Environmental Management System

Peroxide Forming Compounds

Note: This procedure was adapted with permission from the Desert Research Institute.

Purpose:
Peroxide formation in laboratory solutions and reagents by auto-oxidation has caused many laboratory accidents, including unexpected explosions of residues remaining after solvent distillation. Many liquid, a few solid and a few gaseous organic and a few inorganic solid compounds form peroxides over time. Peroxides form by the reaction of the chemical with oxygen allowed in the headspace of chemical containers once the container is opened for the first time. Most organic peroxides are sensitive, to varying degrees, to shock, heat or friction.

The rate of peroxide formation will depend upon the compound. Some peroxides quickly build up to an explosive level and some are only explosive on concentration, such as when a solvent is distilled. Peroxidizable compounds contain a reactive hydrogen atom that is 'activated' by adjacent structural components (see Attachment A). The dangers of peroxide formation can be divided into three groups (see Attachment B, Tables A-C).

Although there is no agreement upon what level of peroxides present a significant hazard, several sources suggest that the "safe" range of peroxide formation is 100 ppm or less. Therefore it is University of Evansville policy that all peroxide forming chemicals be inspected and or tested on regular the schedule. If peroxides are suspected or are detected at a level above 100 ppm, the material must be decontaminated with standard procedures for deperoxidation or discarded as hazardous waste. Test strips for the detection of peroxides may be purchased from various safety-supply vendors, including Lab Safety Supply, VWR and Fisher Scientific. Several chemical methods for the detection of peroxides are also available in the published literature.

Definitions and Scope: This procedure is for departments where peroxide forming compounds are used. Currently that includes the Chemistry Department, and potentially the Biology Department.

Responsibility: Faculty and other designated individuals of the Department of Chemistry and the Department of Biology are responsible for the control methods in this procedure. The Manager/Risk and Environmental Management is responsible for performing periodic audits of this procedure, which includes review of Chemical Inventory Forms and the Peroxide Forming Chemicals Inspection and Testing Logbook.

Procedure, Control and Safe Use of Peroxide Formers: Peroxide formation may be controlled by the following methods:

1. **Ordering chemicals:**
    a. Check in the storeroom and on the peroxide forming chemicals receipts list before ordering any new peroxide formers. This will help ensure that minimum amounts of peroxide formers are on hand, since they have limited safe storage times. Many chemical companies now routinely print an expiration date on containers of the worst peroxide forming chemicals.
    b. Purchase the smallest possible container size for your needs. Inhibitors are added to some chemicals and the purchase of peroxide formers with added inhibitors is encouraged. However, be aware that these free radical inhibitors will be depleted over time as peroxides are formed. Additionally distillation removes the inhibitor. Distilled peroxide forming compounds and those retained for extended periods should be checked for inhibitor concentration and inhibitor added if below the manufacturer's recommended concentration.

2. **Receiving chemicals:**
    a. Look at the list of peroxide forming chemicals in Attachment B of this procedure (stockroom clerk).
    b. Check the appropriate box (Yes or No) on the chemical inventory form.
    c. If the chemical is a peroxide former, check the table on which it is listed (A, B or C)
    d. Attach a peroxide former label to the chemical container
    e. Date all incoming containers of peroxide formers:
        i. Upon receipt
        ii. Upon opening the container
    f. Enter a page for each peroxide-former in the Peroxide Forming Chemicals Inspection and Testing Logbook.

3. **Storing Peroxide Formers:**
    a. Store peroxide forming chemicals in sealed, air-impermeable containers such as dark amber glass with a tight-fitting cap. Iron inhibits the formation of peroxides in some materials, which is why diethyl ether and some other materials are sold in metal cans. Ground glass stoppered bottles and plastic containers are not advisable, however, plastic squeeze bottles may be used for small quantities of some materials, such as 2-propanol, for immediate use.
    b. Containers of peroxide forming chemicals should be stored away from heat and light and protected from physical damage and ignition sources.
    c. Peroxide forming compounds should not be stored at or lower than the temperature at which the peroxide freezes or precipitates, as this will make these compounds extremely sensitive to shock. Note: refrigeration does not prevent (and may not inhibit) peroxide formation.
    d. Store peroxide forming chemicals, especially those listed in Table A, under nitrogen or other inert gas or keep and use them in an inert atmosphere chamber. Note: Some inhibitors actually need small amounts of oxygen to prevent peroxide formation; therefore it is recommended that inhibited chemicals are not stored under an inert atmosphere.

