

INFORMATION ON PEROXIDE-FORMING COMPOUNDS



Peroxides are a class of chemical compounds with unusual stability problems and are one of the most hazardous classes of chemicals routinely handled in the laboratory.

Peroxides can be formed via intentional chemical reactions (i.e., ozonolysis), but just as hazardous is the inadvertent peroxide formation during storage of certain compounds. Some compounds form explosive peroxides and others are polymerizable unsaturated compounds that can initiate a runaway, explosive polymerization reaction. To varying degrees, shock, heat or friction may cause unexpected explosion of peroxidized organic chemicals.

Common classes of compounds that form peroxides include:

- Ethers, acetals, and ketals, especially cyclic ethers and those with primary and/or secondary alkyl groups
- Aldehydes, including acetaldehyde and benzaldehyde
- Compounds containing benzylic hydrogens
- Compounds containing allylic hydrogens, including most alkenes; vinyl and vinylidene compounds, and dienes

Refer to Appendix A for a list of common peroxide forming chemicals and recommendations on safe storage durations

STORAGE AND HANDLING

- The quantity of peroxide-forming chemicals kept should be restricted to the minimum amount needed.
- Store peroxide-formers in airtight bottles, away from light and heat. Avoid using containers with loose-fitting lids and glass ground stoppers.
- Certain peroxide formers, including those in Appendix A List A, should be stored under nitrogen if possible.
- Evaluate for peroxide formation regularly and always prior to distillation. Some materials may need evaluation as often as every 3 months.
- Crystallization, discoloration, and stratification are signs a peroxide former may have become shock sensitive – Do not move the container, and call EH&S promptly at 323-6280.
- If evaporation or distillation is necessary, do not distill to a dry residue. Always leave at least 10-20% residual bottoms.

LABELING

All peroxide-forming compounds should be labeled with date received and date opened. For common peroxide formers, guidance on recommended shelf life and time interval for peroxide evaluation is provided in Appendix A.

Contact the Chemistry Stockroom for labels (Chemistry Department); all others date directly on container.

GENERAL PRECAUTIONS

Chemical selection:

- If possible, use a material that does not form peroxides.
- If possible, purchase peroxide forming chemicals containing an inhibitor such as butylated hydroxytoluene (BHT).

Hazard Control:

- Use fume hood or other appropriate exhaust ventilation if inhalation hazard is anticipated.
- Wear appropriate lab attire and personal protective equipment (PPE).
- Utilize shields, barricades, and additional PPE (such as face shields with throat protectors and heavy gloves) where there is a possibility of explosion or vigorous chemical reaction.



EVALUATING PEROXIDE FORMERS

Prior to using peroxide formers and as needed (see Appendix A), conduct the two-part evaluation for peroxide content:

Part 1. Initial Screening—Verify:

- Identity of chemical
- Date last opened (or if unopened, date received) is known and is within the recommended safe storage period per guidance in Appendix A
- Evaporation of the chemical is known or estimated to be less than 10%
- Use of a flashlight as a light source can be helpful to peer through bottles to determine if crystals, solid masses, cloudiness, string-like formations, layers, or discoloration are present, then there are likely very high levels of peroxides and everyone in the lab should be warned not to touch the chemicals until EH&S has been contacted and consulted.

CAUTION: Never try to force open a rusted or stuck cap on a container of a peroxide-forming chemical.

If any items above cannot be verified, the container should be considered unsafe and should not be disturbed (promptly contact EH&S at 323-6280 for assistance with safe disposal).

Part 2. Peroxide Testing

Containers passing the initial screening (above) may be tested for peroxide content. The best method to test for peroxides involves semi-quantitative analysis using peroxide detection dip strips. The peroxide strips are similar to the use of pH paper and a simple instruction sheet accompanies the strips. If a test strip indicates a peroxide concentration at or above **25 ppm**, the chemical should not be used and should be immediately ticketed for disposal.

Modifications to the dip strip testing method are required to test low volatile organic compounds. For water-miscible chemicals, add three drops of water to one drop of a chemical to be tested. Wet the dip strip, wait until the color stabilizes, and then multiply the result by 4. For water-immiscible chemicals, add three drops of a volatile ether to one drop of a chemical to be tested. Wet the dip strip, wait until the color develops, and then multiply the result by 4. Peroxide testing strips have a limited shelf life (follow storage instructions on container). Refrigeration is not recommended once the container has been opened because water condensing on the strips reduces their effectiveness. The strips should be stored in as dry an environment as possible.

A common test strip used is the Quantofix peroxide test sticks (0-25 ppm range). Available through Sigma Aldrich, Part Number [2249254](#).

< 25 ppm	Considered safe for general use (label bottle with date)
>25 ppm	Avoid handling and contact EH&S for assistance with safe disposal

Appendix A: Peroxide Formers

List A	List B	List C
Form peroxides during storage	Dangerous Peroxide levels can occur during concentration	Peroxides can trigger explosive polymerization
Butadiene *	Acetal	Butadiene **
Chloroprene *	Acetaldehyde	Chlorobutadiene
Divinyl acetylene	Benzyl alcohol	Chloroprene **
Isopropyl ether	Chlorofluoroethylene	Chlorotrifluoroethylene
Potassium amide	Cumene (isopropylbenzene)	Styrene
Potassium metal	Cyclohexene	Tetrafluoroethylene **
Sodium amide	2-Cyclohexen-1-ol	Vinyl acetate
Tetrafluoroethylene *	Cyclopentene	Vinyl acetylene
Vinyldiene chloride	Decahydronaphthalene (decalin)	Vinyl chloride
	Diacetylene (butadiyne)	Vinyl pyridine
	Dicyclopentadiene	Vinyldiene chloride
	Diethylene glycol dimethyl ether (diglyme)	
	Dioxane	** Can form explosive levels of peroxides if stored as a liquid. When stored as gas, peroxide accumulation may cause autopolymerization.
	Ethyl ether	
	Furan	
	4-Heptanol	
	2-Hexanol	
	Methyl acetylene	
	3-Methyl-1-butanol	
	Methyl-isobutyl ketone	
	Methylcyclopentane	
	2-Pentanol	
	4-Penten-1-ol	
	Phenylethanol	
	Tetrahydrofuran	
	Tetrahydronaphthalene	
	Vinyl ethers	
	Other secondary alcohols	

List A chemicals should be tested for peroxide formation before using or discarded after 3 months.

List B chemicals should be tested for peroxides before distillation or evaporation and tested for peroxide formation or discarded after 1 year.

List C chemicals should be tested for peroxide formation or discard liquids after 6 months; and gases after 1 year.

References

Clark, Donald E., Peroxides and Peroxide Forming Compounds, 2000. Texas A&M University. Boston University, <http://www.bu.edu/EHS>

National Research Council, Prudent Practices in the Laboratory, National Academy Press: Washington, DC, 1995.

Kelly, R.J. "Review of Safety Guidelines for Peroxidizable Organic Chemicals," Chemical Health & Safety- American Chemical Society-, 1996, 4(5), 28-36.