



SACRAMENTO
STATE

Peroxide Forming Chemicals

STANDARD OPERATING PROCEDURE (SOP)

Type of SOP: Process Hazardous Chemical Hazardous Class

All personnel who are subject to these SOP requirements must review a completed SOP and sign the associated training record. Completed SOPs must be readily accessible to laboratory personnel. Electronic access is acceptable. SOPs must be reviewed, and revised where needed, as described in the [CSUS Chemical Hygiene Plan](#). Note that not all hazardous chemicals are appropriately addressed in a single control-banded SOP, and some chemicals are subject to several control-banded SOPs. Unique properties of each chemical must be considered before including it into a control band.

Date SOP Written: _____ Approval Date: _____

SOP Prepared by: _____

SOP Reviewed and Approved by (name/signature): _____

Department: _____

Laboratory Supervisor/Principal Investigator: _____

Email: _____ Phone: _____

Emergency Contact(s): _____ Phone: _____

Location(s) Building (s): _____

covered by _____ Lab

SOP: Room #(s): _____ Phone: _____

1. HAZARD OVERVIEW

A number of commonly used chemicals can undergo auto-oxidation to form unstable and dangerous peroxide products. Under normal storage conditions this reaction can be initiated by light, heat, introduction of a contaminant, oxygen, loss of an inhibitor, or concentration. Exposing these organic peroxides to heat, light, friction, or mechanical shock can result in violent explosions that may result in serious injury or death. For this reason, it is important to identify and control chemicals which form potentially explosive peroxides.

Peroxide forming chemicals may also have other hazardous properties including toxicity. Refer to the SDS for the specific chemical to determine specific toxicity and other hazards.

2. PROCESS OF PEROXIDE FORMATION IN CHEMICALS

A wide variety of organic compounds spontaneously form peroxides by a free-radical reaction with molecular oxygen in a process of auto-oxidation. Although ethers are the most notorious in this regard, many other moieties are susceptible to the same process. The rate of peroxide formation is dependent on the specific chemical, exposure to oxygen, and the presence of inhibitors such as butylated hydroxytoluene (BHT).

There are not specific hazard classifications for peroxide forming chemicals defined by Cal/OSHA or GHS. Depending on the danger of peroxide accumulation, peroxide-forming chemicals can be divided into three categories (Group/List A-C).

Listed in Table 1 are three groups of chemicals that form potentially explosive peroxides. Please note that this is not an exhaustive list. Users must consult the chemicals Safety Data Sheet (SDS) and/or other sources of information for the chemicals used (and stored) to determine their peroxide forming potential.

Group A:

- Materials may spontaneously form peroxides that will make the materials shock- or heat-sensitive “on the shelf,” that is, without any further concentration through evaporation or distillation.

Group B:

- Materials that form explosive peroxides upon concentration. Distillation or evaporation of these solvents can cause dangerous concentrations of peroxides.

Group C:

- Materials that contain reactive alkene groups and can undergo runaway polymerization reactions. Peroxides can initiate polymerization leading to the release of large amounts of energy.

Table 1: List of Common Peroxide Forming Chemicals

Group A: Chemicals that form explosive levels of peroxides without concentration^{1,2}		
Divinyl acetylene	Potassium metal	Butadiene ³
Divinyl ether	Potassium amide	Chloroprene ³
Isopropyl ether	Sodium amide	Tetrafluoroethylene ³
Vinylidene chloride		
Group B: Chemicals that form explosive levels of peroxides on concentration^{1,2,4}		
Acetal	Diethyl ether (ether)	4-Methyl-2-pentanol
Acetaldehyde	Diethylene glycol dimethyl ether (diglyme)	2-pentanol
Benzyl alcohol	Dioxanes	4-Penten-1-ol
2-Butanol	Ethylene glycol ether acetates (glyme)	1-Phenylethanol
Cumene	Furan	2-Phenylethanol
Cyclohexanol	4-Heptanol	2-Propanol (Isopropanol, isopropyl alcohol) ⁵
2-Cyclohexen-1-ol	2-Hexanol	Tetrahydrofuran (THF)
Cyclohexene	Methylacetylene (gas)	Tetrahydronaphthalene (Tetralin)
Decahydronaphthalene	3-methyl-1-butanol	Vinyl ethers
Diacetylene	Methylcyclopentane	Other secondary alcohols
Dicyclopentadiene	Methyl isobutyl ketone	
Group C: Chemicals that may autopolymerize as a result of peroxide accumulation^{1,2,6}		
Acrylic acid	Methyl methacrylate	Vinylacetylene
Acrylonitrile	Styrene	Vinyl chloride
Butadiene (gas)	Tetrafluoroethylene (gas)	Vinyl pyridine
Chloroprene (gas)	Vinyl acetate	Vinylidene chloride
Chlorotrifluoroethylene		

¹ Materials other than those listed may form peroxides. Review the references and contact EH&S for further information.

