from movement and can't be disturbed.**

5. *Testing of Peroxides*

(i) Test for the presence of peroxides before each use. A number of methods to detect peroxides are reported in the literature. Three methods of detection commonly used are described below. Some variations to methods B and C are reported in the literature - these tests are not to be used for alkali metals and their amides.

Method A

Commercially available test strips (such as EM Quant® Peroxide Test Strips) may be purchased from most safety or laboratory suppliers for the semi-quantitative detection of peroxides in organic solvents. Please note that these strips have finite ranges.

Method B[1]

(1) Prepare a fresh solution of 10% (by weight) potassium iodide in distilled water.

(2) In a fume cupboard, add 1mL of this solution to approx 10mL of the test chemical in a clear test tube or similar.

(3) Shake well. Observe the colour of the resulting mixture by looking through the side of the tube with a piece of white paper behind it.

(4) Peroxides oxidise the colourless iodide anion (I^-) to elemental iodine (I_2), which gives a purple or brownish solution depending on the solvent.
   - o A pale or barely discernible yellow colour indicates a low concentration of peroxides
   - o Purple, brown or bright yellow indicates a relatively high concentration of peroxides

Variations of this method include using a 20% KI solution and a 1:1 solvent:reagent ratio.

Method C[1]

(1) Prepare the fresh reagent by adding 0.1g of sodium iodide or potassium iodide to 1mL of glacial acetic acid.

(2) Add 1mL of the solvent to the reagent using a clear test tube or similar.

(3) A yellow colour indicates a low concentration of peroxides. A brown colour indicates a relatively high concentration of peroxides.

Prepare a blank sample using a chemical that doesn't form peroxides for both Methods B and C. It has been reported that Method B is often faster than Method C (it may take up to 15 minutes for colour formation in Method C, compared to less than 1 minute for Method B).[1]

5. *Removal of Peroxides*

(i) Peroxides may be removed using one of the 2 methods below.[1]

Method 1

Pass the solvent through a short column of activated alumina. (A suggested amount is 100g of alumina per 100mL of solvent). Retest the solvent to ensure that peroxides have been removed.

Some peroxide may be retained on the column, which should then be disposed of as a flammable material. Solvents purified in this way should be used directly and not stored further as any peroxide-forming inhibitor will probably have been removed.

Method 2

Shake the solvent with a freshly prepared solution of iron (II) sulphate (60g iron (II) sulphate, 6mL concentrated sulphuric acid and 110mL water per litre of ether). Repeat until peroxides are no longer detected after testing.

Shake very gently for the first extraction.

APPENDIX 1 – Common Peroxide-Forming Compounds and their Shelf-Life

Peroxide-forming chemicals can be divided into 4 groups (based on the peroxide formation hazard). Please note that these lists are not exhaustive – check the MSDS before use to determine if there is the possibility of peroxide formation.

The tables below show the generally accepted test and disposal timeframes for these groups. Refer to the MSDS for each chemical to determine the supplier's recommendations.

A. Peroxide Hazard on Storage

These chemicals may form explosive levels of peroxides with exposure to air and without concentration by evaporation or distillation. It is important to limit quantities of these chemicals in the laboratory, and be vigilant in regularly inspecting any holdings.

Some of these materials may be hazardous even if not opened.

Butadiene (liquid monomer) Isopropyl ether Sodium amide	Chloroprene (liquid monomer) Potassium amide Tetrafluoroethylene (liquid monomer)	Divinyl acetylene Potassium metal Vinylidene chloride
CONSULT MSDS FOR SUPPLIER'S RECOMMENDATIONS FOR TEST & EXPIRY PERIODS*		
Generally: Test every 3 months after opening **Dispose of 3 months after date opened** (unless tested and free of peroxides) **Dispose of 1 year after date received**		

B. Peroxide Hazard on Concentration

These chemicals form explosive levels of peroxides when distilled, evaporated or otherwise concentrated.

