ENVIRONMENTAL HEALTH & SAFETY

Peroxide Forming Chemicals

Standard Operating Procedure

Revision Date: 09/14/21

Laboratory Director (LD) Approval is Required Prior to Performing this Procedure

Description [Provide additional information as it pertains to your research protocol]

This standard operating procedure (SOP) outlines the handling and use of peroxide forming chemicals. Review this document and supply the information required in order to make it specific to your laboratory. In accordance with this document, laboratories should use appropriate controls, personal protective equipment, and disposal techniques when handling peroxide forming chemicals.

Process [Write the steps for using the chemical in your research protocol]

Potential Hazards [Provide additional information as it pertains to your research protocol]

Peroxide Formation

Peroxide formation in common laboratory chemicals is caused by an autoxidation reaction. The reaction can be initiated by light, heat, introduction of a contaminant, oxygen or the loss of an inhibitor. Some chemicals have inhibitors such as BHT (butylated hydroxytoluene), hydroquinone, and diphenylamine to slow peroxide formation. Most organic peroxide crystals are sensitive to heat, shock, or friction, and their accumulation in laboratory reagents has resulted in numerous explosions. For this reason, it is important to identify and control chemicals which form potentially explosive peroxides.

Peroxide Forming Compounds

In general, the more volatile the compound, the greater its hazard, since the evaporation of the compound allows the peroxide to concentrate. Peroxide accumulation is a balance between peroxide formation and degradation. Refer to the tables below for some common peroxide forming chemicals and testing procedures.

Organic peroxide forming materials can form shock-sensitive organic peroxide crystals over time or upon exposure to air. **Also check each material's SDS to determine if a chemical can form peroxides, and to check for other hazards.**

Useful Peroxide Forming Materials Links:

- http://www.ilpi.com/msds/ref/peroxide.html
- https://e-reports-ext.llnl.gov/pdf/235232.pdf

- https://ehs.berkeley.edu/lessons-learned/lesson-learned-peroxide-explosion-injures-campus-researcher
- Peroxides and peroxide-forming compounds. D.E. Clark. 2001. Chemical Health and Safety, 8:12-22

NOTE: **This is not an exhaustive list**. Users **must** consult the chemical's SDS and/or other sources of information for the chemicals used (and stored) to determine their peroxide-forming potential.

Table 1 - Peroxidizable Chemicals List (with CAS #s)

Chemical synonyms are provided in italics beneath the chemical name

List A: Chemicals that form explosive levels of peroxides without concentration (3 months)[1]		
Butadiene[2] (106-99-0) • *Pyrrolene* • *Vinylethylene*	Isopropyl Ether (108-20-3) • *Diisopropyl ether* • *Diisopropyl oxide*	Tetrafluoroethylene[2] (116-14-3) • *Perfluoroethylene*
Chloroprene[2] (126-99-8) • *Chlorobutadiene*	Potassium Metal (7440-09-7)	Vinylidene Chloride (75-35-4) • *1,1-dichloroethylene* • *1,1-dichloroethene*
Divinyl Acetylene (821-08-9)	Sodium Amide (7782-92-5)	
List B: Chemicals that form explosive levels of peroxides on concentration (12 months)[1]		
1,1-Dimethoxymethane (109-87-5) • *Methylal* • *Methylene dimethyl ether*	Benzyl alcohol (100-51-6) • *Hydroxytoluene* • *Phenyl carbinol*	Di-n-propoxymethane (505-84-0)
1,2-Epoxy-3-isopropoxy propane (4016-14-2) • *Isopropyl glycidyl ether*	Benzyl n-butyl Ether (588-67-0)	Dioxane (123-91-1) • *Diethylene ether*
1-pentene (109-67-1) • *Propyl ethylene*	Benzyl Ether (103-50-4) • *Dibenzyl ether*	Diethyl Ether (60-29-7) • *Ethyl ether*
1-Phenylethanol (98-85-1) • *sec-phenethyl alcohol*	Benzyl Ethyl Ether (539-30-0)	Ethylene Glycol Dimethyl Ether (110-71-4) • *1,2-dimethoxyethane* • *EGDME* • *Glyme*
2-Butanol (78-92-2) • *Sec-butyl alcohol*	Benzyl 1-naphthyl Ether (607-58-9)	Isoamyl Ether (544-01-4) • *Isopentyl ether*
2-Hexanol (626-93-7) • *n-hexanol* • *Amylcarbinol* • *Caproyl alcohol*	Cumene (98-82-8) • *Isopropyl benzene*	Isophorone (78-59-1)
3-Methyl-1-butanol (123-51-3) • *Iso-amyl alcohol* • *Isopentyl alcohol*	Cyclohexene (110-83-8) • *Tetrahydrobenzene*	Methyl Isobutyl Ketone (108-10-1)
4-Penten-1-ol (821-09-0)	Cyclooctene (931-88-4)	Methyl Acetylene (74-99-7)

