ENVIRONMENTAL HEALTH & SAFETY

UNIVERSITY *of* WASHINGTON

EH&S Guidelines for Peroxide Forming Chemicals

July 20, 2011

EH&S Guidelines for Peroxide Forming Chemicals

Contents

INTRODUCTION

This guide helps you manage your peroxide forming chemicals. It also outlines the procedures for the required stabilization of peroxide forming chemicals and destruction of peroxides prior to disposal.

Peroxides formed in organic compounds can cause serious accidents. In some circumstances, peroxides become low power explosives. In other circumstances, they are sensitive to shock, sparks, and flames. The danger is increased when a peroxide forming chemical is concentrated by distillation or evaporation.

If you use peroxide forming chemicals, you must understand the factors that contribute to peroxide formation. You must also manage your chemicals correctly and periodically test for peroxides.

MANAGEMENT

Manage your peroxide forming chemicals wisely and diligently to avoid having to test and stabilize peroxide forming chemicals in the first place. Follow these steps:

1. Keep chemical containers tightly closed. Chemicals packaged in tightly sealed, unopened containers and stabilized with an added chemical or packed under inert gas will not form dangerous concentrations of peroxides, since oxygen is necessary for formation of peroxides.
2. Keep containers in opaque containers away from light sources. Exposure to light accelerates peroxide formation. Airtight amber glass containers are best. Amber glass protects the chemical from light exposure while allowing you to view the chemical without opening the container.
3. Keep a careful inventory of your peroxide forming chemicals.
4. Label all peroxide forming chemicals with the UW Peroxide Caution Label UOW1716, shown at right. This label is available for free from the Chemistry Stockroom in the basement of Bagley Hall. Or, email your box number to chmwaste@u.washington.edu to request that some be mailed to you. Fill out the date the container was purchased, opened and tested.
5. Monitor the container volume for evaporative loss and test for the presence of peroxides before each use.
6. Test for peroxides regularly, preferably before each use. Assume peroxide forming chemicals contain peroxides unless they have been recently tested. Record the test data for the next user. If the concentration of peroxides exceeds 10 ppm, then see page 5.
7. Store the substance under an inert gas when possible.
8. Properly dispose of chemicals that are past their maximum retention times or that are not needed.
9. Purchase chemicals in the smallest amount practicable.

COMMON PEROXIDES AND MAXIMUM RETENTION TIMES

EH&S recommends that you dispose of peroxide forming chemicals that have been kept longer than their maximum retention times. The maximum retention times begin on the date of opening a manufacturer's bottle or the date of synthesis in your laboratory. Peroxides form at varying rates depending on the chemical, the length of exposure to air and light and the container type. Peroxides can form in freshly distilled and unstabilized ethers within two weeks, in ethyl ether within eight days, and in tetrahydrofuran within three days. Below are lists of peroxide forming chemicals and their maximum retention times.

High Peroxide Hazard DISCARD WITHIN 3 MONTHS	**Medium Peroxide Hazard** DISCARD WITHIN 6 MONTHS or test for peroxides before use	**Low Peroxide Hazard** DISCARD WITHIN ONE YEAR
diisopropyl ether (isopropyl ether) divinylacetylene (DVA) potassium amide sodium amide (sodamide) vinylidine chloride (1,1-dichloroethylene)	acetaldehyde diethyl acetal cumene (isopropylbenzene) cyclopentene decalin (decahydronaphthalene) diacetylene (butadiene) dicyclopenradiene diethyl ether (ether) p-dioxane furan methyl isobutyl ketone methyl acetylene methylcyclopenatane tetrahydrofuran tetralin (tetrahydronaphthalene) vinyl ethers chloroprene (2-chloro-1,3-buta-diene) styrene vinyl acetate vinylpyridine	In general, chemicals with aldehyde or amide groups form peroxides but are not known to accumulate peroxide to dangerous levels.

These lists are not exhaustive. Check the Material Safety Data Sheet (MSDS) of your chemical to determine if it forms peroxides. If so, there will be a warning under the heading Precautionary Labeling or Fire and Explosion Hazard Data on the MSDS. If a substance does not appear on the lists and the MSDS does not indicate that it is a peroxide former, but you suspect that it is a peroxide former, evaluate the molecular structure of the chemical for peroxide forming functional groups and the chemical families of peroxide formers below:

ORGANIC

A. ethers, acetals
B. olefins with allylic hydrogens, chloro- and fluoroolefins, terpenes
C. dienes, vinyl acetylenes
D. aldehydes
E. ureas, amides, lactams
F. vinyl monomers including vinyl halides, acrylates, methacrylates, vinyl esters

INORGANIC

A. alkali metals, particularly potassium
B. alkali metal alkoxides and amides
C. organometallics

EVALUATING AND TESTING FOR PEROXIDES

EHS will not collect any peroxide forming chemicals that has exceeded its retention time (see page 4) unless the peroxide concentration has been reduced to 10ppm or lower. Complete the steps below for each peroxide forming chemical before requesting disposal. Contact EH&S at 206.616.0595 with any questions.

1. Examine chemical for visible crystals

Peroxide crystals tend to form on the inner surfaces of the container. If you do not see crystals, or if the container is metal or opaque, proceed to the next step. If you do see viscous liquid or crystalline solids, do not handle the chemical any further. The crystals may cause an explosion if subjected to impact or friction. Immediately proceed to Step 6 (deactivation by a hazardous materials contractor.)

