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Management and Safety of Peroxide Forming Chemicals

What are peroxide formers?

- They are usually liquid chemicals that can "auto-oxidize" under normal storage conditions to form potentially explosive organic peroxides. Peroxides are characterized by the weak -O-O- single bond and are prone to violent decomposition.
- Their molecular structure has an auto-oxidizable hydrogen atom activated by nearby functional groups.
- Ethers and acetals are the most common peroxide formers.
- Some alkenes, halogenated alkenes, vinyl monomers, dienes, alkylarenes, alkynes, acrylates, secondary alcohols, ketones, aldehydes, ureas, amides, lactams, and alkali metals can also form peroxides.
- They are divided into three major categories based on the conditions needed to form potentially explosive levels of peroxides and are ranked from most to least dangerous: Class A, Class B, and Class C. Other, less easily categorized, peroxide formers are sometimes listed as Class D.
- Known peroxide formers include, but are not limited to, the *examples* below. Check SDS for section "Hazards not otherwise classified (HNOC): May form explosive peroxides."

Class A Chemicals that can form explosive peroxides under normal storage conditions ***without*** concentration	**Class B** Chemicals, through use or storage, that form explosive levels of peroxides ***with*** concentration	**Class C** Vinyl compounds that are able to initiate free radical polymerization of the bulk monomer
Butadiene, liquid monomer	Diethyl Ether (Ethyl Ether)	Butadiene
Chloroprene, liquid monomer	1,4-Dioxane	Chlorobutadiene
Divinylacetylene	Tetrahydrofuran (THF)	Chlorotrifluoroethylene
Isopropyl ether	Acetal	Methyl methacrylate
Potassium metal	Acetaldehyde	Tetrafluorethylene
Potassium amide	Benzyl alcohol	Vinyl acetate
Sodium amide	2-Butanol (*sec*-butyl alcohol)	Vinylacetylene
Tetrafluoroethylene	Cyclohexanol	Vinylpyridine
Vinylidene chloride	Cyclohexene	Vinyladiene chloride
	1,2-Dimethoxyethane (glyme)	
	Dicyclopentadiene	
	Furan	
	Isopropylbenzene (cumene)	
	Methyl acetylene (propyne)	
	3-Methyl-1-butanol (isoamyl alcohol)	
	Methyl isobutyl ketone	
	(1- or 2-) Phenylethanol	
	Vinyl ethers	
	Other Dioxanes	
	Other secondary alcohols (including isopropyl alcohol*)	

***Isopropyl alcohol/isopropanol/2-propanol/IPA *only* needs to be peroxide tested if it will be distilled or otherwise concentrated. IPA used for cleaning or in rotovap cold fingers does not need to be peroxide tested.**

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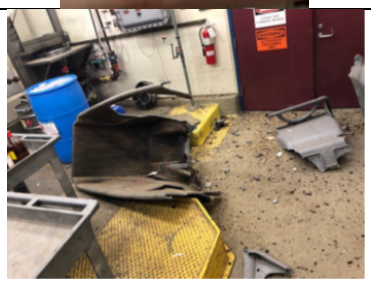
What are the hazards?

- Shock, heat, or friction can lead to peroxides' violent decomposition and explosions which can cause injuries. Examples of recent explosions caused by peroxide forming chemicals are summarized below.

Berkley- A round bottom flask exploded in a student's face while rotovaping unstabilized THF from a nearly empty bottle. The THF was found to have >100 ppm peroxides and concentrating it is believed to have created dry and explosive peroxide crystals. (photo does not show shards from the burst flask)	
University of Minnesota- Methyl methacrylate exploded overnight on a storage shelf leaving only a 'puck' of polymer and approximately the top 5% of the bottle.	
University of Minnesota- Explosion in a waste room when an emptied solvent waste bottle was placed in cart, which ripped the cart to pieces. The likely cause of the explosion was determined to be shock sensitive residue from a peroxide forming chemical deposited inside an empty bottle that would have been stabilized when in solution.	

What causes peroxide formation?