		• *Propyne*
2-Phenylethanol (60-12-8) • *Benzyl carbinol* • *Benzylmethanol*	Decahydronapthalene (91-17-8) • *Decalin* • *DeKalin*	Methylcyclopentane (96-37-7)
List B: Chemicals that form explosive levels of peroxides on concentration (12 months)[1]		
2-Propanol (67-63-0)[5] • *Isopropanol*	Diacetylene (460-12-8)	Other secondary alcohols
4-Heptanol (589-55-9)	Diallyl Ether (557-40-4) • *Propenyl ether*	p-Dibenzyloxybenzene (621-91-0)
4-Methyl-2-pentanol (108-11-2) • *Methyl isobutyl carbinol*	Dicyclopentadiene (77-73-6)	p-Isopropoxypropionitrile (110-47-4)
4-Penten-1-ol (821-09-0)	Diethoxymethane (462-95-3)	Tetrahydrofuran (109-99-9)
Acetal (105-57-7) • *Diethylacetyl* • *ethylidene diethyl ether*	Isoamyl benzyl ether (122-73-6)	Tetrahydronaphthalene (119-64-2) • *Tetralin* • *Tetranap*
Acetaldehyde (75-07-0)	Diethylene Glycoldimethyl Ether (111-96-6) • *Diglyme*	Diethyl acetal (105-57-7)
Allyl Ether (557-40-4)	Dimethoxymethane (109-87-5) • *Methylene dimethyl ether* • *Methylal*	Vinyl Ethers
List C: Chemicals that may autopolymerize as a result of peroxide accumulation (12 months)1,3,4		
Acrylic Acid (79-10-7) • *2-propenoic acid* • *Vinylformic acid* • *Acroleic acid*	Methyl Methacrylate (80-62-6) • *2-propenoic acid*	Vinyl Chloride (75-01-4) • *Chloroethylene*
Acrylonitrile (107-13-1) • *Vinyl cyanide* • *Carbacryl*	Styrene (100-42-5)	Vinylidene chloride (75-35-4) • *1,1-dichloroethylene* • *1,1-dichloroethene*
Butadiene[2] (106-99-0) • *Pyrrolene* • *Vinylethylene*	Tetrafluoroethylene[2] (116-14-3) • *Perfluoroethylene*	2-Vinyl Pyridine (100-69-6)
Chloroprene[2] (126-99-8)	Vinyl Acetate (108-05-4)	4-Vinyl Pyridine (100-43-6)
Chlorotrifluoroethylene (79-38-9)	Vinyl Acetylene (689-97-4)	

1. Safe storage periods are given for an open container of each class of peroxidizable material. Unopened containers from the manufacturer have a safe storage period of 18 months.

2. When stored in liquid form these chemicals may form explosive levels of peroxides without concentration. When stored as a gas, these chemicals may autopolymerize as a result of peroxide accumulation.
3. If chemical from List C is inhibited, do not store under an inert atmosphere. Oxygen is required for inhibitor to function.
4. Uninhibited chemicals from List C have a safe storage period of 24 hours.
5. 2-Propanol does not need to be routinely tested if only used for cleaning. It does need to be tested if it will be distilled or otherwise concentrated.

Engineering Controls **[Provide additional information as it pertains to your research protocol]**

Use fume hood or other appropriate exhaust ventilation if inhalation hazard is anticipated. Utilize shields, barricades, and additional PPE (such as face shields with throat protectors and heavy gloves) where there is a possibility of explosion or vigorous chemical reaction.

Work Practice Controls **[Provide additional information as it pertains to your research protocol]**

- Maintain the smallest amount necessary for ongoing work.
- Purchase peroxide formers with inhibitors added by the manufacturer when possible.
- **Mark the container with the *date it was received* and *the date it was opened*. If tested for peroxides, note the date it was tested.**
- Do not allow materials to evaporate to near dryness unless absence of peroxides has been shown.
- Periodically test containers with peroxide test strips. See testing section below for more information.
    - Note: some peroxide formers (including alkali metals and their amides) should not be tested with standard peroxide tests because they are both water and oxygen-reactive

Note: Never try to force open a rusted or stuck cap on a container of a peroxide-forming chemical.

Testing Procedures

There is a great deal of uncertainty regarding the concentration at which peroxides pose a hazard to researchers. Various sources suggest that the minimum hazardous concentration of peroxides in organic solution is in the range 0.005 - 1.0% (50-10,000 ppm). In most safety literature, a conservative concentration of 100 ppm peroxides is used as a control point.

