UNIVERSITY OF TEXAS ARLINGTON | ENVIRONMENTAL HEALTH & SAFETY

Standard Operating Procedure
Peroxide-Forming Chemicals (PFCs)

Purpose
The purpose of this SOP is to guide Principal Investigators (PIs)/Chemical Owners and laboratory users in the safe handling of Peroxide-Forming Chemicals (PFCs).

Introduction
This document outlines how to store, handle, and test for the presence of peroxides in Peroxide-Forming Chemicals (PFCs). PIs/Chemical Owners are responsible for following these guidelines for the control and safe use of PFCs.

Do not purchase large quantities of PFCs. Purchase only the amount that you will use in a 3-month period.

Purchase PFCs with **inhibitors** added by the manufacturer whenever possible. If the chemical does not contain an inhibitor or stabilizer (e.g., butylated hydroxytoluene or BHT), it can form peroxides more quickly.

Label PFCs with Date Received, Date Opened, Date Tested, and Test Results. EH&S provides appropriate labels.

If a PFC container is not labeled with the date on which it was opened, the opened date will default to the date at which the chemical was received.

How are Peroxides formed:

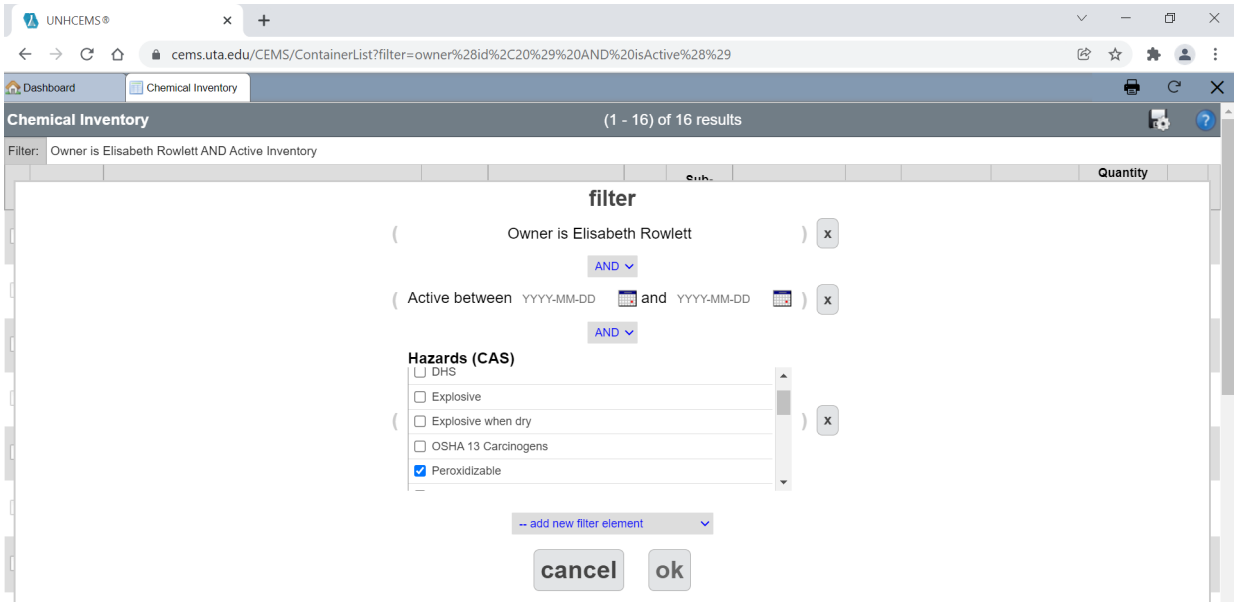
Oxygen	Exposure of peroxide-forming compounds to oxygen always enhances peroxide formation.
Time	Autoxidation generally refers to the slow reaction between organic chemicals and elemental oxygen under mild conditions. Over time, and in the presence of oxygen, chemicals will typically form peroxides. Peroxide-forming chemicals will usually have manufacturer listed expiration dates and institutional storage guidance.
Heat/Concentration	The likelihood of autoxidation increases with concentration or the application of heat. Chemicals that have already formed detectable peroxides should not be heated or concentrated.
Light	Ultraviolet light, including sunlight, promotes both autoxidation and depletion of the inhibitor. Although ultraviolet light catalyzes autoxidation, the reaction cannot proceed in the absence of oxygen.

