

# Fact Sheet

## Peroxidizable Compounds

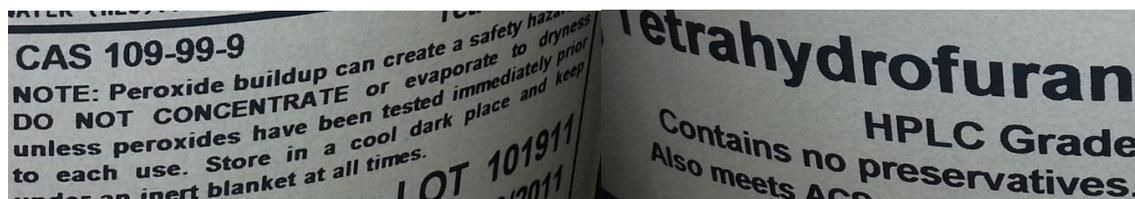
Common organic laboratory solvents, such as ethers or tetrahydrofuran, if not stored or used appropriately, can “auto-oxidize” with atmospheric oxygen under ambient conditions to form organic peroxides (contain a -O-O- bond). These are called peroxide-formers (PF) or peroxidizables. Once formed, organic peroxides are sensitive to thermal or mechanical shock and can be violently explosive in concentrated form or as solids.

### Peroxide formation can be caused by:

Exposure to air, concentration, self-polymerization or may be otherwise internally formed.

### How to identify materials which may form peroxides

- Check container label warning statements. Ex. “**NOTE: Peroxide build up can....**”, “**Contains no preservatives**”, “**HPLC Grade**” “**Stabilized**” or “**Inhibitor-free**”



- Search the [UMN chemical registry](#), if DDC# column shows two numbers followed by the letters ‘PF’, which stand for peroxide-former. Ex **08PF**. May also be a PF if words *Stabilized or Inhibited* are included.
- Check lists of Class A, B, C, and D peroxidizable compounds at end<sup>1</sup>.
- Check for Any OLD organic compounds:
  - “Essentially **all compounds containing C—H bonds pose the risk of peroxide formation** if contaminated with various radical initiators, photosensitizers, or catalysts....Although not a requirement, it is **prudent to discard old samples of organic compounds of unknown origin or history.**”<sup>2</sup>
  - Use Figure 1 from Review of Safety Guidelines for Peroxidizable Organic Chemicals by Richard Kelly, to determine those most likely form peroxides. (Next page) Liquids with a low molecular weight are most likely. Compounds with a low volatility (boiling point > 300°C or vapor pressure < 0.1 mm Hg at 20 °C) are unlikely to concentrate in dangerous levels.

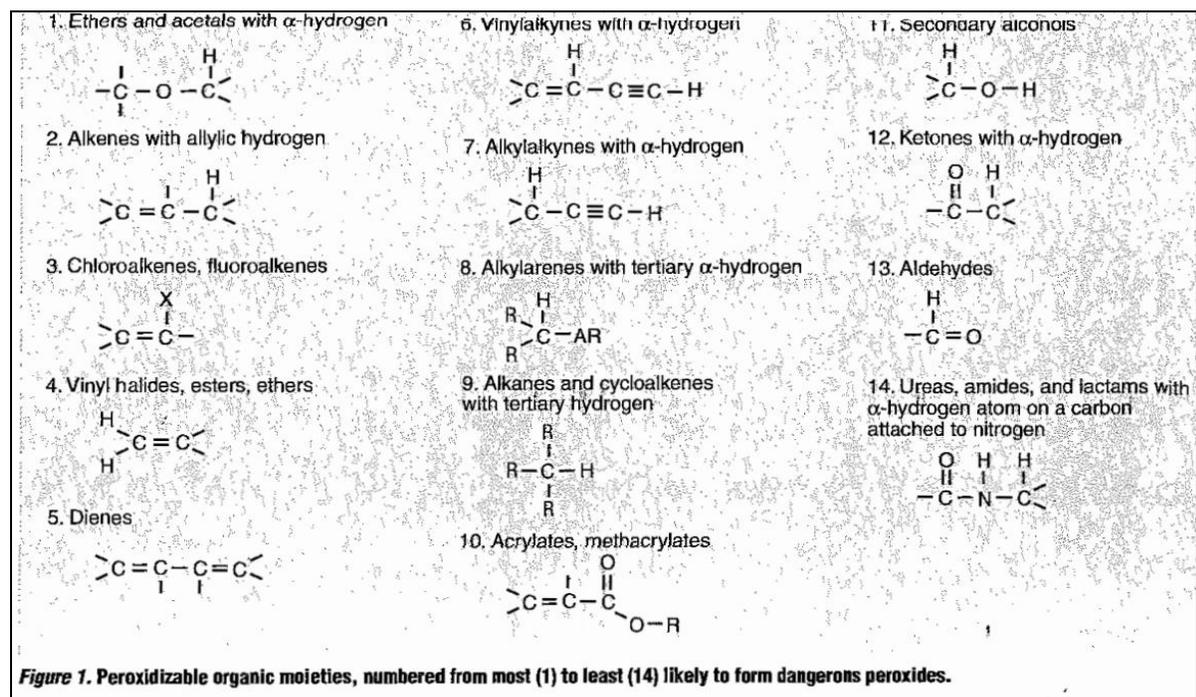
<sup>1</sup> These lists are illustrative not comprehensive. Sources: Jackson et al. (1970) and Kelly (1996)

