"Peroxide-Forming Chemicals" Safety Guidelines

☠WARNING☠: There is a great deal of uncertainty regarding the hazards and safe handling of peroxidizable organic chemicals. These Potentially Explosive Chemicals (PECs)[1] can release tremendous amounts of destructive energy rapidly. If not handled properly, they can pose a serious threat to the health and safety of laboratory personnel, emergency responders, building occupants, chemical waste handlers, and disposal companies.

1) Purpose and Scope

This document discusses the hazards related to Peroxide-Forming Chemicals, including associated solvents, that may be handled, stored and disposed of at Concordia University.

Note that EHS must be informed of the presence in workplaces of any peroxidizable chemicals for which a high level peroxide concentration is suspected or has been determined. The usual stability issues of this class of compounds make them a serious source of fire and explosion hazard that requires careful management ![2]

2) Definition of Peroxide-Forming Chemicals

Peroxide-Forming Chemicals (PFCs) are chemicals that can "auto-oxidize" with atmospheric oxygen under ambient conditions to form organic peroxides (with an O–O bond). Peroxide formation is a spontaneous free-radical reaction that can be initiated by exposure to light, air, or impurities and *via* self-polymerization. Once formed, organic peroxides can be sensitive to light, thermal or mechanical shock, friction, and can be violently explosive in concentrated solutions or in solid forms.[3]

Many oxygenated organic compounds, but not only, become more and more dangerous upon prolonged storage because they tend to form explosive peroxides with age. For instance, these species may form in freshly distilled, undistilled, and unstabilized ethers within less than two (2) weeks.

Numerous lab incidents involving unexpected explosions due to the presence of shock or light sensitive residues after distillation and evaporation processes have been reported.[4] Others were initiated by the formation of friction-sensitive crystals inside or ouside the containers. Although ethers are the most notorious peroxide formers, other peroxidizable organic moieties prone to auto-oxidization are listed in **Figure 1**, numbered from 1 to 14, from most likely to least likely to form peroxides. To this list can be added the inorganic compounds or elements such as alkali metals (K), alkali metal alkoxides and amides, and organometallics.

<u>Note that regarding PFCs, there are no definite data available about the concentration or other specific conditions at which the newly generated peroxides will detonate</u>. Several common test methods may not detect all types of unstable peroxides, and some common deperoxidation procedures may not remove all types of unstable substances. **As a general trend, the more volatile the peroxidizable compound, the easier it is to concentrate the formed peroxides.**

3) Safe work practices with PFCs

3.1 General safety precautions

Purchase:

1) The purchaser must be knowledgeable about the peroxidizability properties of the chemicals. Please check the non-exhaustive list of PFCs, classified according to the related hazards (**Tables 1-4**)[5]
2) Avoid purchasing high-risk chemicals such as diisopropyl ether and consider a safer substitution.
3) Small containers that can be emptied completely are recommended.
4) Keep an inventory of PFCs in the laboratory and DO NOT purchase large quantities of PFCs.
5) When possible, purchase PFCs that have peroxide inhibitors added by the manufacturer (*e.g.*, BHT as a free radical scavenger in diethyl ether). Warning: These inhibitors may lose effectiveness over time once the container has been opened.
6) All PFCs containers must be labeled, displaying the date received and date opened (**Figure 2**).

Storage:

1) A flammable cabinet must be used to store PFCs.
2) Store PFCs in original containers, sealed, opaque and equipped with tight-fitting caps. *Partially empty transparent containers will promote peroxide formation!*
3) DO NOT store PFCs containers near heat, sunlight or ignition sources or in a place that undergoes temperature variations.
4) Always follow the manufacturer's recommendations in regard to storage under inert atmosphere.
5) Regularly inspect all containers for signs of decomposition.
6) Refrigeration DOES NOT inhibit peroxide formation (and may actually increase it)!

Handling and use:

Most explosions directly involving PFCs occur when a material is distilled to dryness!

1) Work inside a certified engineering control (fume hood, glove box, etc.) at all times.
2) Periodically test for the presence of peroxides, as well as before PFCs distillation.
3) DO NOT distill, evaporate or concentrate to dryness: leave at least 10-20% in bottoms.
4) Always stir distillations with a mechanical stirrer or a bubbling inert gas (not air or oxygen-containing mixtures).
5) In the event a PFC container shows obvious crystal formation, discoloration or liquid stratification, **DO NOT handle it or force open the lid because shock or friction can cause explosion**. **Call EHS immediately.**
6) Donation of expired PFCs or presenting a questionable quality is forbidden.