Consequences

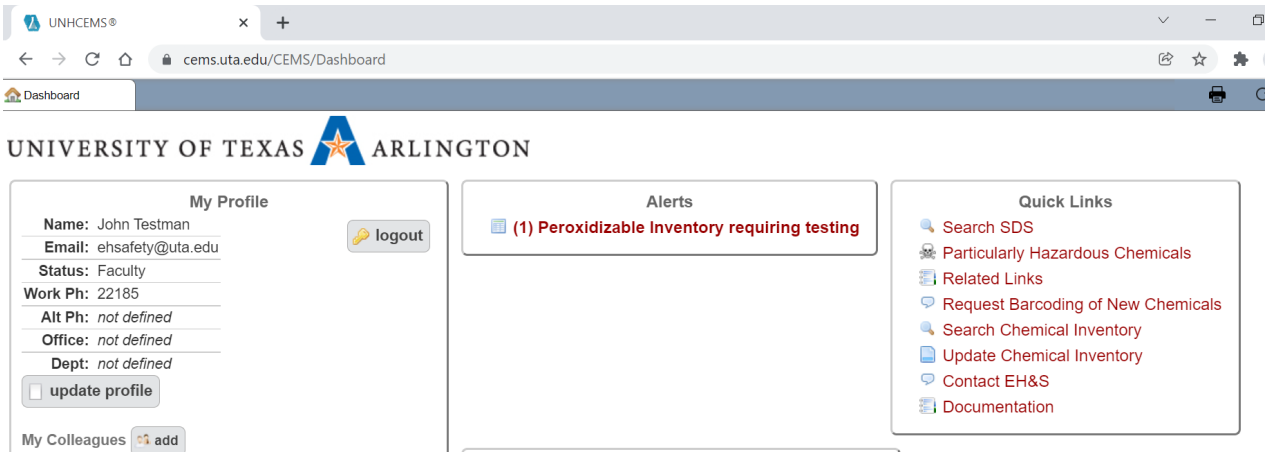
Improper storage or usage of a peroxide-former can result in devastating consequences.

Search and Updates on CEMS

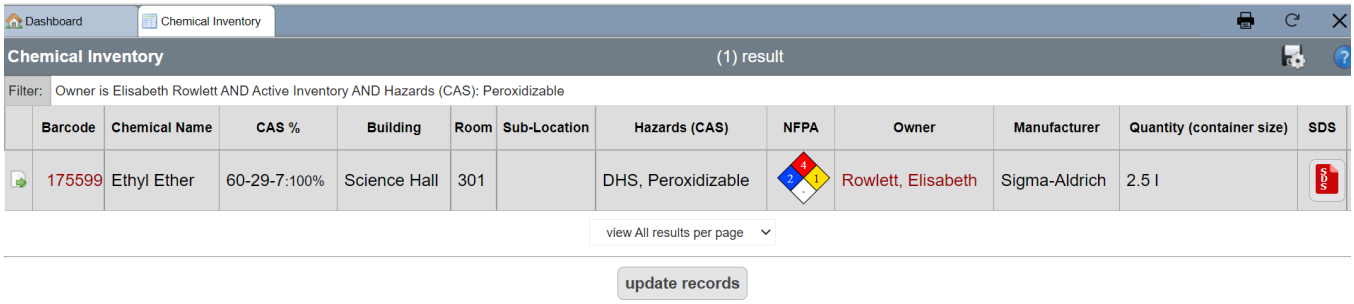
- Confirm that Peroxide-Forming Chemicals are barcoded and included in the inventory on CEMS at http://cems.uta.edu upon receipt and removed from the inventory when discarded.
- To search for PFCs in your laboratory, go to CEMS at http://cems.uta.edu , load the chemical inventory of your lab, and filter the Hazards (CAS)-column for “Peroxidizable”.



