



PEROXIDE-FORMING CHEMICAL SAFETY SUPPLEMENTAL GUIDANCE

I. Purpose

This document provides procedures for managing peroxide-forming chemicals.

II. Objective

The objective of this document is to help prevent hazards to personnel storing/using peroxide-forming chemicals and reduce disposal costs to the university.

III. Scope

The procedure shall apply to all Cal Poly Pomona faculty, staff, and students.

IV. Guidelines:

PEROXIDE-FORMING CHEMICALS

This document is meant to assist responsible parties in managing their peroxide-forming chemicals and it outlines the procedures for purchasing, storage, peroxide testing, and disposing of these chemicals before they become hazardous.

Peroxide-forming chemicals are a class of compounds that can form shock-sensitive explosive peroxide crystals and result in serious accidents if not managed appropriately. They can be sensitive to shock, sparks, heat, and flames as they become low-powered explosives. This danger is increased when these chemicals' peroxide levels increase when exposed to air, light, heat, evaporation/distillation, or contamination from metals.

When using peroxide forming chemicals, responsible parties on campus must develop a standard operating procedure (SOP) for their usage. These parties must understand the factors that contribute to peroxide formation, manage their chemicals correctly, and periodically test for peroxides.

PEROXIDE-FORMING CHEMICALS COMMON TO RESEARCH

Although ethers are the most notorious peroxide formers, other peroxidizable organic materials include acetals, certain allylic alkenes (olefins), chloro- and fluoroalkenes, dienes, aldehydes, amides, lactams, ureas,

some alkylarenes, ketones, vinyl monomers, and some alcohols. Peroxide-forming chemicals can be classified into four groups based on varying conditions and rates of peroxide formation:

- **Group A** – Severe peroxide hazard: May form explosive concentrations of peroxides without concentration by evaporation or distillation even if never opened.
- **Group B** – Concentration hazard: Form explosive peroxides but usually become hazardous when distilled, evaporated, or otherwise concentrated. Note that some of these chemicals are quite volatile and repeated use may allow enough evaporation to occur to concentrate peroxides to explosive levels.
- **Group C** – Shock and heat sensitive: Chemicals which may autopolymerize as a result of peroxide accumulation.
- **Group D** – Peroxidizable chemicals not clearly categorized and therefore not included in Class A, B, or C.

Peroxide-forming chemicals that are most common to research at Cal Poly Pomona can be found listed in the campus’s [Chemical Hygiene Plan](#), APPENDIX G: Peroxide Forming Chemicals Common to Research. **The list is not comprehensive.** If you need assistance determining if a chemical is a peroxide former, please contact **EH&S** at **909-869-4697**:

APPENDIX G: Peroxide Forming Chemicals Common to Research:

TABLE 1. COMMON PEROXIDE-FORMING COMPOUNDS		
Group A- Chemicals that form explosive levels of peroxides without concentration		
(Safe storage time after opening - 3 months)		
Chemical Name	CAS Number	Synonym(s)
1,1-Dichloroethylene	75-35-4	Vinylidene Chloride
2-Chloro-1,3-Butadiene^{1,3}	126-99-8	Chloroprene
Butadiene^{1,3}	106-99-0	
Divinyl Acetylene	821-08-9	
Isopropyl Ether	108-20-3	
Tetrafluoroethylene	116-14-3	
Vinyl Ether	109-93-3	Divinyl ether
Group B- Chemicals that form explosive levels of peroxides on concentration		
(Safe storage time after opening - 12 months)		
Chemical Name	CAS Number	Synonym(s)
2-Butanol	78-92-2	
2-Cyclohexan-1-ol	822-67-3	
2-Hexanol	626-93-7	
2-Pentanol	6032-29-7	
3-Methyl-1-Butanol	123-51-3	Isoamyl alcohol

