

Acadia University/Chemistry

Standard Operating Procedures (SOP) for *peroxide forming chemicals*.

Problem. Some substances are capable of readily forming peroxides when stored for prolonged time in the presence of atmospheric oxygen. The reaction is accelerated by heat and light. These organic peroxides can explode when initiated by heat, shock, electric spark etc., thus posing high propensity for accidents.

Solution. *Peroxide forming substances* must be handled with special care as described in this SOP.

Description of *peroxide forming chemicals*. NOTE: the lists include the most common representatives. Consult MSDS for further details if not sure.

Group A. Chemicals that form explosive levels of peroxides without concentration.

This group can form peroxides in concentrations, e.g. well defined crystalline precipitates, that can readily explode without prior concentration. It is imperative that these materials are handled with extreme care and used shortly (within 3 months) after their acquisition and opening.

- Butadiene
- Chlorobutadiene
- Divinyl acetylene
- Isopropyl ether
- Potassium amide
- Potassium metal
- Sodium amide
- Tetrafluoroethylene
- Vinylidene chloride

Group B. Chemicals that form explosive levels of peroxides on concentration.

This group forms diluted suspensions of low levels of peroxides which become explosive after prior concentration of these materials e.g. due to evaporation or distillation. These materials must be used within 12 months of their acquisition and tested for presence of peroxides before their use, especially for distillations and other procedures resulting in possible concentration of explosive peroxides. They must never be distilled to dryness! Leave at least 10 % liquid at the bottom.

- Acetal
- Acetaldehyde
- Benzyl alcohol
- 2-butanol
- Chlorofluoroethylene
- Cumene
- Cyclohexanol
- 2-Cyclohexen-1-ol
- Cyclohexene
- Cyclooctene
- Cyclopentene
- Decahydronaphthalene
- Diacetylene
- Dichloropentadiene
- **Diethyl ether**
- Diethylene glycol dimethyl ether
- Dioxanes
- Ethylene glycol dimethyl ether
- Furan
- 4-Heptanol
- 2-Hexanol
- Methyl acetylene
- Methyl cyclopentane
- 3-Methyl-1-butanol

- Methyl isobutyl ketone
- 4-Methyl-2-pentanol
- 2- Pentanol
- 4-Penten-1-ol
- 1-Phenylethanol
- 2-Phenylethanol
- **2-Propanol (Isopropanol)**
- **Tetrahydrofuran**
- Tetrahydronaphthalene
- Vinyl ethers
- other secondary alcohols

Group C. Chemicals capable of dangerous polymerization.

This group can undergo very rapid exothermic polymerization when initiated by free radicals that form from accumulated peroxides. If uninhibited, materials must be used shortly after opening (within 24 hours). Inhibited materials must be discarded after 12 months from their acquisition.

- Acrylic acid
- Acrylonitrile
- Butadiene
- Chloroprene
- Chlorotrifluoroethylene
- Ethyl acrylate
- Methyl methacrylate
- **Styrene**
- Tetrafluoroethylene
- Vinyl acetate
- Vinyl acetylene
- Vinyl chloride
- Vinyl pyridine
- Vinylidene chloride

Safe handling practices.

All substances in **Groups A, B and C** must be labelled upon arrival. Label example is shown.

	
	Peroxide Forming Chemical
Ordered for/by: _____	
Date Received: _____	
Date Opened: _____	
Date Expires: _____	
<u>Dispose when peroxide >100 ppm</u>	
<u>Tested by:</u> _____	<u>Result:</u> _____
<u>Tested by:</u> _____	<u>Result:</u> _____

On the label, print clearly the name of the person responsible; date received; date opened and the expiry date.

Before their use, materials in **Group B and C** must be tested for peroxides using a test kit. The name of the person testing, date and peroxide concentration in ppm (mg/L) shall be printed on the label. If the concentration of peroxides exceeds 100 ppm, the materials must be disposed in a safe manner. If the material is expired, it shall be also disposed safely.

Expiry dates: Unopened materials **Group A, B, C** as received from manufacturer expire after **12 months** from the date received.

Opened materials: **Group A**, expire **3 months**; **Group B**, expire **12 months** (or less*); and **Group C**, expire **24 hours if not inhibited or 12 months** (or less*) **if inhibited** from the date opened (*not exceeding 12 months from date received).

If the presence of cloudiness, crystalline deposits or other heterogeneity is revealed visually, the materials shall be immediately disposed in a safe manner.

All these materials shall be stored in a dark, cool place without access of oxygen from air. If opened and exposed to heat and light, the chemicals undergo accelerated peroxide formation and must be regularly tested (**every 3 months**). It is highly recommended to use original manufacturer's containers for their storage. Note that diethyl ether is best stored in iron containers that inhibit formation of hazardous peroxides.

If an old undated container is found, it shall be presumed expired, handled with extreme care and disposed in a safe manner.

Safe disposal.

Label all materials that are suspect of containing peroxides with writing “**Waste containing peroxides**” and concentration of peroxides in ppm if known. Arrange with the person responsible for waste disposal for safe storage and timely disposal of the material making sure to pass any pertaining information about any additional hazards associated with the waste (e.g., visible levels of peroxide deposits at the bottom etc. requiring extreme care when handling and disposing the materials)

References.

R.J. Kelly “Review of Safety Guidelines for Peroxidizable Organic Chemicals”, Chemical Health and Safety (1996) 28-36 [http://www-ehs.ucsd.edu/lab/pdf/kelly_peroxides.pdf]

<https://uwaterloo.ca/chemistry/resources-services/safety-information/standard-operating-procedures-sop-peroxide-forming-compounds> (accessed 07/2021).

<https://www.sigmaaldrich.com/CA/en/technical-documents/technical-article/chemistry-and-synthesis/reaction-design-and-optimization/peroxide-formation> (accessed 07/2021)