ENVIRONMENTAL HEALTH & SAFETY

UNIVERSITY *of* WASHINGTON

EH&S GUIDELINES FOR PEROXIDE FORMING CHEMICALS

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INTRODUCTION

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

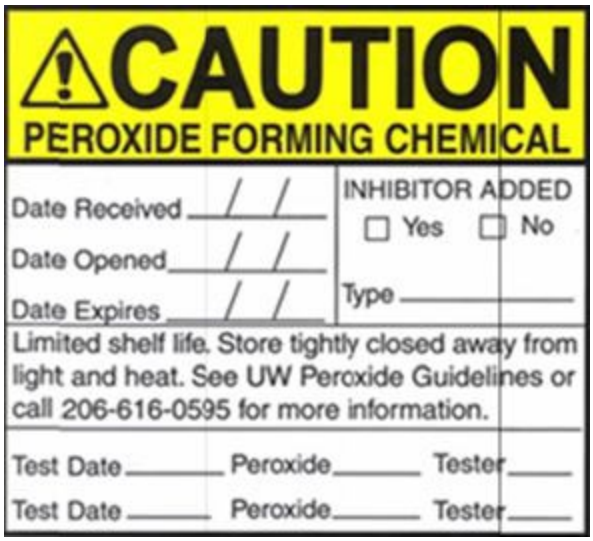
Peroxides formed in organic compounds can cause serious accidents. In some circumstances, peroxides become low power explosives. In other circumstances, they are sensitive to shock, sparks, and flames. The danger is increased when a peroxide forming chemical is concentrated by distillation or evaporation.

If you use peroxide forming chemicals, you must develop a standard operating procedure (SOP) for their use; see our example Peroxide-Forming SOP. You must understand the factors that contribute to peroxide formation, 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, as oxygen is necessary for the formation of peroxides.
2. Keep chemicals 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 in the UW's MyChem inventory system.
4. Label all peroxide forming chemicals with the **UW Peroxide Caution Label** (UOW 1716), shown at right. This label is available for free from the Chemistry Stockroom in the basement of Bagley Hall, or you can email your box number to chmwaste@uw.edu to request that some be mailed to you. Fill out the date the container was purchased, opened and tested.



5. Monitor 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, container type, and the length of exposure to air and light. 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 common peroxide forming chemicals at UW Campuses and their maximum retention times. There are many more peroxide forming chemicals and the Safety Data Sheet (SDS) for your reagent is the best source of information.

Continued on next page.

High Peroxide Hazard DISCARD WITHIN 3 MONTHS (or test for peroxides before use)	Medium Peroxide Hazard DISCARD WITHIN 6 MONTHS (or test for peroxides before use)	Low Peroxide Hazard DISCARD WITHIN ONE YEAR (or test for peroxides before use)
diisopropyl ether (isopropyl ether)	acetaldehyde diethyl acetal	In general, chemicals with aldehyde or amide groups form peroxides but are not known to accumulate peroxides to dangerous levels.
divinylacetylene (DVA)	cumene (isopropylbenzene)	
potassium amide	cyclopentene	
sodium amide (sodamide)	decalin (decahydronaphthalene)	
vinylidine chloride (1,1-	diacetylene (butadiene)	
dichloroethylene)	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	

These lists are not exhaustive. Check the Safety Data Sheet (SDS) for your particular reagent to determine if it forms peroxides. If a substance does not appear on the lists and the SDS does not indicate that it is a peroxide former, but you suspect that it is a peroxide former, you can also 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

EH&S 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 that has exceeded its retention time before requesting disposal. Contact EH&S at 206.616.0595 with any questions.

STEP 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** contact EH&S at 206.616.0595 for guidance on how to proceed.

STEP 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 should not test for peroxides without consulting with EH&S. 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 is 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

STEP 3: TEST FOR PEROXIDES

If the reagent is safe for testing as outlined above, you may use Method A or B described below. 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. These strips are available from many chemical suppliers such as JT Baker and Sigma/Aldrich. Carefully read the instructions provided by the manufacturer. EH&S will provide test strips upon request. Call 206.616.0595 for more information.

Method B (Iodide Test)

The iodide test 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.

STEP 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 as outlined on the EH&S Chemical Waste Disposal webpage.

STEP 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 EH&S will advise how the material must be managed.

STEP 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 may require deactivation 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 Peroxide Forming Chemical Deactivation Request on page 10. Email the completed form chmwaste@uw.edu or mail to EH&S Peroxide Stabilization, Box 354110.

If necessary, 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.

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PEROXIDE FORMING CHEMICAL DEACTIVATION REQUEST

Principal Investigator's Name: _____ **Box #:** _____

Department Administrator's Name: _____ **Box #:** _____

Building Coordinator's Name: _____ **Box #:** _____

Contact Name: _____

Contact Telephone: _____

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:			
APPROX. CONTAINER VOLUME:			

Please return completed information to: EH&S EPO Peroxide Stabilization, Box 354110 or email to chmwaste@uw.edu or call 206.616.0595.