4. **Safe Use of Peroxide Formers:**
    a. Do not distill peroxide forming chemicals without first testing for the existence of peroxides. Most explosions occur when a material is distilled to dryness. Leave at least 10-20% in still bottom. Stir such distillations with a mechanical stirrer or an inert gas. (Air or an oxygen containing mixture should never be used for this purpose.)
    b. Do not evaporate containers that held peroxide forming compounds to dryness for reuse unless it is known that the chemical was peroxide-free.

c. Inspect containers of peroxide forming chemicals regularly looking for signs of precipitation, stratification of liquid, crystal formation or other irregularities. Note: the presence of any of these signs indicates the potential for a shock sensitive container. Do not move the container and contact EH&S as soon as possible.
d. After each use, carefully wipe the container neck, cap and threads with a cloth before resealing.

5. Monitoring and Testing Peroxide Formers:

a. An record of inspections and tests should be kept for all peroxide forming compounds in the Peroxide Forming Chemicals Inspection and Testing Logbook.
b. Each peroxide forming chemical should be placed in a Storage and Testing category according to its type.
c. Each peroxide forming chemical should be inspected, tested and/or discarded according to schedule indicated in the Table below.
d. The date and the result of the inspection, test, or discard should be entered into the Logbook each time it is performed.

Class of Peroxide Forming Compound	**Safe Storage Period**	**Action after indicated time**
Unopened chemicals from manufacturer:	18 months	Visual inspection with testing or discard if indicated. Repeat at 6 month intervals thereafter.
Opened containers:		
Chemicals in Table A.	3 months	Visual inspection. Discard.
Chemicals in Table B	12 months	Visual inspection with testing or discard if indicated. Repeat at 12 month intervals thereafter.
Uninhibited chemicals in Table C.	24 hours	Discard
Inhibited chemicals in Table C. (Do not store under an inert atmosphere)	12 months	Visual inspection with testing or discard if indicated. Repeat at 6 months. Discard after one year.

Evaluation (Inspection and Testing) of Peroxide-Forming Chemicals

Safety Precautions: Personnel handling containers of *outdated* (of unknown age, of unknown origin, not inspected and/or tested within the time period listed in the table above) peroxide forming chemicals must wear chemical goggles, heavy gloves, and a buttoned lab coat. Hearing protection (plugs or muffs), a face shield, and a rubber apron are also recommended. Suspect chemical containers must be transferred, one at a time, to a clean (no other chemicals) lab hood. A blast shield must be used when opening or manipulating containers, and testing peroxide levels. Never attempt to force open a stuck cap on a container. Secondary containment for the chemical should also be utilized if practical. Tongs or other forms of remote handling should be used as much as practical. Verify that an operable safety

shower/eyewash and fire extinguisher are readily accessible. At least one other person not directly involved in handling of the chemicals should be present.

Personnel conducting regular and timely inspection and testing of peroxide forming chemicals should wear goggles, gloves and a lab coat. They should work in a lab hood with at least one other person aware of their actions. Additional precautions should be taken when prudent and indicated by conditions.

With the above precautions and on the schedule in the table above, peroxide-forming chemicals must be evaluated as follows:

1. *Visual Inspection*

   Visually inspect all peroxide forming chemicals before any further evaluation. Containers that exhibit any unusual visual characteristics, such as the examples listed below, should be assumed to contain dangerous levels of peroxides and should not be disturbed. Notify EH&S, who will assist in the further evaluation. If there is any doubt about the safety of handling a chemical container, notify EH&S immediately.

   Liquid Chemicals

   - Crystallization (around the cap or in the liquid)
   - Visible discoloration
   - Liquid stratification

   Note: A flashlight or other light source can be used to increase the visibility of the interior of amber bottles.

   Diethyl ether is commonly sold in steel containers which prevents visual inspection of the liquid. Therefore, diethyl ether containers whose age and use history are unknown should be assumed to contain dangerous levels of peroxides and should not be disturbed.

   Solid Chemicals (potassium metal, potassium and sodium amide)

   - Discoloration and/or formation of a surface crust (for example, potassium metal forms a yellow or orange superoxide at the surface)

   Note: Evaluation of alkali metals and their amides is based on visual criteria only. These substances react strongly with water and oxygen, and standard peroxide tests should not be used.

   Materials meeting the above criteria are considered to be high risk and will have to be disposed of by special means (limit handling and movement; notify EH&S). Only chemicals that pass visual inspection should be evaluated further.

2. *Opening Container* (Note: Never try to force open a rusted or stuck cap on a container of a peroxide-forming chemical.)

a. Only chemicals that meet the below criteria should be opened and tested for peroxides. Chemicals that do not meet one or more of these criteria should be considered to be high risk, and should not be disturbed. Limit handling and movement; notify EH&S.

