



ECKERD COLLEGE

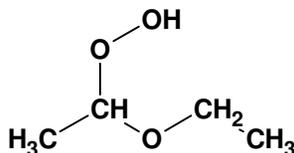
Safe Operating Procedure

(2/04)

USE AND STORAGE OF PEROXIDE-FORMING CHEMICALS

Some common laboratory chemicals can form peroxides. Once peroxides are formed, these chemicals can be extremely sensitive to thermal or mechanical shock and may explode violently. The peroxides are formed through a spontaneous reaction with oxygen. Simply opening the container to remove some of its contents can initiate their formation. Light and heat act to accelerate this process.

Peroxides have an O-O bond as part of their structure. For instance, the peroxide of diethyl ether has the structure shown below.



SAFE HANDLING AND USAGE

- Store all peroxidizable compounds away from heat and light.
- Protect peroxidizable compounds from physical damage and ignition sources.
- Keep a record for all peroxidizable compounds to indicate the date of receipt and the date the container was first opened. At the time of receipt, affix a label indicating the date of receipt, date of opening, and test date. Including a notice such as **Warning-Peroxide Former** can also be helpful.
- 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 peroxidizable solvents. If peroxides are present treat the solvent to remove the peroxides. Failure to remove peroxides can result in their concentration as the distillation process proceeds. Eventually, the peroxides can accumulate to the point of an explosive reaction.
- If crystals are visibly present on or in the container or lid, or if the container has been opened but not tested and is more than two years old, do not open the container. Contact the stockroom supervisor, Fawn Crotty (x8447).
- 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 stockroom supervisor for assistance.
- Do not use any peroxide forming chemical if a precipitate forms or an oily, viscous layer appears.
- Immediately rinse empty containers that once held peroxide-forming solvents. Do not allow residues to evaporate.

In order to counter peroxide formation, manufacturers often add an inhibitor to the chemical. 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 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.

Polymerizable, unsaturated compounds are a related class of chemicals. These chemicals can form peroxides, which can initiate a runaway, explosive polymerization reaction. Examples of chemicals that are prone to forming peroxides are found in the tables at the end of this SOP.

TESTING

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.

Ferrous Thiocyanate Test A drop of the solvent to be tested is mixed with a drop of sodium ferriothiocyanate 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.

TREATMENT

If peroxides are detected, the solvent must be treated prior to use. To ensure safety in handling, transport, and disposal, all solvents containing peroxides must be treated prior to disposal in a hazardous waste container. Any of the following procedures may be used to remove the peroxides. One of the above test procedures should be employed following treatment to ensure that peroxides have been removed.

Method 1 - Activated Alumina Peroxides can be removed by passing the solvent through a short column of activated alumina. This method is effective for both water-insoluble and water-soluble solvents (except low molecular weight alcohols). Since this method does not destroy peroxides the alumina should be flushed with a dilute acid solution of potassium iodide or ferrous sulfate following treatment to remove peroxides from the alumina.

Method 2 - Ferrous Salt Peroxide impurities in water-soluble solvents are easily removed by gently shaking with a concentrated solution of a ferrous salt. A frequently used ferrous salt solution can be prepared either from 60 g of ferrous sulfate + 6 ml concentrated sulfuric acid + 110 ml water; or from 100 g of ferrous sulfate + 42 ml of concentrated hydrochloric acid + 85 ml of water.

COMMON CHEMICAL FAMILIES KNOWN TO BE PEROXIDE FORMERS

Organics

- A. Ethers, acetals.
- B. Olefins with allylic hydrogens, chloro- and fluoroolefins, terpenes, tetrahydronaphthalene.
- C. Dienes, vinyl acetylenes.
- D. Aldehydes.
- E. Ureas, amides, lactams.
- F. Vinyl monomers including vinyl halides, acrylates, methacrylates, vinyl esters.

Inorganics

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

LISTS OF COMMON PEROXIDIZABLE COMPOUNDS

The tables below provide specific examples of common chemicals that present a serious hazard due to peroxide formation. Time limits from the date when the original container is first opened are given as guidelines for testing or discarding of these compounds.

List A: Severe Peroxide Hazard on Storage with Exposure to Air Use within 3 months

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

List B: Peroxide Hazard on Concentration Do Not Distill or Evaporate Without First Testing for the Presence of Peroxides. Use or test for peroxides 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
Ether
Ethylene glycol dimethyl ether (glyme)
Ethylene glycol ether acetates
Ethylene glycol mono-ethers (cellosolves)
Glyme
Furan
Methyl Isobutyl Ketone
Methylacetylene
Methylcyclopentane
Tetrahydrofuran (THF)
Tetralin (tetrahydronaphthalene)
Vinyl ethers

List C: Hazard of Rapid Polymerization Initiated by Internally-Formed Peroxides
 Use or test for peroxides within 6 months

Chloroprene (2-chloro-1,3-butadiene)
Styrene
Vinyl acetate
Vinylpyridine