Applies only to pure materials.

² Data adapted from (Kelly 1996) and (Clark 2001)

³ When stored as a liquid

⁴ WARNING! May become unstable if concentrated intentionally or accidentally by the user.

⁵ Isopropanol/water mixtures below 91% do not form explosive concentrations of peroxides under normal storage conditions.

⁶ If a chemical from group C contains inhibitors, do not store under inert atmosphere.

3. RECEIVING AND SHELF LIFE

All chemicals received must be reviewed to determine whether they are a peroxide former. All peroxide formers must be **labeled upon receipt**. This label must include the date received, the type of peroxide former, how frequently it is to be tested, and space to note when it is first opened. Table 2 lists the safe storage and testing frequencies for peroxide forming chemicals. Never open or test containers of unknown age or those that have visible evidence of peroxides.

Table 2: Safe Storage and Testing Frequencies for Peroxide Forming Chemicals

Safe Storage Period	Group A	Group B	Group C
Open & Uninhibited	3 months	12 months	24 hours
Open & Inhibited	12 months	12 months	12 months
Unopen	12 months	12 months	12 months
Examples	1,3-butadiene, isopropyl ether, Vinylidene chloride	Tetrahydrofuran (THF), Ethers, Isopropanol, Dioxanes, 2-Butanol, Acetaldehyde	1,3-Butadiene, Acrylonitrile, Methyl acrylate, Styrene, Vinyl Chloride
Testing Frequency	Group A	Group B	Group C
Within Safe Storage Period	3 months	6 months	6 months
After Safe Storage Period - Uninhibited	Must dispose by 3 months	Test every 6 months and before each use	Dispose of by 24 hours
After Safe Storage Period - Inhibited	Must dispose by 12 months	Test every 6 months and before each use	Test every 6 months and before each use

STORAGE

Storing peroxide-forming chemicals should be part of a comprehensive chemical storage plan. The SDS for each material should be read to determine specific storage recommendations and conditions. Additional guidance for chemical storage and segregation can be found in the [CSUS Chemical Hygiene Plan](#).

- Refer to Table 2 for the safe storage period for each class of peroxide forming chemicals. Extended storage provides for accumulation of unstable products.
- Storage of peroxide forming chemicals in open, partially empty, or transparent containers greatly increases the risk of peroxide formation. Store away from light and heat. Store in amber bottles if possible.
- Protect from heat, light, friction, static discharge, mechanical shock, contact with a catalyst, physical damage or other conditions listed in the SDS that the chemical may be sensitive to.

4. ADMINISTRATIVE CONTROLS

The following elements are required:

1. Complete the [Laboratory Safety Fundamentals](#) (or approved equivalent) training prior to working in the laboratory;
2. Complete laboratory-specific safety orientation and training on laboratory-specific safety equipment, procedures, and techniques to be used prior to receiving unescorted access to the laboratory;
3. Demonstrate competency to perform the procedures to the Laboratory Supervisor, Principal Investigator (PI), Safety Officer, and/or trainer;
4. Be familiar with the location and content of any applicable Safety Data Sheets (SDSs) for the chemicals to be used (online SDSs can be accessed from [Risk & Safety Solutions](#));
5. Implement good laboratory practices, including good workspace hygiene;
6. Inspect all equipment and experimental setups prior to use;
7. Follow best practices for the movement, handling, and storage of hazardous chemicals (see Chapters 5 and 6 of [Prudent Practices in the Laboratory](#) for more detail). An appropriate spill cleanup kit must be located in the laboratory. Chemical and hazardous waste storage must follow an appropriate segregation scheme and include appropriate labeling. Hazardous chemical waste must be properly labelled, stored in closed containers, in secondary containment, and in a designated location;
8. Do not deviate from the instructions described in this SOP without prior discussion and approval from the PI and/or Laboratory Supervisor.
9. Notify the PI and/or Laboratory Supervisor of any accidents, incidents, near-misses, or upset condition (*e.g.*, unexpected rise or drop in temperature, color or phase change, evolution of gas) involving Peroxide forming chemicals described in this SOP; and
10. Abide by the department or college-specific working alone policy, if applicable.

For Peroxide forming chemicals, the following are also required:

TESTING AND INSPECTING FOR PEROXIDE FORMATION

Visual Inspection

Always perform a visual inspection of a peroxide forming chemical first. Never try to force open a rusted or stuck cap on a container of peroxide-forming chemicals. If there is evidence of possible peroxide formation, testing should not be performed, and EH&S should be contacted immediately to pick up. Evaluation of alkali metals and their amides is based on visual inspection criteria only.

