

PEROXIDE-FORMING CHEMICALS

STANDARD OPERATING PROCEDURE

Type of SOP: Process Hazardous Chemical Hazard Class

Department: _____ **Building:** _____ **Room #:** _____

Principal Investigator: _____ **Phone #:** _____

Prepared By: _____ **Email:** _____ **Date:** _____

1. HAZARD OVERVIEW



EXPLOSIVE



FLAMMABLE

Chemicals in this class are thermally unstable and may undergo exothermic self-accelerating decomposition. They may also be explosive, burn rapidly, be sensitive to impact or friction, or react dangerously with other substances. Therefore, all chemicals in this band are considered highly hazardous.

Organic peroxides can be obtained via:

- A. Purchase or synthesis like benzoyl peroxide, or
- B. Occur spontaneously when certain chemicals are
 - Stored for prolonged periods;
 - Concentrated through distillation, evaporation, or air exposure; or
 - A result of polymerization.

This SOP only deals with the peroxides that can form in the lab. Organic peroxides that are purchased are addressed in a separate NJIT SOP template titled "Organic Peroxides and Self-Reactive Chemicals".

Organic peroxides are organic compounds containing the peroxide functional group (R-O-O-R'), where R = an organic group. These materials are sensitive to oxygen, heat, friction, impact, light, and strong oxidizing and reducing agents.

Peroxide forming chemicals are compounds that undergo auto-oxidation to form organic hydroperoxides and/or peroxides when exposed to the oxygen in air. **Ether bottles that have evaporated to dryness are especially dangerous.** A peroxide present as a contaminant in a reagent or solvent can be very hazardous and can change the course of a planned reaction. Auto-oxidation of organic materials (*solvents and other liquids are most frequently of primary concern*) proceeds by a free-radical chain mechanism. For the substrate R—H, the chain is initiated by ultraviolet light.

The unusual stability problems of this class of compounds make them a serious fire and explosion hazard that requires careful management.

Examples of specific compounds that are prone to forming peroxides:

Acetal	Diisopropyl ether	Sodium amide
Butadiene	Dioxane	Styrene
Cumene	Dimethyl ether	Tetrahydrofuran

Cyclohexene	Divinyl acetylene	Tetrahydronaphthalene
Cyclooctene	Ethyl ether	Tetralin
Decahydronaphthalene	Ethylene glycol dimethyl ether	Vinyl acetate
Decalin	Isopropyl ether	Vinyl acetylene
Diacetylene	Methyl acetylene	Vinyl chloride
Dicyclopentadiene	Methylcyclopentane	Vinyl ethers
Diethylene glycol	Potassium metal	Vinylidene chloride

Most of the above specific examples fall into the following chemical structure types:

- Ethers, especially cyclic ethers and those containing primary and secondary alkyl groups (*Never distill an ether before it has been shown to be free of peroxide.*)
- Aldehydes
- Compounds containing benzylic hydrogen
- Compounds containing allylic hydrogens (C=C-H), including most alkenes; vinyl, and vinylidene compounds
- Compounds containing a tertiary C-H group (e.g., decalin and 2,5-dimethyl hexane)

2. PERSONAL PROTECTIVE EQUIPMENT (PPE)

At minimum, safety glasses, lab coats, and gloves are required. Additional or more protective PPE may be required. Please refer to the NJIT Chemical Hygiene Guide and Hazard Assessment Form to determine the proper PPE for handling corrosive materials.



3. ENGINEERING/VENTILATION CONTROLS

- Use at least one of the following engineering controls:
 - ~ Chemical Fume Hood: Work inside a certified chemical fume hood at all times.
 - ~ Glovebox: Use when inert or dry atmospheres are required.
 - ~ Portable Explosion Shield: May also be required to control the risk of explosion.
 - ~ Gas Cabinet: If the material is classified as a compressed gas.
- Use bonding and grounding equipment to minimize the likelihood of an ignition from static electricity during the transfer of all Class I flammable liquids – see the *Advanced Flammable & Combustible Liquids* SOP in the NJIT SOP library.
- Know where your safety equipment is located (*e.g., fire extinguisher, eye wash/safety shower, and first aid kit*).
- Have the appropriate fire extinguisher available.

Please review the NJIT Chemical Hygiene Guide and the Safe Chemical Fume Hood Use Guide for information on the proper use of a chemical fume hood and criteria for implementing engineering controls.