Disposal:

1) Most of the PFCs have a recommended shelf life and must be discarded within 12 months of opening (or within 18 months if unopened). **Disposal must be done by their expiration dates, whether or not they have been opened. EHS must be contacted.**
2) The identification of suspect containers (crystal formation, expired or untested chemicals, other suspicious observations) **must be communicated to EHS immediately**.
3) Follow the Concordia **EHS Chemical Waste Disposal Guidelines – EHS-DOC-018**.

3.2 Information displayed on WHMIS-related documentation

1) No specific pictogram adopted under the WHMIS regulation.
2) *In the Safety Data Sheet (SDS):* "*May form explosive peroxides*" specified in Hazards Not Otherwise Classified (HNOC class).
3) *On the label:* Presence of Hazards and Precautionary Statements (+ some conditioning considerations): *e.g.*, "*NOTE: Peroxide buildup can create a safety hazard.*", "*DO NOT CONCENTRATE or evaporate to dryness unless peroxides have been tested immediately prior to each use.*", "*Store in a cool dark place and keep under an inert blanket at all times*", "*Contains no preservatives*", "*HPLC grade*", "*Stabilized*", "*Inhibitor-free*".

3.3 Testing PFCs

Never test containers of unknown age or origin. They may contain concentrated peroxides, or present friction-sensitive crystallized forms in the cap threads, which would present a serious hazard when attempting to open the bottle for testing. EHS must be contacted.

a) Even though somewell-known procedures[6] can allow the efficient removal of peroxides from chemicals, **EHS DOES NOT recommend them** because:

- Their safe application requires only low levels of peroxide concentrations be present; and
- The inactivation techniques often employ heat, concentration or additional hazardous reagents making the process risker than simply disposing and purchasing new reagent.

b) A variety of methods are available to test for the presence of peroxides in organic chemicals and most specifically in solvents, for which obtained concentrations are to compare with recognized standards. Despite the lack of scientific validation, **20 ppm** is widely used and recognized as a general control point with respect to minimum hazardous peroxide concentration in a solvent. However, this value must be considered in the context of the solvent in question (more specifically for ethers) and intended applications. **Higher peroxide concentrations must discourage distillations, evaporations or concentrations. EHS must be contacted when higher levels in peroxides are determined to require a specific assistance or disposal**.

Peroxide Test Strips are suitable for the routine semi-quantitative detection and testing of peroxides formed in common inorganic or organic chemicals (solvents) such as diethyl ether, tetrahydrofuran (THF) or *p*-dioxane. While these test strips are available from many suppliers, the most common are from Sigma-Aldrich and named QUANTOFIX®-Peroxide test sticks (Product Z101680 for a 1-100 mg/L range of application)[7], or XploSens PS™ (Product Z683108 for a 0-500 ppm range of application)[8] They allow a fast dip-and-read determination with a straightforward comparison of the resulting color with fields of equal size on color scale on the strip container. *The manufacturer's instructions regarding the storage, use and expiration of test strips must be strictly followed: 1) Avoid exposing the strips to sunlight and moisture, 2) Store unopened packs in a lab refrigerator, 3) Store opened packs in a cool and dry place, and 4) Readings must be taken in a timely manner. False positive results can be caused by strong oxidizing agents and the accuracy of the determination is dependent on the test solution pH.* **It is strongly recommended for PIs and supervisors to aquire these test strips when PFCs are used, stored or handled in their workplaces.**

Protocols involving home-made **Ferrous thiocyanate** methods, **Potassium Iodide** indicator and corresponding variations can also be used.[6]

