

# **Peroxide-Forming Chemicals (PFCs)**

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Peroxide-forming chemicals (PFCs) are some of the most potentially hazardous substances handled in laboratories. PFCs are most often flammable organic liquids which are capable of forming potentially explosive R-O-O-R' peroxide bonds (where R = organic group) upon exposure to air or oxidizing impurities. Peroxides formed in a chemical container are particularly likely to accumulate within the threads of the screw cap, and may explode when subjected to heat, light, friction or mechanical shock (e.g., unscrewing the cap).



It is particularly dangerous to allow these materials to evaporate to dryness, such as during distillation, leaving the crystals of peroxide on the surfaces of the container. In order to stabilize peroxide forming chemicals and to increase the permissible storage length, inhibitors are often added. However, because distillation of such a stabilized liquid will remove the inhibitor, the end product must be stored with care as a potential peroxide-former. Distillation of solvents may act to concentrate peroxides to explosive levels and must not be carried out until the liquid has been tested and proven to be peroxide free. If you notice the formation of crystals on or within a solvent bottle:

- Do not move or open the container.
- Alert others in lab as to the potential hazard.
- Post a sign warning others not to disturb the container.
- Contact the ESD Hazardous Materials Group at (706) 542-5801 for disposal assistance.

Georgia Fire Code requires that all peroxide-forming chemicals be dated upon opening. UGA policy also dictates that these chemicals be dated upon receipt. Peroxide levels should be checked regularly and a log of test results maintained.

<u>Please note:</u> Peroxides may form on the surface of alkali metals and their amides (e.g., lithium, sodium amide). Since they are water reactive, standard peroxide tests should not be performed on these materials. Alkali metals & their amides should be purchased in small quantities and used up as soon as possible.

Types of compounds known to auto-oxidize to form peroxides:

• Aldehydes

- Ethers, especially cyclic ethers and those containing primary and secondary alkyl groups
- Compounds containing benzylic hydrogens
- Compounds containing allylic hydrogens (C=CCH), including most alkenes, vinyl and vinylidene compounds
- Compounds containing a tertiary CH group (e.g., decalin, 2,5-dimethylhexane)



Standard lab coats are required. Flame resistant lab coats should be considered when handling flammable liquids and other hazardous materials that are easily ignited.



Personal Protective Equipment

Nitrile chloroprene or gloves provide typically adequate protection against minor splashes. Consult with your PI or supervisor to determine whether any materials involved in your process require alternative hand protection.



ANSI Z87.1 - Compliant safety glasses or safety goggles if a splash hazard is present.

## Labeling & Storage

PFCs should be stored in a flammable storage cabinet with self-closing hinges or in a refrigerator rated for flammable storage. All PFCs must be stored away from oxidizers and should be marked with receiving date and opening date. If the receiving and opening date is not known, promptly dispose of as hazardous waste. They should be managed in accordance with the following guidelines:

<u>Class I:</u> Unsaturated materials, especially those of low molecular weight that may polymerize violently and hazardously due to peroxide initiation.

<u>Safe storage period</u>: If unopened from manufacturer, up to 18 months or stamped expiration date, if stored in accordance with manufacturer guidelines. After opening, chemicals with inhibitors should not be stored for longer than **12 months**; chemicals without inhibitors should be discarded as hazardous waste as soon as possible after the container is opened.

Acrylic acid	Methyl methacrylate	Vinyl acetylene
Acrylonitrile	Styrene	Vinyl chloride
Butadiene	Tetrafluoroethylene	Vinyl pyridine

Chloroprene Chlorotrifluoroethylene Vinyl acetate

Vinylidene chloride

<u>**Class II**</u>: The following chemicals are a peroxide hazard upon concentration (distillation/evaporation).

<u>Safe Storage period</u>: If unopened from manufacturer, up to 18 months or stamped expiration date, if stored in accordance with manufacturer guidelines. After opening, materials should be discarded or evaluated for peroxides within **12 months** and every 6 months thereafter. If crystals are visible in the solvent or around the cap, call the ESD hazardous materials group (706) 542-5801 immediately to schedule removal of the container from lab.

Acetal	Dicyclopentadiene	Isopropanol
Cumene	Diethylene glycol dimethyl ether	Methyl acetylene
Cyclohexene	Diethyl ether	Methyl cyclopentane
Cyclooctene	Dioxane ( <i>p</i> -dioxane)	Methyl -I-butyl ketone
Cyclopentene	Ethylene glycol dimethyl ether	Tetrahydrofuran
Diacetylene	Furan	Tetrahydronapthelene
		Vinyl ether

<u>Class III:</u> Peroxides derived from the following compounds may explode without concentration.