Acetal 2-Butanol Cyclohexene Diacetylene Diglyme Furan Methyl acetylene Methyl isobutyl ketone 4-Penten-1-ol 2-Propanol Vinyl ethers	Acetaldehyde Cumene 2-cyclohexen-1-ol Dicyclopentadiene Dioxane 4-Heptanol 3-Methyl-1-butanol 2-Methyl-2-pentanol 1-Phenylethanol Tetrahydrofuran Other secondary alcohols	Benzyl alcohol Cyclohexanol Decahydronaphthalene Diethyl ether (ether) Glyme 2-Hexanol Methyl cyclopentane 2-Pentanol 2-Phenylethanol Tetrahydronaphthalene
CONSULT MSDS FOR SUPPLIER'S RECOMMENDATIONS FOR EXPIRY PERIOD*		

C. Hazardous due to Peroxide Initiation of Polymerisation

These chemicals are highly reactive and may auto-polymerise and explode as a result of peroxide accumulation.

Acrylic acid Chloroprene (gas) Styrene Vinyl acetylene	Acrylonitrile Chlorotrifluoroethylene Tetrafluoroethylene (gas) Vinyl chloride	Butadiene (gas) Methyl methacrylate Vinyl acetate Vinyl pyridine
CONSULT MSDS FOR SUPPLIER'S RECOMMENDATIONS FOR EXPIRY PERIOD*		

* Consult the WHS unit if this information is not found in the supplier MSDS

D. Potential Peroxide-Forming Chemicals

These chemicals may form peroxides but cannot clearly be categorised as any of the above.

Acrolein Allyl ether	p-Chlorophenetole Cyclooctene	4,5-Hexadien-2-yn-1-ol 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 n-	p-Di-n-butoxybenzene	Isoamyl ether
Amyl ether	1,2-Dibenzyloxyethane	Isobutyl vinyl ether
Benzyl n-butyl ether	p-Dibenzyloxybenzene	Isophorone
Benxyl ether	1,2-Dichloroethyl ethyl ether	B-Isopropoxy-propionitrile
Benzyl ethyl ether	2,4-Dichlorophenetole	Isopropyl
Benzyl methyl ether	Diethoxymethane	Limonene
Benzyl 1-napthyl ether	2,2-Diethoxypropane	1,5-p-Methadiene
1,2-Bis(2-chloroethoxy)- ethane	Diethyl ethoxymethylene-malonate	Methyl p-(n-amyloxy)benzoate 4-
Bis(2 ethoxyethyl)ether	Diethyl fumarate	Methyl-2-pentanone
Bis(2(methoxyethoxy)-ethyl) ether	Diethyl acetal	n-Methylphenetole
Bis(2-chloroethyl) ether	Diethyketene m,o,p-	2-Methyltetra-hydrofuran
Bis(2-ethoxyethyl) adipate Bis(2-	Diethoxybenzene 1,2-	3-Methoxy-1-butyl acetate
ethoxyethyl) phthalate Bis(2-	Diethoxyethane	2-Methoxy-ethanol
methoxyethyl) carbonate Bis(2-	Dimethoxymethane	Methonxy-1,3,5,7-cyclooctatetraene
methoxyethyl) ether	1,1-Dimethoxyethane	B-Methoxy-propionitrile
Bis(2-methoxyethyl) phthalate Bis(2-methoxymethyl) adipate	Dimethylketene 3,3-Dimethoxypropene	m-Nitro-phenetole 1-Octene
Bis(2-n-butoxyethyl) phthalate	2,4-Dinitrophenetole	Oxybis(2-ethyl acetate)
Bis(2-phenoxyethyl) ether	1,3-Dioxepane	Oxybis(2-ethyl benzoate)
Bis(4-chlorobutyl) ether	Di(1-propynyl)ether	B,B-oxydi-propionitrile 1-
Bis(chloromethyl) ether	Di(2-propynyl)ether	Pentene Phenoxyacetyl
2-Bromomethyl ethyl ether	Di-n-propoxymethane	chloride
B-Bromophenetole	1,2-Epoxy-3-isopropoxypropane	a-Phenoxy-propionyl chloride
o-Bromophenetole p-	1,2-Epoxy-3-phenoxypropane	Phenyl o-propyl ether
Bromophenetole	p-Ethoxyacetho-phenone	p-Phenylphenetone
3-Bromopropyl phenyl ether	1-(2-Ethoxyethoxy)-ethyl acetate	n-Propyl ether
CONSULT MSDS FOR SUPPLIER'S RECOMMENDATIONS FOR EXPIRY PERIOD* TEST FOR PEROXIDES BEFORE USE		

* Consult the WHS unit if this information is not found in the supplier MSDS

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