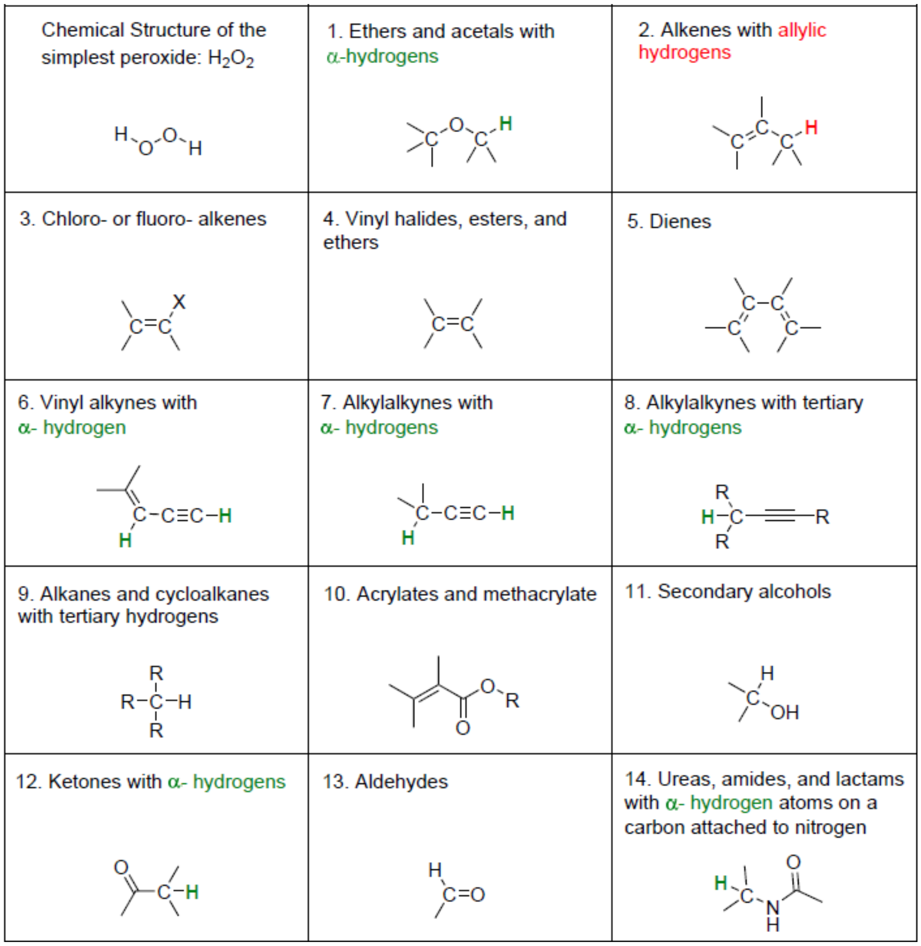

Figure 1. Chemical moieties prone to peroxide formation – Taken from https://safetyservices.ucdavis.edu/safetynet/peroxide-formation-chemicals

WARNING: PEROXIDIZABLE MATERIAL
MAY FORM EXPLOSIVE PEROXIDES

Store in tightly closed original container. Avoid exposure to light, air, and heat.

If crystals, discoloration, or layering are visible, do not attempt to move or open the container.

Test/check for peroxides before distilling or concentrating

This Chemical has a limited shelf life!

Date received ____________________ **Date opened** ____________________

PEROXIDE TEST RESULTS

Date / Test results ____

Date / Test results ____

Date / Test results ____

Contact Concordia EHS for guidance

Figure 2. Sample label that can be displayed on PFCs containers.

Table 1. CLASS A – Chemicals that spontaneously form potentially explosive peroxides <u>without concentration</u> that will make the materials shock- or heat-sensitive «on-the-shelf». **Severe peroxide hazard after prolonged storage, especially after exposure to air**. **DO NOT TEST if expired or suspected to contain peroxides!**

SEVERE PEROXIDE HAZARD - Chemicals have a <u>3-month storage limit (even if unopened)</u>. The list is not all inclusive! Below are the most commonly used PFCs of this Class
• Butadiene *(when stored as an inhibited liquid monomer)* • Chloroprene *(when stored as a liquid monomer)* • Divinyl acetylene • Diisopropyl ether • Tetrafluoroethylene *(when stored as an inhibited liquid monomer)* • Vinylidene chloride • Tetrahydrofuran (THF) without inhibitor • Potassium metal • Potassium and Sodium amide

Table 2. CLASS B – Chemicals that form explosive levels of peroxides <u>on concentration</u> (when evaporated, distilled or concentrated). The formation of peroxides is also highly dependent on the amount of head space (air/oxygen) that exists in the container.

