

### USE AND STORAGE OF PEROXIDE-FORMING CHEMICALS

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(For assistance, please contact EHS at (402) 472-4925, or visit our web site at <http://ehs.unl.edu/>)

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.

#### SAFE HANDLING AND USAGE

- 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.
- 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.
- Keep a record for all peroxidizable compounds to indicate the date of receipt, the date the container was first opened, and disposal date according to peroxide lists provided or information from the Material Safety Data Sheet (MSDS). It is suggested that, at the time of receipt, the container be permanently marked or label affixed (see sample label below) indicating the date of receipt, date of opening, test date(s), and disposal date. Including a notice such as **Warning-Peroxide Former** can also be helpful.
- 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. Call Environmental Health and Safety (EHS), 472-4925, for assistance.

- 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 EHS for assistance.
- Immediately rinse empty containers that once held peroxide-forming solvents. Do not allow residues to evaporate. Do not attempt to open or rinse a container of unknown age and history. Contact EHS for assistance.

## TESTING

The following test procedures may be used on most organic solvents. NONE of these tests should be applied to materials (such as metallic potassium) that may be contaminated with inorganic peroxides. The tests can detect most, but not necessarily all, peroxy compounds, including hydroperoxides. NEVER test containers of unknown age or history.

### ***Iodide Test\****

- Add 1-3 ml of the liquid to be tested to an equal volume of acetic acid, add a few drops of 5% aqueous potassium iodide solution, and shake. The appearance of a yellow to brown color indicates the presence of peroxides. Alternatively, addition of 1 ml of a freshly prepared 10% solution of potassium iodide to 10 ml of an organic liquid in a 25 ml glass cylinder should produce a yellow color if peroxides are present.
- Add 0.5 ml of the liquid to be tested to a mixture of 1 ml of 10% aqueous potassium iodide solution and 0.5 ml of dilute hydrochloric acid to which has been added a few drops of starch solution just prior to the test. The appearance of a blue or blue-black color within a minute indicates the presence of peroxides.

### ***Ferrous Thiocyanate Test***

A drop of the solvent to be tested is mixed with a drop of sodium ferrous thiocyanate 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***

Peroxide detection dip sticks are commercially available from most laboratory equipment supply vendors. Follow the manufacturer's instructions for storing and using the product. Observe any product expiration dates to ensure adequate detection. Note that these strips must be air dried until the solvent evaporates and then exposed to moisture for proper operation.

## TREATMENT

If peroxides are detected, the solvent must be treated prior to use. All solvents containing peroxides must be treated, if safe to do so, prior to requesting collection by EHS to ensure safety in handling, transport, and disposal. 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***

- Ethers, acetals.
- Olefins with allylic hydrogens, chloro- and fluoroolefins, terpenes, tetrahydronaphthalene.
- 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.

### **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. These tables are provided to assist in identification of peroxide-forming chemicals, but are not meant to be a comprehensive listing. Refer to Material Safety Data Sheets for specific information on chemicals in use in the laboratory.

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

Diisopropyl ether (isopropyl ether)
Divinyl Acetylene (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 (isopropyl benzene)
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
Methyl acetylene
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

**Sample Label**

**WARNING: MAY FORM EXPLOSIVE PEROXIDES**

Store, handle and dispose of per EHS SOP, ***Use and Storage of Peroxide-Forming Chemicals***. Keep in tightly-closed, original container. Avoid exposure to light, air, and heat. If crystals, discoloration, or layering are visible, do not open. Contact EHS for guidance.

**THIS CHEMICAL HAS A LIMITED SHELF LIFE**

Date received: \_\_\_\_\_ Date opened: \_\_\_\_\_ Disposal Date: \_\_\_\_\_

**PEROXIDE TEST RESULTS**

(If within the concentration range from 25-100 ppm, material can be used but don't evaporate or concentrate)

Date/Test Results \_\_\_\_\_ (Example) 9/26/05 10 PPM  
Date/Test Results \_\_\_\_\_  
Date/Test Results \_\_\_\_\_  
Date/Test Results \_\_\_\_\_  
Date/Test Results \_\_\_\_\_  
Date/Test Results \_\_\_\_\_

\* Source: National Research Council. *Prudent Practices in the Laboratory*. National Academy Press. Washington, D.C. 1995.