UMassAmherst | Environmental Health & Safety

Peroxide-Forming Materials SOP

What are peroxide-forming materials and what are the hazards?

Peroxide-forming materials are items that can react with molecular oxygen over time under normal conditions of use and storage to form peroxides. Peroxides formed in this way can be potentially shock sensitive and explosive, particularly when dry. Many different materials are capable of peroxide formation, and certain molecular structures are known to exhibit this behavior. Known materials are typically categorized in lists by the hazard level and type of the peroxide formed. List A items are materials that are known to form dangerous peroxides in hazardous levels in normal conditions of storage. List A[1] items include:

- Potassium metal
- Potassium amide
- Sodium amide
- Isopropyl ether
- Vinylidene chloride
- Divinylacetylene
- Butadiene
- Chloroprene
- Tetrafluoroethylene

List B items are materials that are known to form dangerous peroxides at potentially hazardous levels when the material is used or stored in such a way that the peroxides could increase in concentration. Many common laboratory solvents are list B materials, including, but not limited to:

- Diethyl ether
- Tetrahydrofuran (THF)
- 1,4-dioxane
- Decalin
- Cyclohexanol
- Furan
- Glyme
- Diglyme
- Isopropyl benzene
- Tetralin

List C materials are vinyl compounds that form peroxides that are capable of initiating free radical polymerization in the neat vinyl monomer. Polymerization processes that occur in this way can be dangerous as the propogation reaction is exothermic, and the probability of termination reactions occurring decreases as localized viscosity changes due to the polymerization process limit diffusion. Common list C items include, but are not limited to:

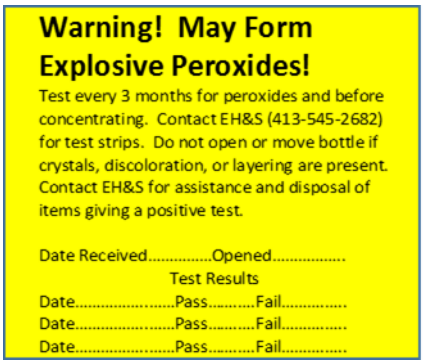
[1] IUPAC names for all peroxide-forming materials listed here are included as an appendix at the end of this document.

- Styrene
- Methyl methacrylate
- Vinyl acetate
- Vinyl chloride
- Acrylonitrile
- Vinyl pyridine

Categorization of materials known to form peroxides led to the understanding that certain molecular structures are prone to peroxide formation. Known structures include the following functional groups that can form stable free radicals and have abstractable hydrogen or that have adjacent carbon bonded to a hydrogen (i.e., hydrogen on the alpha carbon):

- Ethers
- Allylic compounds
- Benzylic compounds
- Aldehydes
- Amides
- Vinyl Compounds, particularly vinyl halides
- Secondary alcohols

UMass has implemented a program for the management of peroxide-forming materials on campus. As part of the program, peroxide-forming materials that are received in CEMS are labeled with the yellow sticker shown on the right so that these can be easily identified. New stickers can be requested through CEMS if needed.



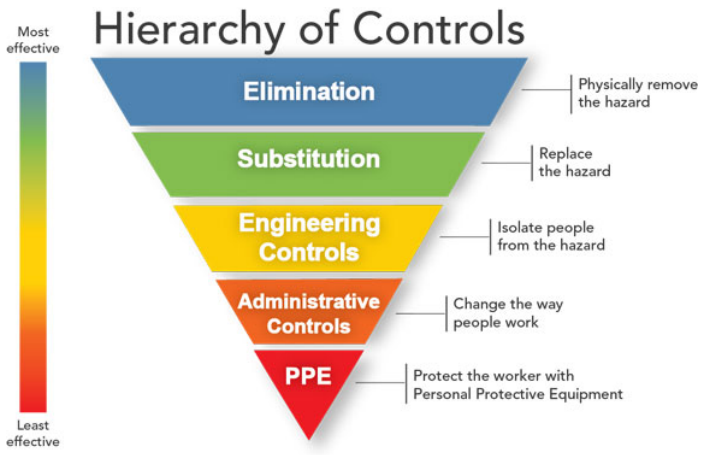
What Activities Could Pose a Risk?

Peroxides that are capable of detonation are most likely to do so when they are solidified or concentrated and exposed to a source of initiation, such as heat, light, or friction. As such, any activities or storage conditions that can concentrate or precipitate peroxides or provide a source of initiation are potentially problematic.

How Can Exposures and Physical Hazards Be Minimized?