By the end of the expiration date (as indicated in Table 2) for a particular peroxide forming chemical, the person using the chemical should either dispose of it or test it for peroxide content. Any container found to have a peroxide concentration greater than or equal to 100 ppm should be disposed of (call EHS at (734) 763-4568 for assistance).

Materials which are older than the suggested shelf life but have been tested and have no detectable peroxides or peroxide concentrations less than 100 ppm may be retained but should be re-tested. Table 1 List A chemicals should be retested monthly while List B chemicals should be retested every three months (see Table 2). *All chemicals which are to be distilled must be tested prior to distillation regardless of age.*

Important note: Researchers should never test containers of unknown age or origin. Older containers are far more likely to have concentrated peroxides or peroxide crystallization in the cap threads and

therefore can present a serious hazard when opened for testing. Please read section below on managing older containers.

There are several methods that are commonly used to detect for peroxides in the laboratory. Perhaps the most convenient method is the use of peroxide test strips which are manufactured by Aldrich and several other suppliers. These strips are simple to use and can be obtained from a chemical supplier. For volatile organic chemicals, the test strip is immersed in the chemical for 1 second; then the tester breathes slowly on the strip for 15-30 seconds or until the color stabilizes.

The color is then compared with a colorimetric scale provided on the bottle. Strips that offer a 1-100 ppm peroxide range are useful for determining if the material is below the control point of 100 ppm. Other testing methods are available. Contact UM-Dearborn Environmental Health and Safety (EHS) at (313) 583-6692 for more information.

Table 2: Safe storage period for peroxidizable chemicals	
Peroxidizable Chemical Classification	**Dispose or Test After:[1,2]**
Unopened chemicals from the manufacturer	18 months
Opened containers	
List A, Table 1 materials	3 months
List B, Table 1 materials	12 months
Uninhibited List C, Table 1 materials	24 hours
Inhibited List C, Table 1 materials	12 months[3]

1. Never open or test containers of unknown origin or age or that have visible evidence of peroxides
2. After initial storage periods peroxide-forming chemicals should be re-tested every three months for List B chemicals and monthly for List A
3. Do not store under inert atmosphere.

Personal Protective Equipment **[Provide additional information as it pertains to your research protocol]**

In order to select the appropriate PPE for the workplace, a Hazard Assessment is conducted. The hazard assessment determines the hazards and potential hazards associated with a task, machinery, or process. The appropriate PPE for the situation may be subsequently determined.

The hazard assessment form may be completed either by the workplace supervisor or the department's EHS representative.

Wear standard nitrile laboratory gloves (or those recommended on the SDS), lab coat, and safety glasses (meeting the requirements of ANSI/ISEA Z87.1) for all work in the laboratory.

Also, refer to the (EHS) Glove Compatibility Chart Web page.

Transportation and Storage **[Provide additional information as it pertains to your research protocol]**

- Store in airtight containers in a dark, cool but not freezing, and dry area.
- Do not permit sources of heat, friction, grinding, or impact near storage areas.
- **Date upon receiving and opening all incoming peroxide forming chemicals and dispose of them immediately upon reaching their expiration date**.
- Some peroxide-formers should be stored under nitrogen (or other inert gas) – consult the chemical's SDS for more information.

Waste Disposal [Provide additional information as it pertains to your research protocol]

Most spent, unused and expired materials are considered hazardous wastes and **must be collected and disposed of within 90-days** by EHS. Contact EHS at (313) 583-6692 for any questions regarding proper waste disposal. Also, refer to EHS Hazardous Waste Web page for more information.

Contact EHS ***immediately*** to arrange for pick-up and disposal if:

- Crystals are found around the lid of the container. Do **NOT** attempt to open the container!
  or
- The container tests positive for peroxides.

Exposures/Unintended Contact [Provide additional information as it pertains to your research protocol]

If the employee is in need of emergency medical attention, call 911 immediately.

For a chemical exposure/injury:

INJURY TYPE	ACTION	NOTES
Exposure-Eyes	1. Immediately flush eyes with plenty of water for at least 15 minutes. 2. *Remove contact lenses, if present and easy to do*. 3. Continue rinsing. 4. Get medical aid.	
Exposure-Skin	1. Flush skin with plenty of water. 2. Remove contaminated clothing and shoes. 3. Get medical aid if irritation develops and persists.	Wash clothing before reuse.
Inhalation (including spills of powder outside of a chemical fume hood)	1. Remove the individual to fresh air. 2. If the individual is not breathing, give artificial respiration. 3. If the individual has difficulty breathing, give oxygen. 4. Get medical aid.	
Ingestion	1. **Do not induce vomiting unless directed to do so by medical personnel**. 2. Get medical aid.	Never give anything by mouth to an unconscious person.
NOTE: If an ambulance is needed, call the University of Michigan- Dearborn campus Department of Public Safety (DPS) at 911, from any campus landline, to request assistance.		