4-Heptanol	589-55-9	
4-Methyl-2-Pentanol	108-11-2	
Acetal	105-57-7	
Acetaldehyde	75-07-0	
alpha-Methyl-Benzyl Alcohol	98-85-1	Phenyl Ethanol
Benzyl Alcohol	100-51-6	
Cyclohexanol	108-93-0	
Cyclohexene	110-83-8	
Cyclooctene	931-87-3	
Cyclopentene	42-29-0	
Decahydronaphthalene	91-17-8	
Diacetylene	460-12-8	
Dicyclopentadiene	77-73-6	
Dioxane	123-91-1	1,4 Dioxane
Ethylene Glycol Dimethyl Ether	110-71-4	Diethylene Glycol Dimethyl Ether and Glyme
Ethyl Ether	60-29-7	Diethyl Ether
Furan	110-71-4	
Isopropyl Benzene	98-82-8	Cumene
Methylcyclopentane	96-37-7	
Methyl Isobutyl Ketone	108-10-1	
Penten-1-ol	821-09-0	
Propyne	74-99-7	Methyl Acetylene
Tetrahydrofuran	109-99-9	
Tetrahydronaphthalene	119-64-2	

Group C- Chemicals which may autopolymerize as a result of peroxide accumulation

(Safe storage time after opening: inhibited chemicals- 12 months; uninhibited chemicals: - 24 hours)

Note: Do not store inhibited chemicals in this group under inert atmospheres

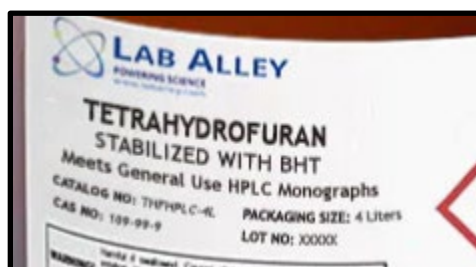
Chemical Name	CAS Number	Synonym(s)
1,1-Dichloroethylene	75-35-4	Vinylidene Chloride
2-Chloro-1,3-Butadiene ^{1,3}	126-99-8	Chloroprene
Acrylic Acid ²	79-10-7	

Acrylonitrile ²	107-13-1	
Butadiene ^{1,3}	106-99-0	
Buten-3-yne	689-97-4	Vinyl acetylene & Butenyne
Chlorotrifluoroethylene	79-38-9	
Methyl Methacrylate ²	80-62-6	
Phenethyl Alcohol	60-12-8	Phenyl Ethanol
Styrene	100-42-5	
Tetrafluoroethylene	116-14-3	
Vinyl Acetate	108-05-4	
Vinyl Chloride	75-01-4	Monochloroethylene
1. When stored as a liquid monomer 2. Although these form peroxides, no explosions involving these monomers have been reported 3. Also stored as a gas in gas cylinders.		

Other means of identifying peroxide-formers in your workplace may include consulting the manufacturer's safety data sheet or SDS ([Risk and Safety Solutions \(RSS\): SDS Application](#)), or by reviewing your Chemical Inventory ([RSS: Chemicals Application](#)).

PURCHASING CONSIDERATIONS

- When possible, purchase peroxide-forming chemicals which contain a peroxide formation inhibitor or stabilizer (e.g., butylated hydroxytoluene or BHT).
- Only purchase quantities of peroxide-forming chemicals that you expect to use before their expiration or within safe storage timeframes.



CHEMICAL INVENTORY REQUIREMENTS

- Peroxide-forming chemicals are to be included in the [RSS: Chemicals Application](#) chemical inventory upon receiving, and later removed from the inventory when discarded as hazardous waste using [RSS WASTE](#). When managing a peroxide former on your chemical inventory, the received date, expiration date, opened date, and last tested date should be recorded on the chemical inventory.

LABELING REQUIREMENTS

- All containers of peroxide-forming chemicals must be labeled with the date received, the date opened, expiration date, and dates of routine peroxide testing. Also include on the label if an inhibitor has been added. If you need stickers, please contact **EH&S at 909-869-4697**. Please see the sticker below:

CAUTION	
SHOCK-SENSITIVE PEROXIDE FORMER	
Date Received ___/___/___	INHIBITOR ADDED?
Date Opened ___/___/___	<input type="checkbox"/> YES <input type="checkbox"/> NO
Date Expires ___/___/___	Type _____
Peroxide Testing	
Date _____ Tester _____ Peroxide Conc. _____	
Date _____ Tester _____ Peroxide Conc. _____	
Date _____ Tester _____ Peroxide Conc. _____	
If peroxide concentration exceeds 0ppm, please contact EH&S for further guidance	