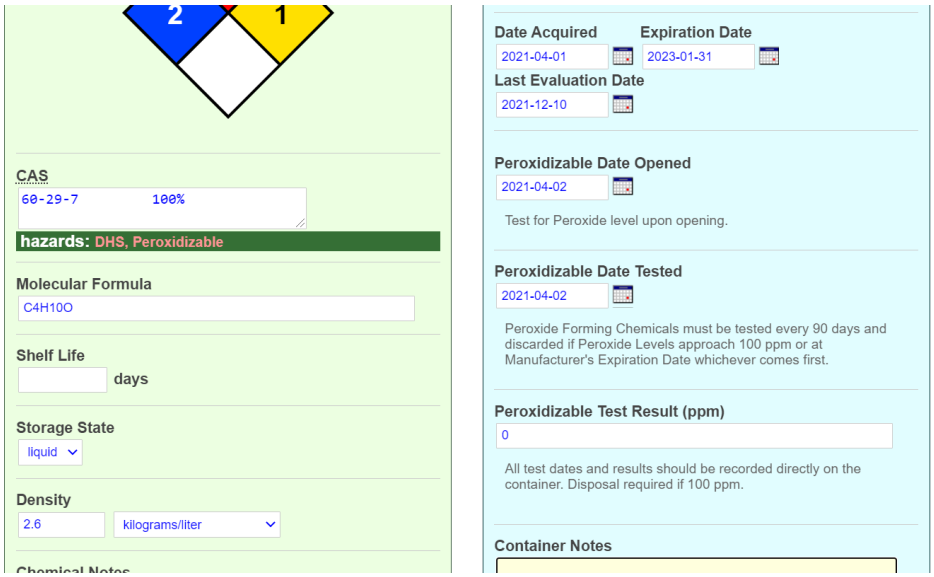
- To see which Peroxidizables are due for testing, go to Alerts-window on your CEMS Dashboard and click on the link (X) Peroxidizable Inventory requiring testing:



- Open the Container Record by clicking on the barcode:



- Fill out fields “Peroxidizable Date Opened”, “Peroxidizable Date Tested”, and “Peroxidizable Test Result (ppm):



- Click on “save” in the upper right corner.

Classes of PFCs and Storage
Peroxide-Forming Chemicals are divided into classes according to the conditions required for peroxide formation.
In all cases, EH&S requires prompt disposal of any Peroxide-Forming Chemical that are past the manufacturer’s expiration date.

Class A – Severe Peroxide Hazard

These are chemicals that form explosive levels of peroxides without concentration. These are the most hazardous of the peroxide formers and can form explosive peroxide levels even if not opened.
Unopened Container: Dispose or test within 18 months of receipt or at manufacturer’s expiration date, whichever comes first.
Opened Container: dispose within 90 days if there is no manufacturer’s expiration date.
Dispose at the manufacturer’s expiration date if this date exceeds 90 days since receipt. Inspect and test after opening and every 90 days until manufacturer’s expiration date. Failure to test every

90 days requires immediate disposal of the container.

Butadiene (liquid monomer)	Potassium metal
Chloroprene (liquid monomer)	Sodium amide
Divinylacetylene	Tetrafluoroethylene (liquid monomer)
Isopropyl ether	Vinylidene chloride
Potassium amide	

Note: Potassium metal, Potassium amide & Sodium amide are solid chemicals and cannot be tested with a peroxide testing strips so they must be stored appropriately (away from light) and frequently visually inspected for peroxide formation.

Class B – Concentration Hazard

These compounds form explosive peroxides when distilled, evaporated, or otherwise concentrated.

Unopened Container: Dispose or test within 18 months of receipt or at manufacturer's expiration date, whichever comes first.