If there is any doubt about the severity of the injury, seek immediate medical attention.

Contact EHS for advice on symptoms of chemical exposure, or assistance in performing an exposure assessment.

Report all work related accidents, injuries, illnesses or exposures to Work Connections within 24 hours by completing and submitting the Illness and Injury Report Form. Follow the directions on the EHS website's Illness, Injuries and Accidents page to obtain proper medical treatment and follow-up.

Complete the Incident and Near-Miss Report form.

Treatment Facilities

Concentra: Allen Park clinic -- Campus Employees, non-emergencies
Mon-Fri 8:00 am - 5:00 pm
17500 Federal Drive, Suite 750
Allen Park, MI 48101
(313) 982-1376

After hours, go to Concentra: Romulus clinic, non-emergencies
24 hours a day/ 7 days a week
10912 Wayne Rd.
Romulus, MI 48174
(734) 955-7000

Henry Ford Medical Center: Fairlane – emergencies only (UM-D Police will assist by calling EMS)
19401 Hubbard Drive
Dearborn, MI 48126
(313) 928-8278

Spill Procedure **[Provide additional information as it pertains to your research protocol]**

- When a spill occurs, personal safety should always come first.
- Alert and clear everyone in the immediate area where the spill occurred.

For additional information regarding spill response procedures, refer to the EHS Hazardous Waste Spill Response Web page.

Minor Spill Response

A **minor (small) chemical spill** is one that the laboratory staff is capable of handling safely without the assistance of safety and emergency personnel, i.e., (less than 1 Gallon or 3.5 Liters, inside a fume hood). In the event of a minor chemical spill, use the following information for a safe cleanup process.

- Alert people in immediate area of spill.
- If spilled material is flammable, turn off ignition and heat sources. Don't light Bunsen burners or turn on other switches.

- Open outside windows, if possible.
- Use proper personal protective equipment (PPE) as indicated above.
- Avoid breathing vapors from spill.
- Confine spill to as small an area as possible.
- **Do not wash spill down the drain**.
- Use appropriate spill kits/sorbents to absorb spill. Collect contaminated materials and residues and place in container. Contact EHS (313) 583-6692 for proper disposal.
- Clean spill area with water.

Major Spill Response

Report large chemical spills greater than 1 Gallon or 3.5 Liters in corridors or common areas, e.g., hallways, elevators, eating areas, rest rooms, offices, etc., to U-M Dearborn Department of Public Safety (DPS) by calling 911, from any landline campus phone.

A **major (large) chemical spill** requires active assistance from emergency personnel. Do not attempt to clean up a peroxide forming chemical spill that occurs outside a fume hood, or a major spill. In the event of a major chemical spill, use the following information for a safe spill response process.

- Attend to injured or contaminated persons and remove them from exposure.
- Alert people in the laboratory to evacuate.
- If spilled material is flammable, turn off ignition and heat sources. Don't light Bunsen burners or turn on other switches.
- **Call UM-D DPS at *911* immediately for assistance.**
- Close doors to affected area.
- Post warning signs (e.g., "Danger- Chemical Spill. Do Not Enter") or use red Danger tape to keep people from entering the area.
- Have person available that has knowledge of incident and laboratory to assist emergency personnel.

Emergency Reporting

Report all emergencies, suspicious activity, injuries, spills, and fires to the UM-Dearborn DPS by calling 911. Register with the University of Michigan Emergency Alert System via Wolverine Access.

Training of Personnel

All personnel are required to complete the ***General Laboratory Safety Training*** session (**BLS025w** *or equivalent*) via the EHS My LINC. Furthermore, all personnel shall read and fully adhere to this SOP when handling the chemical.

Certification

I have read and understand the above SOP. I have received approval from my Lab Director to perform this procedure. I agree to contact my Lab Director if I plan to modify this procedure.

NAME	SIGNATURE	UMID #	DATE

Lab Director Revision Date

Major Revisions (Tracking purposes only -- Do not print as part of SOP)

DATE	REVISION
09-19-18	Updated EHS name and logo and format and revised the Exposure/unintended contact section (AKJ)
03-18-19	Updated links, certification and formatting (DML).
05—04-20	Updated links, formatting (LS)
08-25-21	Removed 2-methyl-1-butanol and added 3-methyl-1-butanol to List B chemicals in Table 1. Added note that 2-Propanol does not need to be routinely tested if only used for cleaning and is not distilled or otherwise concentrated (LS)
9-14-21	Updated procedures to indicate UM-D contacts and local clinics (TAP)