



UCCS SAFE OPERATING PROCEDURE

44. SAFE STORAGE AND HANDLING OF PEROXIDE FORMING CHEMICALS

(For assistance, please contact [Environmental Health & Safety](#))

Much of the information here is adapted from the publication, *Prudent Practices in the Laboratory, Handling and Management of Chemical Hazards, Updated Edition*, National Research Council. Some common laboratory chemicals can form peroxides. Once peroxides are formed, these chemicals can become extremely sensitive to thermal or mechanical shock and may explode violently. Peroxides are formed through a spontaneous reaction with oxygen. Simply opening the container can initiate peroxide formation, while light and heat act to accelerate the process.

Manufacturers may add an inhibitor to peroxide forming chemicals to counter peroxide formation. For many peroxide-forming solvents, butylated hydroxy toluene (BHT) is commonly added. BHT 'scavenges' oxygen in the solvent and prevents it from reacting with the solvent to form peroxides. Over time, BHT or other inhibitor in the solvent can become exhausted allowing peroxides to form. Distilling the solvent can completely remove the BHT and make the solvent immediately susceptible to peroxide formation.

Examples of chemicals that are prone to forming peroxides are found in the tables at the end of this SOP. In order to limit peroxide formation, manufacturers often add an inhibitor to the chemical, which 'scavenges' oxygen from solution and prevents it from reacting to form peroxides. Over time, the inhibitor can become exhausted allowing peroxides to form. Distillation can eliminate the inhibitor and result in susceptibility to peroxide formation.

Polymerizable, unsaturated compounds are a related class of chemicals that can form peroxides and initiate a runaway, explosive polymerization reaction.

Safe Handling and Usage

- When received, label indicating date of receipt, date of opening, and test date. > Attach a highly visible notice: **WARNING -- PEROXIDE FORMER.**
- Keep a record to indicate date of receipt and date the container was first opened. > Store away from heat and light.
- The best method for managing potential peroxide forming chemicals is to purchase them in quantities that will allow them to be completely used before they have to be tested for formation of peroxides and/or before their expiration dates. Most potential peroxide forming chemicals have a shelf life of 18 months if **not opened** and 12 months once **opened and exposed to air**, unless noted otherwise.
- Store all peroxidizable compounds in tightly closed, air-impermeable, light-resistant containers, away from light, heat, direct sunlight, sources of ignition, oxidizers, and oxidizing agents. Refer to the SDS, storage under Nitrogen may be advisable.
- Make sure caps are replaced promptly after use. Store in the original manufacturer's container whenever possible. Protect containers from shock, friction, and do not shake.



- Protect from physical damage and ignition sources.
- If a peroxide-forming chemical or container is of unknown age or history, if crystals or solid masses are visibly present on or in the container or lid, or if the chemical shows discoloration, string-like formations, or liquid stratification, do not open the container. Contact EHS for assistance..
- Do not use any peroxide forming chemical if a precipitate forms or an oily, viscous layer appears.
- Most peroxides are not volatile. Loss of solvent via an ill-fitting lid can concentrate any peroxides that are present. A nearly empty container, for which the solvent cannot be accounted, may be a hazard. Contact Environmental Safety.
- Use, dispose, or test for peroxides according to the appropriate time limits listed in Lists A through C below, or in accordance with the Material Safety Data Sheet.
- Test for peroxides before distilling or evaporating peroxide forming solvents. If peroxides are present, treat the solvent to remove the peroxides. Failure to remove peroxides can result in concentration during distillation, and could result in accumulation to the point of an explosive reaction.
- Immediately rinse empty containers that once held peroxide-forming solvents. Do not allow residues to evaporate.
- Organic peroxides are a special class of compounds that are very hazardous in low concentrations. They are generally produced from auto-oxidation of solvents that are exposed to air and light. They are extremely sensitive to heat, friction, impact and light.
- Do not heat solutions containing peroxides in volatile solvents because the solvent may vaporize, thereby increasing the concentration of the peroxide.
- Do not use metal spatulas to handle solid peroxides. Ceramic, teflon, or wooden spatulas may be used if they do not generate a static charge.
- Do not permit open flames near peroxides.
- Avoid friction, grinding and all forms of impact near peroxides, especially solid peroxides. Do not use screw cap lids with glass bottles, or ground glass joints to contain peroxides. Polyethylene bottles that have screw cap lids may be used.
- Store peroxides at the lowest possible temperature, but not lower than the freezing point, as peroxides in this form are extremely shock-sensitive.

Testing

CAUTION: Testing should ONLY be performed by a chemist properly trained in the procedure.

The following test procedures may be used on most organic solvents. However, there is not a suitable, simple test procedure for detection of peroxides in substances such as alkali metals, alkali metal alkoxides, amides, or organometallics.



Iodide Test Add 0.5-1.0 ml of the solvent to be tested to an equal volume of glacial acetic acid to which has been added about 0.1 g of sodium iodide or potassium iodide crystals. A yellow color indicates a low concentration of peroxide in the sample; a brown color indicates a high concentration. A blank determination should be made. Always prepare the iodide/acetic acid mixture at the time the test is made, because air oxidation slowly turns the blank to a brown color.