Chemical Fume Hood Glovebox Biological Safety Cabinet Other _____

Room Location of Unit(s): _____

4. SPECIAL HANDLING PROCEDURES AND STORAGE REQUIREMENTS

- At least one other person should be present in the same laboratory, or nearby, when any work involving peroxide forming chemicals is carried out.
- Eliminate or substitute a less hazardous material when possible.
- Design your experiment to use the smallest amount of material possible to achieve the desired result.
- Verify your experimental set-up and procedure prior to use.
- Ensure all equipment is appropriate for the task.
- Avoid inadvertent incompatibles:
 - Heat sources, open flames and oxidizers
 - Consult Faculty/PI and EHS if work involves large quantities.
- Conduct distillation, extraction or crystallization, and other processes that concentrate the organic peroxides only when it is explicitly known safe to do so.
- Reduced temperature can impede the peroxide-scavenging ability of added preservatives and may actually increase peroxide formation. Reduced temperature may also decrease the solubility of any solid peroxides that have formed, thereby increasing the hazard.

Hazard Class-Specific Practices:

- Diethyl ether **must** be used in a fume hood.
- THF-containing mobile phase **must** be prepared in the fume hood, but may be used outside of the fume hood on HPLC equipment as long as the mobile phase supply container is covered.
- Refrigeration of diethyl ether is not recommended.

Storage:

- Purchase and use the minimum amount of material necessary to perform your research.
- Label peroxide-forming materials clearly and promptly with the date upon receipt or synthesis. Dispose of old materials when past their expiration date. For many ethers, this is usually in the **6 to 12 months** range.
- The presence of peroxides in some cases is indicated by the appearance of a **precipitate or oily layer** in the container.
- Store all peroxide forming materials inside of a flammable cabinet.
- Review your inventory frequently to prevent peroxide-forming chemicals from becoming unsafe.
- **Do not** handle old or expired peroxide-forming materials that are discovered. Inform your Faculty/PI and EHS immediately, and dispose of the item as a hazardous waste.

- Ether solvents stored in solvent drying cartridge manifolds can be excluded since these are kept air-free under a positive pressure of inert gas. The dangers associated with ether solvents depend on and can be exacerbated by these factors:
 - Exposure to air (oxygen)
 - Exposure to light
 - Temperature
 - Friction
 - Shock
 - Concentration
 - Chemical structure
 - Distillation that removes stabilizers
 - Slow evaporation of volatile ethers over time
 - Impurities

5. INCIDENTS AND ACCIDENTS

Absorb spillages with sand, earth or other non-combustible material. Collect the spill-sand mixture in an appropriate waste container then clean the surface using a suitable cleaning agent. Please review the SDS, verify with the manufacturer, or contact EHS for proper spill procedures for the specific peroxide.

Laboratory personnel are to report all occupational injuries or illnesses to Faculty/PI as soon as practical. The Faculty/PI and laboratory personnel must submit the required paperwork to NJIT EHS Department. See the the Emergency Response Guidelines posted in the laboratory or Emergency Procedures section of the NJIT CHG for proper procedures involving an injury, exposure, fire, or release/spill of a hazardous material.

In the event of an emergency, DIAL 9-1-1 to activate emergency response personnel.

6. SPILL AND DECONTAMINATION

If there are incidental drips of peroxidizable solvent on the fume hood work surface, secure ignition sources, and lower the sash to allow for evaporation. If bench paper becomes contaminated, it **must** be removed, replaced and disposed of as hazardous waste.

Wear proper PPE. Please review the SDS, verify with the manufacturer, or contact EHS for proper decontamination procedures. Dispose of all used contaminated disposables in the appropriate waste stream following the Waste Disposal Section of the NJIT CHG.

Decontamination Solution(s): _____

Additional Spill / Decontamination Requirements:

7. WASTE DISPOSAL

Follow the practices and procedures in accordance with the NJIT Laboratory Waste Management Program to properly dispose of waste.

Additional Waste Disposal Requirements:

8. PRIOR APPROVAL/REVIEW

9. DESIGNATED USE AREA

Designated Use Area Location(s): _____

10. SAFETY DATA SHEETS

Location of SDS: _____

11. LAB-SPECIFIC INFORMATION (required) ([Examples](#) of appropriate content)