Evidence of possible peroxide formation includes:

For liquids:

- Solids or crystals on the lid or around the cap
- Visible discoloration
- Liquid stratification

For solids:

- Formation of surface crust (ex: potassium metal forms a yellow or orange superoxide at the surface)
- Discoloration of the solid

Testing Procedure

Follow the testing frequency guidelines outlines in Table 2 which include testing before distilling or evaporating peroxide forming chemicals and periodic testing. Visually inspect all peroxide formers prior to testing or use. Only chemicals that pass visual inspection should be tested. The most convenient method for testing for peroxide formation is to use peroxide test strips that are a semi-quantitative colorimetric method. Read and follow the manufacturer's instructions to use peroxide test strips. Here are the generic steps:

- Dip the test strips into the test solution for 1 second.
- Shake off any excess liquid.
- Wait for a period of time (manufacturer specific) before comparing test field with color scale.
- Take the value which matches closest with the colored test field.
- To test for hydroperoxides in organic solvents, the test zone is wetted with one drop of water after the evaporation of the solvent.
- Record the testing date and results on the label.

Actions

- Less than 20 ppm: You may keep the chemical until its safe storage period and continue testing periodically according to the frequency in Table 2.
- Around 20 ppm: Request disposal from EH&S. Create waste tag through WASTE and indicate peroxide levels.
- Above 50 ppm: Contact EH&S immediately for pickup.

5. PERSONAL PROTECTIVE EQUIPMENT (PPE)

At a minimum, long pants (covered legs) and closed toe/closed heel shoes (covered feet) are required to enter a laboratory or technical area where hazardous chemicals are used or stored.

In addition to the minimum attire required upon entering a laboratory, the following PPE are required for work with Peroxide forming chemicals:

- A. Eye Protection: Eye protection is required for all work with Carcinogens.
 - i. At a minimum ANSI Z87.1-compliant safety glasses are necessary.
 - ii. Splash goggles may be substituted for safety glasses, and are required for processes where splashes are foreseeable or when generating aerosols.
 - iii. Ordinary prescription glasses will NOT provide adequate protection unless they also meet the Z87.1 standard and have compliant side shields.
- B. Body Protection: At a minimum a chemically compatible laboratory coat that fully extends to the wrist is necessary.
 - i. Flame resistant lab coats should be used when working with chemicals or processes that increase the risk of fire. Avoid wearing synthetic clothing when possible.
 - ii. For chemicals that are corrosive and/or toxic by skin contact/absorption additional protective clothing (*e.g.*, face shield, chemically resistant apron, disposable sleeves, etc.) are required where splashes or skin contact is foreseeable.
- C. Hand Protection: Hand protection is needed for the activities described in this SOP. Define the type of glove to be used based on: A) the chemical(s) being used, B) the anticipated chemical contact (*e.g.*, incidental, immersion, etc.), C) the manufacturers' permeation/compatibility data, and D) whether a combination of different gloves is needed for any specific procedural step or task.

6. SPILL AND EMERGENCY PROCEDURES

Follow the guidance for chemical spill cleanup from the [CSUS Chemical Hygiene Plan](#), unless specialized cleanup procedures are described below. Emergency procedure instructions for CSUS campus are contained in the campus [Chemical Hygiene Plan](#) and in building specific [Emergency Action Plans](#).

For spills of solid materials, DO NOT dry sweep.

7. WASTE MANAGEMENT AND DECONTAMINATION

Hazardous waste must be managed according to the [CSUS Chemical Hygiene Plan](#). Hazardous waste must be stored in compatible containers that are in good condition, must be stored in secondary containment in a designated area, and must be properly labeled. In general, hazardous waste must be removed from your laboratory within 9 months of the accumulation start date. Hazardous waste pick up requests must be completed through the RSS WASTE application ([Risk & Safety Solutions](#)) or EH&S [Hazardous Waste Pickup Request Form](#). If there is evidence of peroxide formation or the peroxide forming chemical tested at 50 ppm peroxides or greater, contact EH&S immediately.

8. DETAILED PROTOCOL

Documentation of Standard Operating Procedure Training

(Signature of all users is required)

- ✓ Prior to using **Carcinogens**, laboratory personnel must be trained on the hazards described in this SOP, how to protect themselves from these hazards, and emergency procedures.
- ✓ Ready access to this SOP and to a Safety Data Sheet for each hazardous material described in the SOP must be made available.
- ✓ The Laboratory Supervisor must ensure that their laboratory personnel have attended appropriate laboratory safety training or refresher training within the last three years.
- ✓ Training must be repeated following **any** revision to the content of this SOP. Training must be documented. This training sheet is provided as one option; other forms of training documentation (including electronic) are acceptable but records must be accessible and immediately available upon request.

Designated Trainer: *(signature is required)*

I have read and acknowledge the contents, requirements, and responsibilities outlined in this SOP:

Name	Signature	Trainer Initials	Date