Opened Container: dispose **inhibited** chemicals in this group within 12 months unless testing indicates peroxides less than 100 ppm (or 100 mg/L), or at the manufacturer's expiration date, whichever comes first. Inspect and test for peroxide formation after opening and at least every 90 days thereafter.

Failure to test every 90 days after 12 months of opening requires immediate disposal of the container.

Uninhibited chemicals in this group should be discarded **within 90 days of opening**.

Acetal	2-Hexanol
Acetaldehyde	Methylacetylene
Benzyl alcohol	3-Methyl-1-butanol
2-Butanol	Methylcyclopentane
Cumene	Methyl isobutyl ketone
Cyclohexanol	4-Methyl-2-pentanol
2-Cyclohexen-1-ol	2-Pentanol
Cyclohexene	4-Penten-1-ol
Decahydronaphthalene	1-Phenylethanol
Diacetylene	2-Phenylethanol
Dicyclopentadiene	2-Propanol
Diethyl ether	Tetrahydrofuran
Diethylene glycol dimenthyl ether (diglyme)	Tetrahydronaphthalene
Dioxanes	Vinyl ethers
Ethylene glycol dimethyl ether (glyme)	Other secondary alcohols
4-Heptanol	

Class C – Auto-Polymerization Hazard

These chemicals are highly reactive and can auto polymerize as a result of internal peroxide accumulation. The peroxides formed in these reactions are extremely shock and heat sensitive.
Unopened Container: Dispose or test within 18 months of receipt or at manufacturer's expiration date, whichever comes first.
Opened Container: dispose **inhibited** chemicals in this group within 12 months unless testing indicates peroxides less than 100 ppm (or 100 mg/l), or at the manufacturer's expiration date, whichever comes first. Inspect and test for peroxide formation after opening and at least every 90 days thereafter.
Failure to test every 90 days after 12 months of opening requires immediate disposal of the container.
Do not store **inhibited** chemicals in this group under inert atmosphere.
Uninhibited chemicals in this group should be discarded **within 24 hours of opening**.

Acrylic acid	Tetrafluoroethylene (gas)
Acrylonitrile	Vinyl acetate
Butadiene (gas)	Vinylacetylene (gas)
Chloroprene	Vinyl chloride (gas)
Chlorotrifluoroethylene	Vinyl pyridine
Methyl methacrylate	Vinylidene chloride
Styrene	

Class D – Chemicals that may form peroxides but cannot clearly be placed in tables A-C.

Unopened Container: Dispose or test within 18 months of receipt or at manufacturer's expiration date, whichever comes first.
Opened Container: dispose within 12 months unless testing indicates peroxides less than 100 ppm (or 100 mg/L), or at the manufacturer's expiration date, whichever comes first. Inspect and test for peroxide formation after opening and at least every 90 days thereafter.
Failure to test every 90 days after 12 months of opening requires immediate disposal of the container.

Acrolein	2,4-Dinitrophenetole
Allyl ether	1,3-Dioxepane
Allyl ethyl ether	Di(1-propynyl)ether
Allyl phenyl ether	Di(2-propynyl)ether
p-(n-Amyloxy)benzoyl chloride	Di-n-propoxymethane
n-Amyl ether	1,2-Epoxy-3- isopropoxypropane
Benzyl n-butyl ether	1,2-Epoxy-3- phenoxypropane