<u>Safe storage period</u>: If unopened from manufacturer, up to 18 months or stamped expiration date, if stored in accordance with manufacturer guidelines. After opening, it is recommended that these chemicals be discarded or evaluated for peroxides no more than **3 months** after opening.

**Organic** Divinyl ether Isopropyl ether Divinyl acetylene Vinylidene chloride Inorganic Potassium metal Potassium amide Sodium amide (sodamide)

## **Peroxide Level Testing**

If test strips are to be employed to determine peroxide levels, they should cover the range from 0 - 100 ppm. The following peroxide levels should be used to determine activities that are deemed safe.

0-25 ppm - Material is safe to use or distill.

26-99 ppm - Material is safe to use, but should not be distilled.

Above 100 ppm - Material should be disposed of and not used in lab.

If a peroxide-forming chemical is found to be more than one year out of date for either storage or testing (3 months out of date for opened Class III peroxide formers), notification will be sent to the PI of record for the laboratory via their laboratory inspection report. PIs will also be notified that they have two weeks to either (1) test the material and verify that peroxide levels are below 100 ppm, or (2) dispose of the material properly. Failure to comply with this request may result in the material being removed for disposal. If the receipt date or opening date cannot be determined, then testing is not recommended. Please dispose of as hazardous waste.

The laboratory must keep record of the dates, and the results obtained in the different tests, regardless of the method used to carry this out. Peroxide-forming chemical labels are available through the Office of Research Safety, and can be provided upon request.

Date Received		Inhibitor Added?	
Date Opened Date Expires		YES	NO
	e! Store tightly clos Call ESD at 542-580		
neat sources. c			
	Peroxide	Tester	
Test Date	Peroxide Peroxide	Tester Tester	

## Engineering Controls, Equipment & Materials

**Fume Hood** Use a fume hood to keep exposure as low as possible when using these chemicals. If your protocol does not permit the handling of such materials in a fume hood, contact the Office of Research Safety (ORS) to determine whether additional respiratory protection is warranted.

#### Cautions & Considerations

**Static Electricity** When transferring flammable liquids between containers greater than 4L (1 gallon) containers should be grounded, and the source container should be bonded to the receiving container during transfer. If possible, transfer flammable chemicals from glass containers to glassware or from glass container/glassware to plastic. Transferring these types of chemicals between plastic containers or unbonded metal containers may lead to a fire hazard due to static electricity.

#### Housekeeping

**Spills** Notify others in the area of the spill, including your supervisor. Evacuate the location where the spill occurred and call 911. Any exposure must be reported to ORS at 706-542-5288. Remain onsite at a safe distance to answer questions from first responders.

	Once any standing material has been wiped away, clean contaminated surfaces with soap and water. Dispose of contaminated paper towels as solid hazardous waste.	
	Any waste from this chemical class should be disposed of through the UGA Hazardous Waste Program. For assistance with arranging a waste pickup, you may contact the Environmental Safety Division (ESD) at 706-542-5801. Prior to pick up, any container used to hold hazardous waste should be labeled with the following:	
	<ul> <li>"Hazardous Waste",</li> <li>the chemical contents, and</li> <li>one or more of the following waste characteristics recognized by EPA: Ignitable, Corrosive, Reactive, or Toxic.</li> <li>In addition, any liquid hazardous waste must be stored in secondary</li> </ul>	
	containment trays until picked up by ESD.	
	First Aid & Emergencies	
Fire	Use a Class B or CO <sub>2</sub> extinguisher to put out a small fire.	
Skin Eye Conta	Remove contaminated clothing and accessories; flush affected area with ct water. If symptoms persist, get medical attention.	
Inhalation	Move person into fresh air. If symptoms persist, get medical attention.	
Ingestion	Rinse mouth with water. If symptoms persist, get medical attention.	

## References

<u>Prudent Practices in the Laboratory: Handling and Management of Chemical Hazards,</u> National Research Council, 2011

*"Review of Safety Guidelines for Peroxidizable Organic Chemicals,"* <u>Chemical Health &</u> <u>Safety</u> – American Chemical Society, 1996, 4(5), 28-36.

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