Indiana State University	ISU Laboratory Safety Guideline
	Working with Organic Peroxides and Storage Guidelines
	Date: December 2012

Organic peroxide is a compound containing the -O-O- structure and is considered a structural derivative of hydrogen peroxide. Organic peroxides are one of the most hazardous materials handled in the laboratory. These peroxides are low powered explosives that are sensitive to shock, sparks or other accidental ignition due to the weak –O-O bond. Organic compounds such as ethers can react with oxygen to form unstable peroxides. Peroxide formation can also occur under normal storage conditions when compounds become concentrated by evaporation or when mixed with other compounds.

Types of Compounds known to form peroxides:

- Ethers containing primary and secondary alkyl groups (never distill an ether before it has been shown to be free of peroxide)
- Compounds containing benzylic hydrogens
- Compounds containing allylic hydrogens (C=C-CH)
- Compounds containing a tertiary C-H group (e.g., decalin and 2,5-dimethlyhexane)
- Compounds containing conjugated, polyunsaturated alkenes and alkynes (e.g., 1,3-butadiene, vinyl acetylene)
- Compounds containing secondary or tertiary C-H groups adjacent to an amide (e.g., 1-methyl-2-pyrrolidinone

Prudent Practices in the Laboratory: Handling and Management of Chemical Hazards, Updated Version

General Procedures for working with Peroxide-forming chemicals:

- Be aware of the use of peroxide-forming chemicals when designing or conducting a new experiment.
- If possible, purchase material containing an inhibitor such as butylated hydroxytoluene (BHT).
- Date the container when received, opened and tested.
- Consult *Prudent Practices* or other resources for storage shelf-life and testing procedures.
- Restrict quantities ordered to the minimum amount needed.
- Store in airtight bottles, away from light and heat. Avoid using containers with loose-fitting lids and glass ground stoppers.
- Segregate from incompatible chemicals.
- Evaluate for peroxide formation regularly and always prior to distillation.
- Crystallization, discoloration, and stratification are signs a peroxide-former may have become shock sensitive. DO NOT MOVE the container. Call OES at x4022 for assistance.
- If the experiment requires evaporation or distillation, do not distill to a dry residue. Always leave at least 10-20% residual in the bottom of container.
- Metal spatulas should not be used. Only ceramic or plastic spatulas should be used. Contamination by metal can cause explosive decomposition.
- Unused peroxides and peroxide forming materials should never be returned to the stock container.
- Wear proper personal protective equipment, including safety eyewear and face shields.
- Conduct work in a chemical fume hood.
- Never try to force open a rusted or stuck cap on a container or a peroxide-forming chemical.

Individual labs are required to develop a lab-specific protocol for working with Peroxide forming materials.

Resources: Handbook of Chemical Health and Safety, American Chemical Society

Prudent Practices: Handling and Management of Chemical Hazards, Updated Version

University of California, Irvine: Environmental Health and Safety

Classes of Chemicals That Can Form Peroxides Upon Aging and Testing and Shelf-life Information

Class 1:	**Unsaturated materials, especially those of low molecular weight, may polymerize violently and hazardously due to peroxide initiation**
Discard or test for peroxides after six months:	• Acrylic acid • Acrylonitrile • Butadiene • Styrene • Tetrafluoroethylene (TFE) • Vinyl acetate • Vinyl acetylene (MVA) • Vinyl chloride • Vinyl pyridine • Vinylidene chloride

Class 2:	**Peroxide hazard dependent on concentration; do not distill or evaporate without first testing for the presence of peroxides**
Discard or test for peroxides after six months:	• Acetal • Cumene (isopropylbenzene) chlorobutadiene (chloroprene) • Chlorotrifluoroethylene • Methyl methacrylate • Cyclohexene • Cyclooctene • Cyclopentene • Diacetylene (butadiene) • Dicyclopentadiene • Diethylene glycol dimethyl ether (diglyme) • Diethyl ether • Dioxane • Ethylene glycol dimethyl ether (glyme) • Furan • Methyl acetylene • Methyl cyclopentane • Methyl isobutyl ketone • Tetrahydrofuran (THF) • Tetralin (tetrahydronaphthalene) • Vinyl ethers

Class 3:	**Peroxides derived from the following compounds may explode without concentration**
Discard within three months	**Organic:**

	• Divinyl ether • Divinyl acetylene (DVA) • Isopropyl ether • Vinylidene chloride (1,1-dichloroethylene) **Inorganic:** • Potassium metal • Potassium amide • Sodium amide (sodamide)

Above information on common peroxide formers and storage limits taken from *Prudent Practices in the Laboratory: Handling and Disposal of Chemicals*, pp. 54-55.

Procedures for Detection of Peroxides

Before distilling or purifying any known or suspected peroxide-former, check it carefully for the presence of peroxides. Either of the following tests will detect most (but not all) peroxy compounds including all hydroperoxides:

1. Add 1-3 ml of the liquid to be tested to an equal volume of acetic acid, add a few drops of 5% aqueous KI solution, and shake. The appearance of a yellow to brown color indicates the presence of peroxides.

2. Add 0.5 ml of the liquid to be tested to a mixture of 1 ml of 10% aqueous KI solution and 0.5 ml of dilute HCl 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.

3. The easiest method of detecting peroxides in common solvents is to use peroxide test strips that are semi-quantitative and give readings in the range from 0 - 25 ppm. These strips are available from most chemical suppliers. Check your department stockroom

Test Results:

>03-30 parts per million (ppm) - Expired compounds testing within this range offer little or no threat of violent reaction on the given test date. For compounds testing in this range, the investigator should consider the addition of fresh inhibitor to retard the auto-oxidation process and the container should be tightly sealed to prevent air and light exposure.

>30 and <80 ppm - Expired or mismanaged compounds originally inhibited by the supplier which test within this range may well be on the way to posing a threat to the operations of the laboratory. Several documented major exothermic reactions have occurred during the reduction of peroxides in drums, bottles, cans and laboratory ware within this range.

>80 ppm - Any suspect container testing in excess of the limits of standard peroxide test strips must be considered to be potentially shock sensitive. High peroxide concentrations may occur without the presence of visible crystals.

Removal of Peroxides

Low concentrations of peroxides can generally be removed by filtering the contaminated material through a column of chromatography-grade basic alumina. Several methods are available for the "deperoxidation" of ether solvents; for a discussion, see Burfield, D. R. J*. Org. Chem.* 1982, *47*, 3821.