Benxyl ether	p-Ethoxyacetho-phenone
Benzyl ethyl ether	1-(2-Ethoxyethoxy)-ethyl acetate
Benzyl methyl ether	2-Ethoxyethyl acetate
Benzyl 1-napthyl ether	(2-Ethoxyethyl)-o-benzoyl benzoate
1,2-Bis(2-chloroethoxy)- ethane	1-Ethoxynaphthalene
Bis(2 ethoxyethyl)ether	o,p-Ethoxyphenyl isocyanate
Bis(2(methoxyethoxy)- ethyl) ether	1-Ethoxy-2-propyne
Bis(2-chloroethyl) ether	3-Ethoxyopropionitrile
Bis(2-ethoxyethyl) adipate	2-Ethylacrylaldehyde oxime
Bis(2-ethoxyethyl) phthalate	2-Ethylbutanol
Bis(2-methoxyethyl) carbonate	Ethyl B-ethoxy- propionate
Bis(2-methoxyethyl) ether	2-Ethylhexanal
Bis(2-methoxyethyl) phthalate	Ethyl vinyl ether
Bis(2-methoxymethyl) adipate	Furan
Bis(2-n-butoxyethyl) phthalate	2,5-Hexadiyn-1-ol
Bis(2-phenoxyethyl) ether	4,5-Hexadien-2-yn-1-ol
Bis(4-chlorobutyl) ether	n-Hexyl ether
Bis(chloromethyl) ether	o,p-Iodophenetole
2-Bromomethyl ethyl ether	Isoamyl benzyl ether
beta-Bromophenetole	Isoamyl ether
o-Bromophenetole	Isobutyl vinyl ether
p-Bromophenetole	Isophorone
3-Bromopropyl phenyl ether	B-Isopropoxy- propionitrile
1,3-Butadiyne	Isopropyl
Buten-3-yne	Limonene
Tert-Butyl ethyl ether	1,5-p-Methadiene
Tert-Butyl methyl ether	Methyl p-(n-amyloxy) benzoate
n-Butyl phenyl ether	4-Methyl-2-pentanone
n-Butyl vinyl ether	n-Methylphenetole
Chloroacetaldehyde diethylacetal	2-Methyltetra-hydrofuran
2-Chlorobutadiene	3-Methoxy-1-butyl acetate
1-(2-Chloroethoxy)-2- phenoxyethane	2-Methoxy-ethanol
Chloroethylene	Methonxy-1,3,5,7- cyclooctatetraene
Chloromethyl methyl ether	B-Methoxy-propionitrile
beta-Chlorophenetole	m-Nitro-phenetole
o-Chlorophenetole	1-Octene
p-Chlorophenetole	Oxybis(2-ethyl acetate)
Cyclooctene	Oxybis(2-ethyl benzoate)

Cyclopropyl methyl ether	b,b-Oxydipropionitrile
Diallyl ether	1-Pentene
p-Di-n-butoxybenzene	Phenoxyacetyl chloride
1,2-Dibenzyloxyethane	a-Phenoxypropionyl chloride
p-Dibenzyloxybenzene	Phenyl o-propyl ether
1,2-Dichloroethyl ethyl ether	p-Phenylphenetone
2,4-Dichlorophenetole	n-Propyl ether
Diethoxymethane	n-Propyl isopropyl ether
2,2-Diethoxypropane	Sodium 8,11,14-eicosa-tetraenoate
Diethyl ethoxymethylene- malonate	Sodium ethoxyacetylide
Diethyl fumarate	Tetrahydropyran
Diethyl acetal	Triethylene glycol diacetate
Diethyketene	Triethylene glycol dipropionate
m,o,p-Diethoxybenzene	1,3,3-Trimethoxy- propene
1,2-Diethoxyethane	1,1,2,3-Tetrachloro-1,3- butadiene
Dimethoxymethane	4-Vinyl cyclohexene
1,1-Dimethoxyethane	2,4,5-tri- chlorophenoxyacetate
Dimethylketene	Vinylene carbonate
3,3-Dimethoxypropene	Vinylidene chloride

NOTE: These tables represent prominent organic and inorganic compounds that are able to form peroxides under the right conditions. The tables are not comprehensive. You should refer to the Safety Data Sheet (SDS) or other reference material, contact the chemical manufacturer, or contact EH&S (817-272-2185) to determine if the chemicals you are using are potential PFCs.

General Precautions for Storage and Handling of PFCs

1. Know the properties and hazards of all chemicals you are using through adequate research and study. Read the label and Safety Data Sheet (SDS).

2. Wear proper personal protective equipment, including safety glasses, face shield, lab coat, gloves, and if possible utilize a safety shield.