Ferrothiocyanate Test A drop of the solvent to be tested is mixed with a drop of sodium ferrothiocyanate reagent, which is prepared by dissolving 9 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in 50 ml of 18% hydrochloric acid. Add 0.5-1.0 g granulated zinc followed by 5 g sodium thiocyanate. When the transient red color fades, add 12 g more of sodium thiocyanate and decant the liquid from the unused zinc into a clean, stoppered bottle. Pink or red coloration indicates the presence of peroxides.

Peroxide Test Strips Test strips are commercially available from a number of vendors. Fisher Scientific currently offers a potassium iodide/starch test strip. VWR offers more elaborate test kits manufactured by EM Science and J.T. Baker. Follow the manufacturer's instructions for using the strips/kits to ensure adequate colorimetric detection.

Results:

0-30 ppm (KI reagent turns slightly yellow): Little or no threat of violent reaction. Should be stabilized with hydroquinone, t-butyl catechol or ferrous sulfate (between 1 and 250 ppm or about 0.1 mg inhibitor/ Liter of solvent).

30-80 ppm (KI reagent turns brilliant yellow): Expired or mismanaged compounds that may pose a threat to persons and structures. The available literature shows that attempts to stabilize these compounds may initiate exothermic reactions that may pose a threat to persons and structures. Tag the container for EH&S Hazardous Waste pickup and contact EHS.

Greater than 80 ppm: (KI reagent turns brilliant yellow to red): Expired or mismanaged compounds that pose a threat to persons and structures. Do not attempt to stabilize. Tag the container for EH&S Hazardous Waste pickup

Common Chemical Families Known to be Peroxide Formers

➤ Organics

- Ethers, acetals.
- Olefins with allylic hydrogens, chloro- and fluoro-olefins, terpenes, tetrahydronaphthalene. o Dienes, vinyl acetylenes.
- Aldehydes.
- Ureas, amides, lactams.
- Vinyl monomers including vinyl halides, acrylates, methacrylates, vinyl esters.

➤ Inorganics

- Alkali metals, particularly potassium
- Alkali metal, alkoxides and amides
- Organometallics.

Common Peroxide Forming Compounds

These tables provide specific, but not all-inclusive, examples of chemicals that present a serious hazard due to peroxide formation. **Time limits are based on the date the original container is first opened or when the material is first synthesized, and are guidelines for testing or disposal.** Peroxides form at varying rates depending on the substance, length of exposure to air or light, and the type of container.

List A: Severe Peroxide Hazard on Storage with Exposure to Air

Use or test within 3 months

Diisopropyl ether (isopropyl ether)	Divinylacetylene (DVA)
Potassium metal	Potassium amide
Sodium amide (sodamide)	Vinylidene chloride (1,1-dichloroethylene)
Divinyl ether	

Peroxide hazard after prolonged storage.
Form potentially explosive peroxides without concentrating.
All have been responsible for fatalities.

List B: Peroxide Hazard on Concentration

DO NOT DISTILL OR EVAPORATE WITHOUT FIRST TESTING FOR PEROXIDES.

Use or test within 6 months

Acetaldehyde diethyl acetal (acetal)	Butadiene
Cellosolve	Cumene (isopropylbenzene)
Cyclohexene	Cyclopentene
Decalin (decahydronaphthalene)	Diacetylene (butadiene)
Dicyclopentadiene	Diethyl ether (ether)
Diethylene glycol dimethyl ether (diglyme)	Dioxane, p-Dioxane
Ether	Ethylene glycol dimethyl ether (glyme)
Ethylene glycol ether acetates	Ethylene glycol mono-ethers (cellosolves)
Ethylene Glycol Dimethyl Ether (Glyme)	Furan
Methyl Isobutyl Ketone	Methylacetylene
Methylcyclopentane	Tetrahydrofuran (THF)
Tetralin (tetrahydronaphthalene)	Vinyl ethers

These compounds form peroxides with age. Exposure to air is necessary for peroxide formation. Light promotes peroxide formation in the presence of oxygen. Manage containers to minimize headspace or inert container contents. Do not attempt to test



containers outside of safe storage limits. Concentration of peroxides by distillation or evaporation is typically necessary for explosivity. However, concentrations of peroxides that have caused crystallization or have phase separation are extremely dangerous

List C: Hazard of Rapid Polymerization Initiated by Internally Formed Peroxides

Use or test within 6 months

Chloroprene (2-chloro-1, 3-butadiene)	Styrene
Vinyl acetate	Vinylpyridine
Chlorotrifluoroethylene	Chlorobutadiene
Tetrafluoroethylene	Acrylonitrile
Vinyl Chloride	Vinyl Acetylene

Chemicals which are a hazard due to peroxide initiation of polymerization.
The peroxide forming potential increases for liquids of this group

THE SINGLE MOST EFFECTIVE APPROACH TO HANDLING PEROXIDE FORMERS IS TO ELIMINATE THESE MATERIALS FROM LABORATORIES. When use of these chemicals is required, modification of the process and substitution of less hazardous chemicals should be practiced for hazard minimization.

Containers should be monitored for evaporation and tested for the presence of peroxides prior to each use. Record test data for the next user. PEROXIDE FORMERS SHOULD ALWAYS BE CONSIDERED TO CONTAIN PEROXIDES, AND HANDLED WITH THE APPROPRIATE PRECAUTIONS.

Last reviewed by Cynthia Norton on December 14, 2015