- Susceptible chemicals autoxidize to form peroxides through the free-radical reaction of a hydrocarbon and molecular oxygen under mild conditions.
- Autoxidation is initiated by UV-light, a free radical source, contaminants, or the peroxide itself and is always enhanced by presence of oxygen.
- Peroxide formation often begins with the formation of the hydroperoxide, which may undergo further reactions leading to the formation of more difficult to detect unstable higher order peroxides.
- Peroxide formation is unpredictable and erratic. There have been instances of unopened chemical containers with 10-100ppm of detectable peroxides.

What can be done to prevent peroxide formation?

- **Avoid purchasing uninhibited peroxide forming chemicals whenever possible**
  - Many peroxide forming chemicals are sold with antioxidant, free-radical scavenging inhibitors.
    - Inhibitors include*: 2,6-di-tert-butyl-p-methylphenol/butylated hydroxy toluene (BHT), hydroquinone, diphenylamine, 1-naphthol, stannous chloride, ferrous sulfate, polyhydrophenols, aminophenols, arylamines, and other phenolic compounds*.
- **Whenever possible, store and work under an inert atmosphere (i.e. nitrogen blanket) to reduce peroxide formation of class A & B peroxide formers.**
  - Phenolic inhibitors used in some class C peroxide formers need some oxygen to work and should *not* be stored under an inert gas.

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How to manage peroxide forming chemicals:

- Buy the minimum practical quantities of inhibited peroxide forming chemicals so they can be used up within manufacturer's expiration date or one (1) year and avoid storing inhibited peroxide forming chemicals for more than five (5) years, even if unopened. Inhibitors are depleted during long-term storage, which can lead to rapid peroxide formation.

- Purchased uninhibited peroxide formers should be used within manufacturer's expiration date or used "fresh" (less than one week) if distilled/redistilled by the lab. Always test uninhibited peroxide forming chemicals prior to working with them.

- Upon receipt of a peroxide forming chemical, place a current BU peroxide testing label on the container and record the date received and date opened on the label. Promptly add the reagent to BioRAFT's ChemTracker inventory.

- Always practice "first in, first out" when opening and using peroxide formers.

- Designate a single storage location for all peroxide formers in the lab to avoid "forgetting" one.

- Store peroxide formers in tightly closed original containers or amber glass bottles. Avoid loose fitting caps and ground glass stoppers.

- Store peroxide formers in a cool, dry, and dark location- usually a flammables cabinet. Only store peroxide formers in an explosion proof fridge/freezer if recommended by the manufacturer. Low temperatures can cause peroxides to crystalize/"crash out" of solution.

- Avoid contaminating peroxide forming chemicals. Do not return reagents to stock bottles, do not use rubber stoppers/septa for long term storage, and avoid inserting items, i.e. pipettes, into stock bottles.

- Do not allow them to dry out. Never concentrate peroxide forming chemicals near dryness- always leave at least 20% of starting volume when distilling these reagents.

When to test for peroxides:

- Test on a quarterly basis (every 3 months) after manufacturer's expiration date or one (1) year from receipt, whichever comes first. Record quarterly test results on BU's peroxide testing label.

- Test uninhibited peroxide formers after manufacturer's expiration date and before and after distilling.

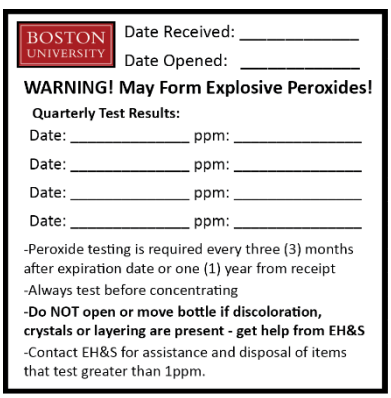
- Always test before concentrating (i.e. distilling, rotovapping, recrystallizing, cooling near freezing/melting point) peroxide forming solvents. Remember to test solvents in solvent drying systems and stills.

How to track peroxide testing:

- Get the current year's BU peroxide testing label from EHS:
  2021 Pink, 2022 Orange, 2023 Yellow, 2024 Green, 2025 Blue

- Place a new sticker on *every* container, old stock and new purchases, of peroxide forming chemicals in the laboratory *every* year.