- The identity of the chemical is known.
- The age of the chemical (since manufacture) is known.
- Evaporation of the chemical is thought to be less than 10% - if this is in question, assume that evaporation has occurred and that high peroxide levels may be present.

b. Additionally, the following classification-specific criteria must be met:

List A Chemicals

- Previously opened chemicals not used in the preceding 3 months must be less than 6 months old.
- Chemicals unopened from the manufacturer must be less than 2 years old. If this is in question, assume the container has been opened.

List B and List C (liquids) Chemicals

- Opened chemicals not used in the preceding 12 months must be less than 5 years old.
- Chemicals unopened from the manufacturer must be less than 10 years old. If this is in question, assume the container has been opened.

Chemicals not meeting the minimum criteria for opening and testing will be considered to be high risk and must be disposed of by special means. Limit handling and movement; notify EH&S.

If after opening the container, visual irregularities such as those listed in section 1 are apparent, assume that dangerous levels of peroxides are present. Gently cover the container to minimize evaporation, limit handling and movement, and notify EH&S as soon as possible.

3. *Peroxide testing*

For chemicals that have been determined to be safe to open, measure the peroxide concentration using commercial peroxide test strips. Wet chemical detection methods are also available; however, the test strips are gentler, easier, faster, and have greater sensitivity and accuracy, and therefore are recommended for most applications. Laboratory personnel are responsible for performing peroxide testing of peroxide forming chemicals present in their laboratories or storage areas. EM Quant Peroxide test strips manufactured by EM Science (E. Merck) are available from many suppliers (such as Fisher Scientific, Lab Safety and VWR). Chemicals that contain peroxide levels that exceed the test strip detection range may be diluted with a miscible, peroxide-free, solvent and retested.

Disposal of peroxide forming chemicals

1. Chemicals with a peroxide concentration of less than 30 ppm can be disposed of by contacting the Manager, Risk and Environmental Management. Laboratory personnel are responsible for decontaminating chemicals that contain greater than 30 ppm peroxides prior to disposal.

2. Chemicals with a peroxide concentration greater than 800 ppm are considered high risk, and require disposal by special means. DO NOT attempt to decrease peroxide concentration. Limit handling and movement of the chemical container. Notify the Manager, Risk and Environmental Management at extension 2697.

3. Peroxide forming chemicals with a peroxide concentration greater than 100 ppm must be disposed of. (Exception: a container of a chemical on list B with a peroxide concentration of less than 800 ppm, can be decontaminated and maintained for future use upon the approval of the responsible principal investigator or laboratory supervisor).

4. Chemicals with a peroxide concentration less than 800 ppm must be decontaminated to reduce the peroxide concentration to less than 30 ppm before disposal. Peroxides can be removed by chemical treatment or column separation (1,2,5). Verify treatment with testing. Notify the Manager, Risk and Environmental Management of treatment and subsequent peroxide concentration when submitting request for waste removal.

Preparation of Peroxide Formers for Disposal

Water-insoluble peroxide formers (ethers, hydrocarbons, etc.) can be decontaminated by several chemical methods (1,2,5). Reduction of the peroxides generally takes only a few minutes. Re-test the peroxide former after decontamination to verify that the peroxide concentration is less than 30 ppm. Dispose of the decontaminated peroxide former as soon as possible through EH&S (report final peroxide concentration). An alumina column is used as the standard procedure to decontaminate water-soluble peroxide formers (1,2). Contact EH&S for guidance on decontamination of these chemicals.

In some instances it may be permissible to dilute the peroxide concentration to below 30 ppm by mixing the peroxide former with a chemically compatible chemical waste stream or chemical solvent. Contact the Manager, Risk and Environmental Management prior to diluting any peroxide former in preparation for disposal. After diluting the peroxide former, verify that the peroxide concentration of the resulting mixture is less than 30 ppm, and then dispose of the waste mixture through the Manager, Risk and Environmental Management (report final peroxide concentration).

Associated Documents and References

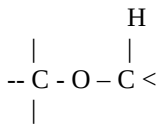
1. Kelly, R. J., "Review of Safety Guidelines for Peroxidizable Organic Chemicals", *Chem. Health Saf.* **1996**, 3(5), 28-36
2. Jackson, H. L.; McCormack, W. B.; Rondestvedt, C. S.; Smeltz, K. C.; Viele, I. E. *J. Chem. Educ.* **1970**, 47(3), A175-88
3. Clark, D. E., "Peroxides and Peroxide Forming Compounds", *Chem. Health Saf.* **2001,** 8(5), 12-21
4. National Safety Council, Recognition and Handling of Peroxidizable Compounds, **1987**, Data Sheet I-655-Rev. 87