CONCENTRATION HAZARD - These chemicals must be discarded <u>within 12 months of opening</u>. Test for peroxide formation must be performed periodically (*e.g.*, every 3 months) or before concentration process. The list is not all inclusive! Below are the most commonly used PFCs of this Class		
• Acetal • Acetaldehyde • **Benzyl alcohol** • 2-Butanol • Cumene • Cyclohexanol • 2-Cyclohexen-1-ol • **Cyclohexene** • Decahydronaphthalene • Diacetylene • **Dicyclopentadiene**	• **Diethyl ether** • **Diethylene glycol dimethyl ether (diglyme)** • **Dioxanes** • **Ethylene glycol dimethyl ether (glyme)** • 4-Heptanol • 2-Hexanol • Methylacetylene • 3-Methyl-1-butanol • Methylcyclopentane • Methyl isobutyl ketone	• 4-Methyl-2-pentanol • 2-Pentanol (isopropyl ether • 4-Penten-1-ol • 1-Phenylethanol • 2-Phenylethanol • **2-Propanol** • **Tetrahydrofuran (THF)** • Tetrahydronaphthalene • **Vinyl ethers** • **Other secondary alcohols**

Note: In bold are noted some of the solvents that are the most commonly used at Concordia University. Quantofix® peroxides test sticks should be available in workplaces where these chemicals are handled to perform peroxides quantification regularly.

Table 3. **CLASS C – These chemicals are highly reactive and <u>can autopolymerize</u> as a result of internal peroxide accumulation.** Chemicals without inhibitors MUST be stored under inert gas. Chemicals with inhibitors CANNOT be stored under inert gas as the inhibitors require oxygen.

SHOCK AND HEAT SENSITIVE - These chemicals must be discarded <u>within 12 months of opening</u>. The list is not all inclusive! Below are the most commonly used PFCs of this Class		
• Acrylic acid	• Methyl methacrylate	
• Acrylonitrile	• Styrene	• Vinyl chloride (gas)
• Butadiene (gas)	• Tetrafluoroethylene (gas)	• Vinylpyridine
• Chloroprene	• Vinyl acetate	• Vinylidene chloride
• Chlorotrifluoroethylene (gas)	• Vinylacetylene (gas)	

Table 4. **CLASS D: POTENTIAL PFCs - Other peroxidizable chemicals which can not be placed into the other three (3) classes but nevertheless require handling with precautions.**

<u>There are over 200 organic and inorganic compounds capable of forming peroxides under specific conditions</u>.[9]

These chemicals must be tested regularly. The list is not all inclusive (only refers to most common PFCs at Concordia University)!		
		• Vinylidene chloride
• Acrolein	• Benzyl ethyl ether	• Cyclooctene
• *m*- or *p*-Anisaldehyde	• 2-Chlorobutadiene	• Diallyl ether
• Benzyl ether	• Diethylacetal	• Ethyl vinyl ether
• *p*-Bromoanisole	• *p*-Dioxane	• *m*-Methoxyphenol
• Isopentyl ether	• Furan	• *n*-Propyl ether
• Tetrahydropyran	• Limonene	• Tetraethyleneglycol monomethylether
• Allyl ether	• Tetraethylene glycol	

Should you have any concerns about the use, handling, storage, or disposal of PFCs at Concordia University, please contact EHS: Email: ehs@concordia.ca; Telephone: 514-848-2424 ext. 4877

Preparation date: October 2019
Revision date: December 2023

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1) a) Guidelines for Explosive and Potentially Explosive Chemicals Safe Storage and Handling - University of California, Berkeley; b) Clarck, D. E., PEROXIDES AND PEROXIDE FORMING COMPOUNDS - Texas A&M University – *Consulted on December 14th, 2023.*

2) Expired chemicals found at U of A were detonated 2 months after being found - University of Alberta – *Consulted on December 14th, 2023.*

3) Mason, D. *Those pesky peroxides … J. Chem. Health Saf.*, **2014**, *21*, 3, 13-15 – https://pubs.acs.org/doi/10.1016/j.jchas.2013.12.011.

4) a) Peroxide Explosion Injures Campus Researcher - University of California, Berkeley*; b)* Dangers of Peroxide Formers—Explosion at UMN; c) Management and Safety of Peroxide Forming Chemicals – Boston University – *Consulted on December 14th, 2023.*

5) Adapted from www.sigmaaldrich.com/chemistry/solvents/learning-center/peroxide-formation.html

6) Kelly, R.J. *Review of Safety Guidelines for Peroxidizable Organic Chemicals*, ACS–*Chemical Health & Safety*, **1996**, *4*, 33-36 –- https://pubs.acs.org/doi/10.1021/acs.chas.8b03515.

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8) https://www.sigmaaldrich.com/CA/en/product/aldrich/z683108 – *Consulted on December 14th, 2023*.

9) Peroxide-Forming and Other Time-Sensitive Chemicals - Washington University in St.Louis (EHS) – *Consulted on December 14th, 2023*.