SAFE STORAGE REQUIREMENTS

- Always consult the manufacturer's safety data sheet (SDS)/container labeling regarding storage practices and expiration dates.
- Dispose of peroxide forming chemical containers prior to their expiration date.
- Ensure containers of peroxide forming chemicals are kept tightly sealed to avoid unnecessary evaporation, as this inhibits the stabilizers that are sometimes added.
- Visually inspect containers periodically to ensure that they are free of interior and exterior contamination or crystallization. If crystallization is present inside or on the exterior of a container, **do not handle the container. Secure the area. Contact EH&S immediately at 909-869-4697.**
- If old containers of peroxide forming chemicals are discovered in the laboratory, past the expiration date, or if the date of the container is unknown, **do not handle the container. Contact EH&S immediately at 909-869-4697.**

EVALUATION AND TESTING FOR PEROXIDES

- Discard peroxide-forming chemicals prior to their **expiration date**.
- Peroxide levels should be routinely tested following manufacturer guidelines, the chemical hygiene plan, and this guide.

- Peroxides should be removed from actively used stock and secondary containers by following laboratory practices prior to designating containers as hazardous waste.
- EH&S will not collect any peroxide forming chemicals for hazardous waste disposal that have exceeded their retention time unless the peroxide concentration has been tested at 0 ppm.
- As a best management practice, all uninhibited peroxide formers should be tested prior to usage.
- **Prior to distillation or evaporation:** confirm that peroxide-forming solvents have been tested for peroxide formation. Follow the guidelines below:

Peroxide Concentration:	Action:
≤ 20 ppm	Considered safe for general use
20-100 ppm	Not recommended for distilling or concentrating
> 100 ppm	Avoid handling and contact EH&S x4697 for guidance

STEP 1: Examine chemical for visible crystals

Peroxide crystals tend to form on the inner surfaces of the container and around the mouth/lid of the container. If you do not see crystals, or if the container is not transparent, proceed to the next step. If you do see viscous liquid or crystallization, **do not handle the chemical any further**. The crystals may cause an explosion if subjected to impact or friction. **Secure the area. Immediately contact EH&S at 909-869-4697 for guidance on how to proceed.**

Please see the pictures below of peroxide-former crystallization examples:



STEP 2: Determine whether it is safe to test for peroxides

If crystallization, layering, discoloration, wispy structures, ice-like structures, or viscous liquid is present on the container, do not test for peroxides. **Do not handle the container and secure the area. Contact EH&S immediately at 909-869-4697.**

If the contents of the container have evaporated significantly compared to the original volume, do not test for peroxides without consulting with EH&S. If you do not know the history of the chemical, **do not handle the container.**

- **Unopened containers from manufacturer:** Discard by the manufacturer's expiration date and test for peroxides following manufacturer's recommendations. At the latest, all peroxide-forming chemicals should be disposed of by 18 months from receiving the chemical. Record expiration date on the bottle/container.
- **Group A Peroxide Hazard:** Test for peroxide formation before using or discard container when ≤ 3 months from the open date. Test for peroxides and record testing prior to disposal.
- **Group B Peroxide Hazard:** Test for peroxide formation or discard container when ≤ 12 months from the open date. Once open, containers should be retested every 3 months and record testing.
- **Group C Peroxide Hazard (Inhibited):** Test for peroxide formation or discard when ≤ 12 months from the open date. Once open, containers should be retested every 3 months and record testing.
- **Group C Peroxide Hazard (Uninhibited):** Discard container when ≤ 24 hours from opening. Test prior to discarding and record results on the container label.

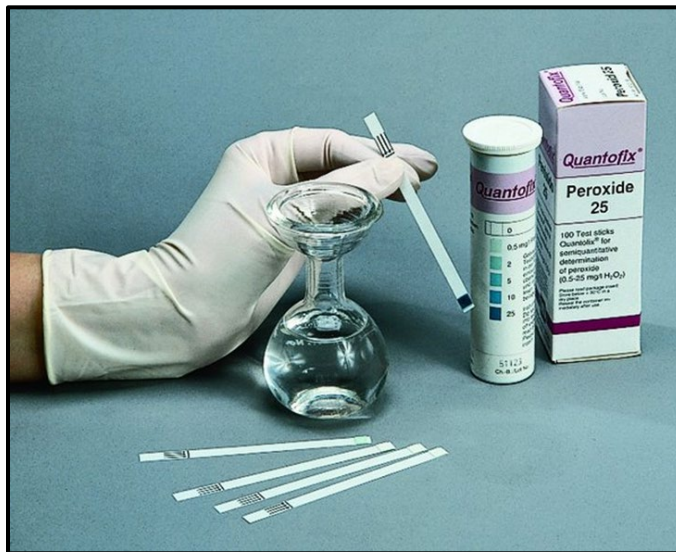
STEP 3: Testing for Peroxides

If the reagent is safe for testing as outlined above, you may use peroxide test strips to test the container. Faculty, staff, and students may test for peroxides if they have been trained and the chemical is not expired or exceeds the safe storage guidelines.

