# **PEROXIDES & PEROXIDE-FORMING CHEMICALS**

## INTRODUCTION

A peroxide is a chemical that contains a peroxo (O-O) unit, one that has the chemical formula of O2²¯. Peroxide-forming chemicals (PFCs) are chemicals that react with oxygen, even at low concentrations (or that can “auto-oxidize” with atmospheric oxygen under ambient conditions) to form peroxides. Peroxide formation can be initiated by exposure to air, heat, light, self-polymerization, or solvent impurities.

## How To Identify Peroxide-Forming Chemicals?

* Peroxide-forming chemicals invariably contain an auto-oxidizable hydrogen atom that is activated by adjacent structural components.
* Review PubChem and Safety Data Sheet (SDS) for warning statements such as “May form explosive peroxides on exposure to air”. (Found under Safety & Hazards or Hazard Identification sections).
* University of Minnesota maintains a [list of peroxide forming chemicals](https://docs.google.com/spreadsheets/d/1VBSj95JyKZ33Q9VS7Z6jMDBv50b3j2Awa3GFc0xGbuE/edit#gid=1451024088).

## Hazards

* Peroxides are generally potentially explosive, highly flammable, and extremely sensitive to shock, heat, sparks, friction, impact, and UV light.
* *Refer to SDS and other reference materials for specific hazards and controls measures per PFC.*

## Best Practices

* **Label containers with date received and date opened.**
* Purchase/use stabilized solvents where possible.
* Limit inventories to what is immediately needed. If a lab frequently uses peroxide forming chemicals, instead of purchasing large amounts all at once, develop an ordering schedule to limit excess chemicals that may degraded before being used and will require disposal.
* Purchase 5L containers or smaller. For containers greater than 5L, the lab must consult with the OEHS Chemical Hygiene Officer prior to purchasing.
* Use “first-in, first-out” inventory system, and only one open container at a time.
* Regularly test for peroxide formation, such as by using test strips like [XploSens PS](https://www.sigmaaldrich.com/US/en/product/aldrich/z683108) or [Supelco Peoxide Test](https://www.emdmillipore.com/US/en/product/Peroxide-Test%2CMDA_CHEM-110081) (review manufacturer’s user guide for limitations and incompatible substances) or conduct literature review to identify appropriate test methods. Preferably this should be done before each use but is especially important as the chemical gets closer to its expiration date. Concentrations ≥ 100 PPM are typically considered hazardous, and the chemical should be disposed through OEHS.
* Use uninhibited solvents immediately after opening.
* Dispense and use the smallest amount possible.
* Do not use metal tools which may contact the chemical.
* Keep away from open flames and other heat sources.
* Remote handling, personal protective equipment, and explosion-proof barricades (including the fume hood sash) should be used to minimize close contact with reactants, reaction mixture or products.
* Do not return unused material to its original container.
* Train on lab-specific policies and safe work practices.

## Storage Requirements

* Store PFCs in original, airtight bottles away from light and heat in a marked flammable area (e.g. flammable cabinets, explosion proof refrigerators). After dispensing the PFC, it is recommended to “blow-out” the air in the bottle using an inert atmospheric gas.
* Do not use storage containers with loose fitting lids and ground glass stoppers.
* Store PFCs at the lowest possible temperature, above their solubility or freezing point. Refrigerated storage must be ONLY in explosion-proof refrigerators.
* Refer to SDS and other reference material regarding stabilizers, storage under inert gas, and peroxide formation testing methods.

## Warning!

*If a container of PFC has visible solid precipitate in the liquid; very fine, spun glass-wool appearance in the liquid; incrustation around cap; layer separation (an oily viscous layer); visible discoloration/cloudiness; or container is excessively old:*

* Do not attempt to move or open suspect container
* Warn co-workers and supervisors of hazard
* Restrict access to surrounding area
* Call OEHS (7-1200) immediately!

## Disposal

* Dispose of PFCs on or before expiration date as hazardous chemical waste via OEHS
* Do not mix with other chemical waste.
* Pure peroxides must be diluted with appropriate solvent prior to disposal.
* Spilled peroxides should be absorbed with inert absorbent material (e.g. vermiculite) as soon as possible.
* Submit a waste pick-up to OEHS as soon as possible.

