



Peroxide Forming Chemicals

Principal Investigator (PI) Approval is Required Prior to Performing this Procedure

Description

This standard operating procedure 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.

Potential Hazards

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>
- http://ccehss.berkeley.edu/sites/default/files/pdf/section7_insert17.pdf
- 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

List A: Chemicals that form explosive levels of peroxides without concentration (3 months)¹

| | | |
|--------------------------|-----------------|----------------------------------|
| Butadiene ² | Isopropyl Ether | Tetrafluoroethylene ² |
| Chloroprene ² | Potassium Metal | Vinylidene Chloride |
| Divinyl Acetylene | Sodium Amide | |

List B: Chemicals that form explosive levels of peroxides on concentration (12 months)¹

| | | |
|--------------------------------|---|--------------------------------|
| 1,1-Dimethoxymethane | Benzyl alcohol | Di-n-propoxymethane |
| 1,2-Epoxy-3-isopropoxy propane | Benzyl n-butyl Ether | Dioxane |
| 1,2-Dibenzoyloxyethane | Benzyl Ether | Diethyl Ether |
| 1-Phenylethanol | Benzyl Ethyl Ether | Ethylene Glycol Dimethyl Ether |
| 2-Butanol | Benzyl 1-naphthyl Ether | Isoamyl Ether |
| 2-Hexanol | Cumene | Isophorone |
| 2-Methyl-1-butanol | Cyclohexene | Methy Isobutyl Ketone |
| 2-Penten-1-ol | Cyclooctane | Methyl Acetylene |
| 2-Phenylethanol | Decahydronaphthalene | Methylcyclopentane |
| 2-Propanol | Diacetylene | Other secondary alcohols |
| 4-Heptanol | Diallyl Ether | p-Dibenzoyloxybenzene |
| 4-Methyl-2-pentanol | Dicyclopentadiene | p-Isopropoxypropionitrile |
| 4-Penten-1-ol | Diethoxymethane | Tetrahydrofuran |
| Acetal | Diethyl acetal isoamyl benzyl ether | Tetrahydronaphthalene |
| Acetaldehyde | Diethylene Glycoldimethyl Ether (diglyme) | Vinyl Ethers |
| Allyl Ether | Dimethoxymethane | |

List C: Chemicals that may autopolymerize as a result of peroxide accumulation (12 months)^{1,3,4}

| | | |
|--------------------------|----------------------------------|----------------------|
| Acrylic Acid | Methyl Methacrylate | Vinyl Acetylene |
| Acrylonitrile | Styrene | Vinyl Chloride |
| Butadiene ² | Tetrafluoroethylene ² | Vinyl Pyridine |
| Chloroprene ² | Vinyl Acetate | Vinyladiene chloride |
| Chlorotrifluoroethylene | | |

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.

Engineering Controls

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

- 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 Environment, Health and Safety (EHS) at (810) 766-6763 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 tested at frequent intervals (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 EHS at (810) 766-6763 for more information.

| Peroxidizable Chemical Classification | Dispose or Test After:¹ |
|--|---|
| 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 ² |

¹ Never open or test containers of unknown origin or age or that have visible evidence of peroxides

² Do not store under inert atmosphere.

Personal Protective Equipment (PPE)

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. Contact EHS at (810) 766-6763 to obtain a copy of the Hazard Assessment

Form. The form may be completed by Environment, Health and Safety, workplace supervisor, laboratory supervisor or principal investigator.

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 [OSEH's Glove Compatibility Charts webpage](#).

Transportation and Storage

- 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

Most spent, unused and expired materials are considered hazardous wastes and **must be collected and disposed of within 90-days** by EHS. Contact Environment, Health and Safety (EHS) at (810) 766-6763 for waste containers, labels, manifests, waste collection and for any questions regarding proper waste disposal. Also refer to UM-Flint Hazardous Waste Management Program and EHS webpage <http://www.umflint.edu/ehs/environment-health-and-safety> for more information.

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

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

Exposures/Unintended Contact

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

In general, flush affected eyes or skin with water for at least 15 minutes, then seek medical attention (see below).