5. National Research Council, *Prudent Practices in the Laboratory: Handling and Disposal of Chemicals*; National Academy Press: Washington, D. C., **1995**; pp. 162-163.
6. National Research Council, *Prudent Practices in the Laboratory: Handling and Management of Chemical Hazards*; National Academy Press: Washington, D. C., **2001**.
7. Kelley, R. J., "Peroxidizable Organic Chemicals", Handbook of Chemical Health and Safety, Chapter 52, ACS, **2001**

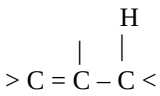
Revision #	Date Issued	Changes

Attachment A—Peroxidizable Organic Moieties*

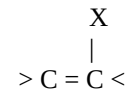
1. Ethers and acetals with α-hydrogen



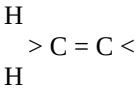
2. Alkenes with allylic hydrogen



3. Chloroalkenes, fluoroalkenes

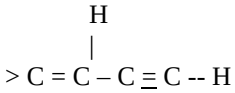


4. Vinyl halides, esters, ethers

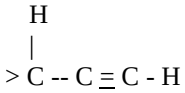


5. Dienes

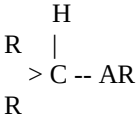
6. Vinyl alkynes with α-hydrogen



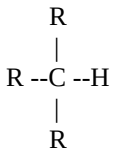
7. Alkylalkynes with α-hydrogen



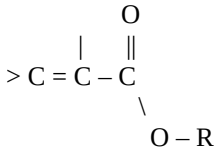
8. Alkylalarenes with tertiary α-hydrogen (benzylic hydrogen)



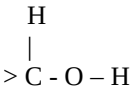
9. Alkanes and cycloalkanes with tertiary hydrogen



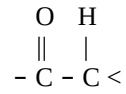
10. Acrylates, methacrylates



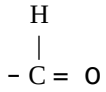
11. Secondary Alcohols



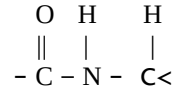
12. Ketones with α-hydrogen



13. Aldehydes



14. Ureas, amides and tactams with α-hydrogen on a carbon attached to nitrogen



***Numbered from "Most" to "Least" likely to form dangerous peroxides.**

Attachment B—Tables of Peroxide Forming Compounds

Table A--Chemicals that form explosive levels of peroxides without concentration.

Butadine[a]	Isopropyl ether	Sodium amide (sodamide)
Chlorobutadiene (chloroprene)[a]	Potassium amide	Tetrafluoroethylene[a]
Divinylacetylene	Potassium metal	Vinylidene chloride

Table B--Chemicals that form explosive levels of peroxides upon concentration. A test for peroxide should be performed if concentration is intended or suspected.**

Acetal	Dicyclopentadiene	2-Pentanol
Acetaldehyde	Diethyl ether (ethyl ether)	4-Methyl-2-pentanol
Benzyl alcohol	Diethylene glycol dimethyl ether (diglyme)	4-Penten-1-ol
2-Butanol (*sec*-butanol)	Dioxanes (*p*-dioxane)	1-Phenylethanol
Cumene (isopropylbenzene)	Ethylene glycol dimethyl ether (glyme)	2-Phenylethanol
Cyclohexanol	Furan	2-Propanol (isopropyl alcohol)
2-Cyclohexen-1-ol	4-Heptanol	Tetrahydrofuran (THF)
Cyclohexene	2-Hexanol	Tetrahydronaphthalene (tetralin)
Cyclooctene	Methylacetylene	
cyclopentene	3-Methyl-1-butanol (isoamyl alcohol)	
Decahydronaphthalene (decalin)	Methylcyclopentane	Vinyl ethers
Diacetylene	Methyl isobutyl ketone (4-methyl-2-pentanone)	Other secondary alcohols

****This list is illustrative, not comprehensive. Refer to Attachment A and MSDS information for further guidance.**

Attachment B—Tables of Peroxide Forming Compounds

Table C—Unsaturated monomers may autopolymerize as a result of peroxide accumulation if inhibitors have been removed or are depleted.

Acrylic acid[b]	Ethyl acrylate	Vinyl acetate
Butadiene[c]	Methyl methacrylate[b]	Vinyl chloride
Chlorobutadiene (chloroprene)[c]	Styrene	Vinylpyridine
Chlorotrifluoroethylene		

NOTES:

[a] When stored as a liquid monomer.

[b] Although these chemicals form peroxides, no explosions involving these monomers have been reported.

[c] When stored in liquid form, these chemicals form explosive levels of peroxides without concentration. They may also be stored as a gas in gas cylinders. When stored as a gas, these chemicals may autopolymerize as a result of peroxide accumulation.