3. Segregate PFCs from incompatible materials.

4. Store PFCs away from ignition sources. Protect PFCs from flames, static electricity, and other sources of heat.

5. DO NOT OPEN a container of a PFC that has obvious crystal formation or liquid stratification. Do not handle the container or force open the lid. Treat the reagent

as potentially explosive material. Immediately call EH&S for assistance (817-272-2185).

6. Store PFCs (especially those in Table A) under nitrogen or other inert gas, or keep and use them in an inert atmosphere chamber.

   Note: Some inhibitors actually need small amounts of oxygen to prevent peroxide formation and it is recommended that inhibited chemicals are not stored under an inert atmosphere.

7. Store PFCs in sealed, air-impermeable containers such as dark amber glass with a tight-fitting cap. DO NOT store these chemicals in open, partially empty, or transparent containers as these conditions promote formation of peroxides. Containers of PFCs should also be stored away from heat and light and protected from physical damage and ignition sources.

8. Test prior to distillation or evaporation. Less than 25 ppm: considered safe for general use. 25-100 ppm: not recommended for distilling or otherwise concentrating. 100 ppm: avoid handling and contact EH&S immediately to arrange disposal.

9. Avoid distillation of PFCs without first testing for the presence of peroxides in the material. Most explosions with the use of PFCs occur when a material is distilled to dryness. Leave at least 10-20% of PFC undistilled. Stir such distillations with a mechanical stirrer or a bubbling inert gas. Air or an oxygen-containing mixture should never be used for bubbling or stirring.

10. Contamination: some contaminants such as heavy metals, metal oxide salts, alkaline materials (e.g. amines), strong acids, and many varieties of dust and dirt can cause the uncontrolled decomposition of peroxides. This condition can lead to pressure build up, explosions, and/or fire. In order to prevent accidental contamination, never return a peroxide former to its original storage container once withdrawn.

11. Do not use metal spatulas or magnetic stirring bars (which may leach out iron) with peroxide forming compounds, since contamination with metals can lead to explosive decomposition. Ceramic, Teflon, or wooden spatulas and stirring blades are usually safe to use.

12. Never open or test containers of unknown origin or age, or those that have evidence of peroxide formation.

Quantitative Peroxide Testing

- You can purchase Peroxide Test kit/sticks/strips from most safety or laboratory supply houses. Some examples include Sigma-Aldrich, Fisher Scientific, and VWR Scientific.

- Wear proper personal protective equipment, including safety glasses, face shield, lab coat, gloves, and if possible utilize a safety shield.

- Perform testing in a chemical fume hood.
- Make sure there are no solids or crystals in either the liquid or around the cap of PFC. If they are present, do not open or move the container. Contact EH&S (817-272-2185) for disposal.
- To use most Peroxide Test sticks/strips, simply immerse the stick/strip into the suspect material and then compare the color on the strip to the calibration chart that comes with the test kit. This gives a quantitative peroxide concentration, usually in ppm.

  Caution: these strips have finite ranges. You may need to buy several different test kits to cover all possible ranges; read the product information or call the manufacturer for more information.

- Correctly fill out the label shown below and attach it to the container.

PEROXIDE FORMING CHEMICAL

Date Received__11/27/2020 **Date Opened**__1/27/2021
Date/Test Results__1/27/2021 __0 ppm_____
Date/Test Results__4/20/2021 __50 ppm_____
Date/Test Results__7/15/2021 __100 ppm_____

The example chemical was opened within the 18 months allowable unopened storage time. The initial test after opening was satisfactory. Subsequent tests every 90 days were satisfactory until the test on 7/15/2021, as this test result was 100 ppm. At that time the chemical must be disposed of as soon as possible.

Disposal of PFCs

Submit Waste Pickup Request via CEMS http://cems.uta.edu.

If crystals are present in either the liquid or around the cap of the container with PFC do not open or move the container. Contact EH&S at 817-272-2185 for disposal.