- **Eyes:** In case of contact, immediately flush eyes with plenty of water for at least 15 minutes. *Remove contact lenses, if present and easy to do.* Continue rinsing. Get medical aid.
- **Skin:** In case of contact, flush skin with plenty of water. Remove contaminated clothing and shoes. Get medical aid if irritation develops and persists. Wash clothing before reuse.
- **Ingestion:** If swallowed, **do not induce vomiting unless directed to do so by medical personnel.** Never give anything by mouth to an unconscious person. Get medical aid.
- **Inhalation:** If inhaled, remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Get medical aid.

 ***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 UM-Flint DPS. Additionally, employees and supervisors must be sure to report the injury to EHS and complete and submit the [Illness and Injury Report Form](#) to WorkConnections within 24 hours. Follow the directions on the WorkConnections website [Forms Instructions](#) to obtain proper medical treatment and follow-up.

If you were involved in or observed an incident or near miss, please complete the [EHS Laboratory Incident and Near-Miss Report Form](#). This will be valuable in improving laboratory safety on UM-Flint campus.

TREATMENT FACILITIES:

| <u>MAJOR INJURIES</u> | <u>MINOR INJURIES –During Business Hours</u> | <u>MINOR INJURIES –After Business Hours</u> |
|---|--|---|
| <p>Genesys Hospital One Genesys Parkway Grand Blanc, MI 48439 (810) 606-5710</p> <p>Hurley Medical Center One Hurley Plaza Flint, MI 48503 (810) 262-9000</p> <p>McLaren Hospital Flint 401 South Ballenger Hwy Flint, MI 48532 (810) 342-2000</p> | <p>Genesys Occupational Health Network 1460 Center Rd. Burton, MI 48509 (810) 715-4620 Mon. to Fri. 7:30 am to 10 pm Sat. & Sun. Noon to 8 pm</p> <p>McLaren Flint-Burton OCC Center 1459 S. Center Rd. Burton, MI 48509 (810) 496-0900 Mon. - Fri. 8 am to 8 pm Sat & Sun 10 am to 2 pm</p> | <p>Downtown Flint 420 S. Saginaw St. Flint, MI 48502 (810) 762-1550</p> <p>Genesys East 1096 S. Belsay Rd, Suite F Burton, MI 48509 (810) 743-3351</p> <p>Genesys North 4154 W. Vienna Rd Clio, MI 48420 (810) 686-7397</p> <p>Genesys South 8447 N. Holly Rd Grand Blanc, MI 48439 (810) 603-0856 Mon. - Fri. 6 to 10pm / Sat. & Sun. 1-10pm</p> |

Click [here](#) for more information on the UM – Flint Emergency Preparedness and Response Plan.

Spill Procedures

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

A **minor (small) chemical spill** is one of a known chemical 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*). A **major/large chemical spill** requires active assistance from emergency personnel.

Spill Response Steps:

MINOR CHEMICAL SPILL

- 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 at (810) 766-6763 for proper disposal.
- Clean spill area with water.

MAJOR CHEMICAL SPILL

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 the University of Michigan-Flint DPS at 911.

- 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 University of Michigan – Flint Public Safety Department (DPS) at 911 immediately for assistance.**
- Close doors to affected area.
- Post warnings to keep people from entering the area.
- Have person available that has knowledge of incident and laboratory to assist emergency personnel.

Additional Spill Links:

- www.oseh.umich.edu/pdf/chemspil.pdf
- <http://www.oseh.umich.edu/emer-chemical.shtml>.

Report all emergencies, suspicious activity, injuries, spills, and fires to the UM-Flint Department of Public Safety (DPS) at 911 from any university telephone or (810) 762-3333 from cell phone or non-university telephone. Register with the [University of Michigan Emergency Alert System](#) via Wolverine Access. Also, preprogram the UM-Flint DPS telephone number (810) 762-3333 into your cell phone for quick, easy use.

Training of Personnel

All personnel are required to complete Laboratory Safety Training. Documentation of the training is required. This training can be accomplished by completing the ***Comprehensive Laboratory Safety*** session (**BLS009** or equivalent) via [MyLINC](#), or UM-Flint EHS on-line training or other equivalent approved by EHS. 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 agree to contact my Supervisor or Lab Manager if I plan to modify this procedure.

| Name | Signature | UM ID # | Date |
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Principal Investigator _____

Revision Date _____