Peroxide formers should be tested following the guidance in **STEP 2**. Peroxide formers should also be **tested prior to distillation and evaporation practices** to ensure they are within acceptable levels for a given laboratory standard operating procedure.

Peroxide-forming chemicals require testing prior to being designated as hazardous waste to verify that they do not exceed 0 ppm. **Hazardous waste from peroxide formers will not be accepted by EH&S if levels are above 0 ppm.**

Test Strips: Peroxide test strips detect inorganic and organic compounds that contain a peroxide or hydroperoxide group. Test strips are suitable for the routine testing. Carefully read the instructions provided by the manufacturer. Hydroperoxide detection in organic solvents may require the addition of water to the sample being tested. An example of a peroxide test strip is: QUANTOFIX® Peroxide Test Strips 0 – 100 ppm:



STEP 4: Stabilization of Peroxides

When testing peroxide levels using test strips, responsible parties should periodically stabilize their chemical from additional formation of peroxides if feasible and part of their standard operating procedures (SOPs). Procedures should include the addition of an applicable inhibitor for the chemical requiring further stabilization. For example, butylated hydroxytoluene (BHT) is a common stabilizer added to Tetrahydrofuran (THF). The date the compound is tested and further stabilized should be recorded on the bottle and in [RSS Chemicals](#). It is important to note that a stabilizer such as BHT will not destroy peroxides already present. Once you have stabilized the chemical, label the substance with the peroxide concentration, and indicate the date that you stabilized it.

STEP 5: Removal of Peroxides

Responsible parties should maintain Standard Operating Procedure (SOPs) for removing peroxides for the peroxide formers they use in the laboratory when peroxide levels are detected upon testing. Removal of peroxides may be needed for laboratory practices and experiments. **Do not perform peroxide removal practices on containers testing above 100 ppm.** For additional guidance, please contact EH&S at 909-869-4697.

DISPOSAL OF PEROXIDE FORMERS

Peroxide-forming hazardous waste may be managed using [RSS WASTE](#). However, peroxide formers must be tested prior to designating the chemical as hazardous waste and peroxide levels need to be at 0 ppm to be collected by the campus's hazardous waste collection vendor CleanEarth. When making hazardous waste collection requests using [RSS WASTE](#), please type "peroxide former" in the comments section of the waste tag creation:



Hazard Class*
(Check all that apply)

- Flammable
- Corrosive Acid (pH \leq 2)
- Corrosive Base (pH \geq 12.5)
- Toxic
- Reactive
- Oxidizer
- Extremely Hazardous

Comments

Peroxide former

In addition, responsible parties must complete and provide **CleanEarth's Peroxidizable/Polymerizable Evaluation Form** for chemicals tested at 0 ppm peroxide levels that are within 60 days of expiring, expired, or exceeded safe storage guidance in this document. This form will be submitted through [EH&S's Peroxidizable Evaluation Form: Hazardous Waste](#) smartsheet.

When a peroxide former container forms crystals or viscous liquid, is expired, has an unknown history, has exceeded the safe storage guidelines described in this document, or if the container contents test above 0 ppm peroxides, the container may require deactivation and disposal by a contractor arranged by EH&S. This is a service outside the scope of normal campus hazardous material collection/disposal and this additional service will fall on the responsible party to pay. To help avoid these charges, please follow the guidelines found in this document.

If you do see viscous liquid or crystallization, do not handle the chemical any further. **Secure the immediate area around the chemical so that it is protected from any unnecessary movement or disturbances and immediately contact EH&S at 909-869-4697 for guidance on how to proceed.**

REFERENCES:

[Prudent Practices in the Laboratory](#), updated edition, National Research Council, 2011

[Review of Safety Guidelines for Peroxidizable Organic Chemicals](#), Richard J. Kelly; Chemical Health & Safety 1996, 3(5), 28-36