2. Determine whether it is safe to test for peroxides

If the contents of the container have evaporated to less than 10% of the original volume, you may not test for peroxides. If you do not know the history of the chemical, you can test its contents if it is one of the following:

- for chemicals with a low peroxide hazard, the container is opened and <2 years old or unopened and <3 years old
- for chemicals with a medium peroxide hazard, the container opened and <1 year old or unopened and <2 years old
- for chemicals with a high peroxide hazard, the container is opened and <6 months old or unopened and <1 year old.

If the chemical is not safe for you to test, proceed to Step 6 (deactivation by a hazardous materials contractor).

3. Test for peroxides

Test for peroxides in peroxide forming chemicals that may be tested as determined above. Use Method A or B described below, as appropriate. Faculty, staff and students may test for peroxides if the chemical is not expired. If the chemical is expired, only faculty and staff may test for peroxides.

Method A (Test Strip)

Peroxide test strips detect inorganic and organic compounds that contain a peroxide or hyperperoxide group. Test strips are suitable for the routine testing of peroxides formed from simple ethers such as diethyl ether, tetrahydrofuran, and p-dioxane. Use the EM Quantitative Peroxide Test, a color-metric dipstick test developed by Merck. Carefully read the instructions provided by the manufacturer. EHS will provide test strips upon request. Call 206.616.0595 for more information.

Method B (Iodide Test)

The iodide test (6) is suitable for the testing any peroxide forming chemical.

1. Wear chemical resistant gloves, a laboratory coat and eye protection. Work in a fume hood.
2. Dissolve 100 mg of potassium iodide in 1 ml of glacial acetic acid.
3. Add the mixture to 1 ml of the chemical being tested. Use a 10 ml graduated cylinder.
4. Determine the color of the resulting mixture by looking through the side of the cylinder with a piece of white paper behind the cylinder.

- A pale or barely discernable yellow color indicates a peroxide concentration of 0.001 – 0.005%.
- A bright yellow or brown indicates a peroxide concentration of 0.01% or greater.

If the peroxide concentration is less than 0.001% (10 ppm), go to the next step. If the peroxide concentration exceeds 0.001% (10 ppm), the chemical must be stabilized prior to collection by EH&S; see Step 5.

4. Stabilization of peroxides by laboratory personnel

Even if the concentration of peroxides is less than 0.001% (10 ppm), you should periodically stabilize your chemical from additional formation of peroxides if feasible. To do so, add at least 1 gram of butylated hydroxytoluene (BHT) per liter of chemical. BHT is an antioxidant that slows the oxidation of peroxide forming chemicals. BHT will not destroy peroxides already present.

Once you have stabilized the chemical, label the substance with the peroxide concentration and indicate the date that you stabilized it. Store the substance properly or manage as hazardous waste (submit a Chemical Collection Request at http://www.ehs.washington.edu/forms/epo/1470.pdf.)

5. Destruction of peroxides by laboratory personnel

If you feel comfortable deactivating the peroxides yourself, contact EH&S at 616-0595 for suitable methods. If you are not able or willing to deactivate the peroxides, proceed to Step 6 (deactivation by a hazardous materials contractor.)

6. Destruction of peroxides by a hazardous materials contractor

If you see crystals or viscous liquid in the container or are not comfortable testing and stabilizing your chemical, it must be deactivated by a hazardous materials contractor arranged by EH&S. First, secure the area near the chemical so that no one will disturb it. Then complete the following forms:

1. Peroxide Forming Chemical Deactivation Request (see next page).
2. Chemical Collection Request (http://www.ehs.washington.edu/forms/epo/1470.pdf)

Mail both forms to EH&S Peroxide Stabilization, Box 354110 or fax them to 206.685.2915.

EH&S will contact you and arrange for a hazardous materials contractor. Deactivation will be at the expense of the laboratory of origin. While awaiting deactivation, secure and label the area where the peroxide forming chemical is stored. Protect the substance from any unnecessary movement.

REFERENCES

1. Jackson, H. L. “Safety in the Chemistry Laboratory,” Journal of Chemical Education, 41 (1964), A575.
2. Prudent Practices for Disposal of Chemicals from Laboratories, National Academy Press, Washington, D.C., 1981, Pg 57 ff.
3. Jackson, H.L. et al. “Safety in the Chemistry Laboratory,” Journal of Chemical Education, 47, (1970), A175.
4. Burfield, David R. “Deperoxidation of Ethers,” Journal of Organic Chemistry, Vol. 47, No. 20, (1982), 3821 ff.
5. Prudent Practices for Disposal of Chemicals from Laboratories, National Academy Press, Washington, D.C., 1983, Pg 242 ff.
6. Armour, M.A., Browne, L.M., Weir, G.L., Hazardous Laboratory Chemicals Disposal Guide. CRC Press, Alberta, 1991, Pg 285 ff.

PEROXIDE FORMING CHEMICAL DEACTIVATION REQUEST

Principal Investigator's Name _____ Box # 35_____

Department Administrator's Name _____ Box # 35_____

Building Coordinator's Name _____ Box # 35_____

Contact Person's Name _____ Box # 35_____

Contact Person's Telephone Number _____

Budget Name _____ Budget # _____

Location of Material(s):	Building	Room

	Chemical 1	Chemical 2	Chemical 3
Chemical name			
Manufacturer and lot #			
Expiration date on container			
Type/condition of container			
Date of purchase of container			
Date of last usage			
Approximate container volume			

Please return completed information to:

EH&S EPO Peroxide Stabilization
Box 354110
Fax 206.685.2915
Phone 206.616.5835