- Test for peroxides on a quarterly basis and record results on the label.



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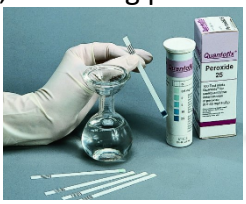
How to determine if peroxides are present:

- First, visually inspect containers of peroxide formers for obvious peroxide formation in the bottle or around the cap. With glass containers use a flashlight to back or side light the bottle. Look for:
  - Cloudiness
  - Layering or discoloration
  - Wisp-like structures in clear liquid
  - Chips, ice-like structures, or solid mass of precipitated peroxide crystals
  - Gross contamination

- **Do not open, do not touch** a bottle of liquid peroxide forming material if solid precipitates or crystals are seen in the bottle or along the bottle's cap. Immediately contact EHS to arrange disposal.

- If no visible peroxide formation, test using peroxide test strips from Millipore-Sigma, VWR, or Fisher.



- **Follow manufacturer's sampling instructions when testing**.

- General peroxide test strip sampling and testing instructions:
  - Working in a chemical fume hood, briefly wet indicator square on test strip with the solvent, then shake to remove the excess.
  - When testing organic solvents, add 1 drop of distilled water to the test area per instructions.
  - A change from white to a color (even faint) within the testing time period indicates a positive result.
    - *Caution: Test strips sitting in the open for extended periods of time may react with the air.*

- WARNING- test strip results are considered only semi-quantitative and, based on the type of peroxide present, can have differing (often low) sensitivity, or changes in indicator color, or development time.

What to do if peroxides are detected?

- **Do not open, do not touch** a bottle of liquid peroxide forming material if gross peroxide contamination is visible in the bottle or along the bottle's cap. **Immediately contact EHS to arrange disposal.**

- **A positive test (>1 ppm) indicates that the reagent should be appropriately disposed of as hazardous waste.**
  - Move reagent to Satellite Accumulation Area (SAA), tag it with a red hazardous waste sticker, and place a BioRAFT waste pick-up request.

EHS Contacts:

- **CRC EHS Office 617-353-4094**
  Mike Puim, Associate Director of Environmental Management, mpuim@bu.edu, 617-353-1993
  Dawn Hengl, Chemical Safety Officer, dmhengl@bu.edu, 617-353-4941

- **MED EHS Office 617-358-7840**
  Mike Dean, Associate Director of Environmental Management, mikedean@bu.edu, 617-358-9448

- **After hours emergencies**: Call Control at **617-353-2105 (CRC)** or **617-414-4444 (BUMC/BMC)**

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References:

- **Boston University Chemical Hygiene Plan**
- **Management of time sensitive chemicals (I): Misconceptions leading to incidents**
  Jim Bailey, David Blair, Lydia Boada-Clista, Dan Marsick, David Quigley, Fred Simmons, and Helena Whyte; Chemical Health & Safety 2004, 11 (5), 14-17
- **Management of time-sensitive chemicals (II): Their identification, chemistry and management**
  Jim Bailey, David Blair, Lydia Boada-Clista, Dan Marsick, David Quigley, Fred Simmons, and Helena Whyte; Chemical Health & Safety 2004, 11 (6), 17-24
- **Peroxides and peroxide-forming compounds**
  Donald E. Clark; Chemical Health & Safety 2001, 8 (5), 12-22
- **Control of peroxidizable compounds**
  H. L. Jackson, W. B. McCormack, C. S. Rondestvedt, K. C. Smeltz, and I. E. Viele; Journal of Chemical Education 1970, 47 (3), A175
- **Review of Safety Guidelines for Peroxidizable Organic Chemicals**
  Richard J. Kelly; Chemical Health & Safety 1996, 3(5), 28-36
- **UMASS Amherst Environmental Health & Safety Peroxide Forming Materials SOP**
- **University of Minnesota University Health and Safety Guidance Document Peroxide-Forming Chemicals (PFCs)**