When working with any hazardous material or process, always conduct a thorough risk assessment and employ the hierarchy of controls to minimize risk. Some specific applications of the hierarchy of

controls to the unique hazards of peroxide-forming compounds are listed below. Always apply the controls in the order of most effective to least effective (see graphic), and apply as many controls as possible to reduce the risk to the lowest achievable level.



Elimination/Substitution

- Avoid working with peroxide-forming materials whenever possible.

Engineering Controls

- Work must be conducted in fume hoods, glove boxes, or other appropriate enclosures when using open containers of volatile liquids.

Administrative Controls

- Avoid storing peroxide formers at low or high temperatures. Low temperatures can cause peroxides to precipitate. High temperatures can accelerate peroxide formation. Peroxide-forming materials should be stored at the temperature recommended by the manufacturer that is listed on the container or in the SDS.
- Clean the rim of bottles after pouring to ensure peroxides do not accumulate around cap threads, particularly for volatile items that can evaporate.
- Ensure that peroxide-forming materials do not become contaminated. Materials that can generate free radicals can initiate peroxide formation. Do not insert pipets or other items into stock containers. Do not return dispensed material to stock containers. Do not seal permanent storage containers with rubber stoppers or septa as this can lead to contamination of the material. Refer containers of potentially contaminated items for hazardous waste disposal.
- Never handle containers of peroxide-forming materials that show evidence of crystallization, layering, or discoloration.
- Ensure laboratory personnel are thoroughly trained on the hazards of peroxide-forming compounds, hazard mitigation techniques, and emergency procedures.
- Avoid concentrating peroxide-forming materials whenever possible. Techniques that involve concentrating these items, such as rotovapping, distillation, recrystallization, or other procedures that involve evaporation are potentially hazardous if peroxides are present. Use only the minimal amount of heating necessary for performing evaporation to ensure this occurs in a controlled fashion. Warm water baths are great options for low-boiling solvents like diethyl ether.
- Perform peroxide testing every three months on peroxide-forming materials. Peroxides can be tested in materials by means of commercially available test strips that contain a peroxidase enzyme (that decomposes the peroxide) and a redox active indicator (that reacts with the

decomposed peroxide to produce a blue colored compound). Other methods for testing peroxides exist, however, the test strips are easy to use and accurately detect all types of peroxides (i.e., fully organic peroxides and organic hydrogen peroxides). Many wet methods only detect the presence of organic hydrogen peroxides and can miss the presence of the typically more dangerous fully organic peroxides. Test strips are available by request through CEMS. Please see the Peroxide-forming Materials Management Program for additional information: https://ehs.umass.edu/peroxide-forming-materials-management-program. It is also recommended that peroxide-forming materials are tested for peroxides prior to concentrating. Promptly refer any item giving positive peroxide tests for hazardous waste disposal.

- Use materials containing stabilizers whenever possible. Stabilizers, such as BHT (butylated hydroxytoluene) and ethanol, can be added to peroxide-forming materials to scavenge free radical species that lead to peroxide formation. Always purchase and use stabilized materials when possible. It is important to understand that even stabilized materials can form peroxides and eventually stabilizers will be depleted over time. As such, even stabilized materials must be tested for peroxide formation every three months.
- Avoid storing peroxide-forming materials past the manufacturer's expiration date. Peroxide formers should be completely used or discarded before the expiration date, however, expired items may be kept and used if it can be demonstrated through testing that these are free of peroxides.
- Store peroxide-forming compounds away from heat and light and avoid conditions that might create friction. Light can help to initiate peroxide formation and can also initiate dangerous peroxide decomposition. Store peroxide formers away from light and in light blocking containers (i.e., amber glass, aluminum cans). Do not use ground glass joint stoppers for storage containers.
- Avoid storing or using peroxide-forming materials in ways that cause exposure to oxygen. Minimizing exposure to oxygen reduces the rate and quantity of peroxide formation. Minimize exposure to oxygen. Store and use materials under a blanket of inert gas (e.g., sure sealed containers, solvent dispensing systems) or in an inert atmosphere (e.g., glovebox) whenever possible. Keep containers tightly closed when not in use. Never use squirt bottles for peroxide-forming compounds.

Personal Protective Equipment

- Always wear appropriate eye protection. Chemical splash goggles and safety glasses rated for impact (ANSI Z87+) should be worn.
- A lab coat must be worn for all work with peroxide-forming materials.
- Wear appropriate gloves. For liquid suspensions, ensure glove selection is based on the solvents and other materials that are used. Remove and dispose of contaminated gloves promptly.