## Exposure Contacts

* **Principal Investigator (PI):** *(Add phone number)*
* **WSU Public Safety:** 313-577-2222, emergency transportation
* **Henry Ford Occupational Health – Harbortown**

3300 East Jefferson, Suite 100

Detroit MI 48207

(313) 656-1618

Monday – Friday 8:00 AM to 6:30 PM

If Henry Ford Occupational Health Center is closed or for serious injuries, visit:

**Henry Ford Hospital – Emergency Room**

2799 W. Grand Blvd.

Detroit MI 48202

(313) 916-8742

OR

**Detroit Receiving Hospital - Emergency Room**

4201 St. Antoine St, Detroit, MI 48201

Phone: (313) 745-3000

* **Office of Environmental Health and Safety:** 313-577-1200, spills or clean-up

## For More Information

1. Kelly, R.J. Review of Safety Guidelines for Peroxidizable Organic Compounds. Chemical Health and Safety 1996 (Sept/Oct), 28-36.
2. Bretherick’s Handbook of Reactive Chemical Hazards, 7th ed.
3. Prudent Practices in the Laboratory. Washington, D.C.: The National Academies Press.
4. Clark, D., Peroxides and Peroxide - Forming Compounds, Journal of Chemical Health and Safety 2001, 8 (5), 12-21.
5. [Peroxide Forming Solvents](https://www.sigmaaldrich.com/US/en/technical-documents/technical-article/chemistry-and-synthesis/reaction-design-and-optimization/peroxide-formation). Millipore Sigma.

## Storage Guidelines for Peroxides and Peroxide Forming Chemicals

| **MATERIAL** | **MAXIMUM STORAGE PERIODS** |
| --- | --- |
| Unopened container from manufacturer | 6 months for Class A materials, generally 18 months for others; check manufacture’s information. |
| Opened Class A | 3 months (except potassium metal, see below) |
| Opened Class B | 12 months. If uninhibited, either store under inert atmosphere or test for peroxides on a regular schedule. |
| Uninhibited Class C | 24 hours max, small quantities only. |
| Inhibited Class C | 12 months under air (unless also in Class A, when 3-month period applies). Do NOT store under inert atmosphere, as the polymerization inhibitor may only work in the presence of oxygen. |
| Potassium metal | Highly variable ageing depending on storage conditions. Visually check for crusting every 3 months. |

**Note**: Inhibited and uninhibited refers to the presence or absence of a peroxide-inhibitor.

## Classes of Peroxides and Peroxide-Forming Chemicals

**CLASS A** Peroxide-Formers – SEVERE PEROXIDE HAZARD. These compounds spontaneously decompose and become explosive with exposure to air without concentration. All have been responsible for fatalities. Diisopropyl ether is especially notorious and should never be used as a solvent.

Butadiene (liquid); Chloroprene (liquid); Diisopropyl ether; Divinylacetylene; Potassium amide; Potassium metal; Sodium amide (sodamide); Tetrafluoroethylene (liquid); Vinylidene chloride; Isopropyl ether

**CLASS B** Peroxide-Formers – Form low concentrations of peroxides (less than 1%). Any operation involving evaporation or distillation will concentrate the peroxides, which may become dangerously explosive.

Acetaldehyde; Benzyl alcohol; Benzyl ethers; Bis (2-methoxyethyl) ether (diglyme); 2-Butanol; Cumene; Cyclohexene; Decahydronaphthalene (decalin); Dicyclopentadiene; Diethyl ether; Dioxane(s); 1,1-Diethoxyethane (acetal); Furan; Methyl isobutyl ketone; Tetrahydrofuran (THF); 1,2 Dimethoxyethane (glyme); Tetrahydronaphthaline (tetralin); Vinyl ethers; Other secondary alcohols

**CLASS C** Peroxide-Accumulation. Accumulation of peroxides may result in violent polymerization of monomers.

Acrylic acid; Acrylonitrile; Butadiene (gas); Chloroprene (gas); Chlorotrifluoroethylene; Methyl methacrylate; Styrene; Tetrafluoroethylene (gas); Vinylacetylene; Vinyl acetate; Vinyl chloride; Vinylidene chloride; Vinylpyridine

**CLASS D** Other Known and Suspected Peroxide Formers - All compounds containing C-H groups activated towards radical reactions are potentially susceptible to peroxidation, although whether peroxides will decompose as fast as they are formed or accumulate to dangerous levels is hard to predict. In approximate order of decreasing danger, known susceptible compounds include the following:

Ethers and acetals; Alkenes with allylic-H; Chloro- and fluoroalkenes; Vinyl halides and esters; Dienes; Vinylalkynes; Alkylalkynes; Alkylarenes with tertiary-H; Acrylates, methacrylates; Secondary alcohols; Ketone; Aldehydes; Ureas/amides/lactams with N-C-H moiety