Waste Handling

All lab waste containing peroxide-forming compounds should be handled as hazardous waste. Items that fail peroxide testing should be immediately referred for hazardous waste disposal. To have the waste picked up by EH&S staff, complete a Hazardous Materials Pickup Request Form in CEMS.

Exposure and Spill Procedure

In the event of a spill involving a peroxide-forming compound that does not involve the contamination of a person, the material may be cleaned up if it is safe to do so following the general procedure for small spills detailed in the University's Chemical Hygiene Plan.

- Ensure that cleaning up the material will not generate airborne dust or aerosols.
    - Spills of highly volatile solvents outside of enclosures (fume hoods or other enclosure devices) should be immediately referred to EH&S (413-54-2682) and the area should be evacuated. Do not permit entry to the area until EH&S arrives.
- Place all items used for cleanup in a labeled hazardous waste container and request a pickup through CEMS.
- If at any point you are uncomfortable cleaning up the spill or require assistance, stop and call EH&S (413-545-2682).

Exposures to hazardous materials should follow the general procedures for exposures outlined in the University's Chemical Hygiene Plan.

For a major exposure, detonation, or fire requiring the use of a drench shower or eyewash:

- Have someone call 911 (report the building name, room number, and street address) or 413-545-3111 (or simply 5-3111 from a campus line) to report the incident and request medical help. Have someone obtain the SDS for the material (if there is one) and provide it to the first responders when they arrive, if possible.
- Help the affected individual to position their head over the eyewash and activate it, or position them under the drench shower and activate it as appropriate.
    - Always ensure your own safety before helping others. Only help if it is safe for you to do so.
    - Wear gloves, safety glasses, and a lab coat.
- If using an eyewash: Instruct the affected individual to open their eyes and roll them around while the water is flowing. Help them to hold their eyes open if necessary and safe to do so.
- If using a drench shower: Remove all clothing from the affected area while under the shower.
- Flush the affected area for 15 minutes with water.

For minor exposures such as a spill to readily accessible extremities (e.g., hand):

- Flush the affected area in a sink equipped with potable water for at least 15 minutes.
- Go to University Health Services (UHS) for medical evaluation, and tell them you have had a lab exposure.
- Provide the SDS for the material if possible.

- Notify EH&S (413-545-2682) as soon as possible and complete the lab incident form (https://ehs.umass.edu/lab-incidents-and-lab-incident-report-form).

References and Additional Resources

- Jackson, H. L.; McCormack, W. B.; Rondestvedt, C. S.; Smeltz, K. C.; Viele, I. E. J. *Chem. Educ.* **1970**, 47, A175-A188.
- Kelly, R. J., Review of Safety Guidelines for Peroxidizable Organic Chemicals. *J. of Chemical Health and Safety* **1996**, 3, 28-36.
- Clark, D., Peroxides and Peroxide-forming Compounds. *J. of Chem. Health and Safety* ***2001****, 8 (5), 12-22.*
- NRC (National Research Council), *Prudent Practices in the Laboratory, Handling and Management of Chemical Hazards,* National Academy Press: Washington, DC, 2011.

APPENDIX A: IUPAC Names and CAS Numbers For Included Peroxide-Forming Materials

LIST A:

- Potassium (7440-09-7)
- Potassium amide (17242-52-3)
- Sodium amide (7782-92-5)
- 2-[(Propan-2-yl)oxy]propane (108-20-3**)**
- 1,1-Dichloroethene (75-35-4)
- 1,5-Hexadien-3-yne (821-08-9)
- 1,3-Butadiene (106-99-0)
- 2-Chloro-1,3-butadiene (126-99-8)
- 1,1,2,2-tetrafluoroethene (116-14-3)

LIST B:

- Ethoxyethane (60-29-7)
- Oxolane (109-99-9)
- 1,4-Dioxacyclohexane (123-91-1)
- Decahydronaphthalene (91-17-8)
- Cyclohexanol (108-93-0)
- 1,4-Epoxybuta-1,3-diene (110-00-9)
- Dimethoxyethane (110-71-4)
- 1-Methoxy-2-(2-methoxyethoxy)ethane (111-96-6)
- (Propan-2-yl)benzene (98-82-8)
- 1,2,3,4-tetrahydronaphthalene (119-64-2)

LIST C:

- Ethenylbenzene (100-42-5)
- methyl 2-methylpropenoate (80-62-6)
- Ethenyl ethanoate (108-15-4)
- Chloroethene (75-01-4)
- Prop-2-enenitrile (107-13-1)
- 2-Ethenylpyridine (100-69-6)