<sup>2</sup> Ask your advisor for lab-specific definition of age. From Prudent Practices pg 72. OSHA cites “Prudent Practices” because of its wide distribution and acceptance and because of its preparation by recognized authorities in the laboratory community through the sponsorship of the NRC.

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## CLASSES of Peroxidizable Compounds (Listed in order of most likely to form organic peroxides)



**Class A-** Chemicals that form explosive levels of peroxides without concentration. Class A chemicals should be discarded within 3 months of receipt. Example: *Isopropyl ether*

**Class B-** These chemicals can form peroxides if concentrated. Class B Chemicals without inhibitors<sup>3</sup> should be tested for peroxides: (1) If intending to distill or evaporate (2) Every 6 months after opening (3) If the chemical is unopened but has been in long-term storage. Example: *Tetrahydrofuran, vinyl ethers and secondary alcohols*

**Class C-** Chemicals that may autopolymerize without an inhibitor. Liquids test after 6 months, Gases dispose after 1 yr. Example: *Acrylic Acid, Methyl methacrylate,*

NOTE- Inhibitors for Class C chemicals require the presence of oxygen.

Inhibitor present in a purchased chemical or added to lab synthesized sample	Requires oxygen	Test every 6 months after opening
No inhibitor present. It was removed from commercial sample or never added to a lab synthesized sample	Store under inert gas	Add inhibitor, within 24 hr prior to disposal

**Class D-** Additional chemicals that may form peroxides.

**A list of chemicals and their peroxidation class is included at the end**

<sup>3</sup> Class B compounds with inhibitors do NOT require testing, unless it has been in long-term storage  
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## BEST PRACTICES WITH PEROXIDIZABLE MATERIALS

### Purchase:

- Limit to what will be used within one month for Class A and others within a year.
- Select materials
  1. with peroxide stabilizers or inhibitors (free-radical scavengers that terminate the chain reaction) e.g BHT<sup>4</sup>,
  2. Inhibitor-free chemicals should be purchased in septum-capped bottles stored under inert gas (N<sub>2</sub> or Ar)

### Storage:

*Reminder- All organic materials should be stored away from light, tightly closed (free from oxygen, and concentration via evaporation), separated from oxidizers and free from catalytic contaminants such as Co<sup>2+</sup>.*

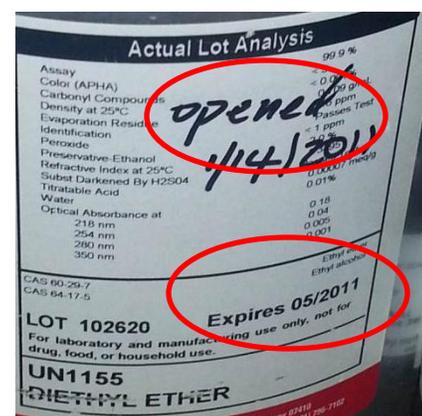
- Store away from heat, light, ignition sources, and oxidizers.
- Use up open containers first, open in order of receipt.
- Glass bottles should be amber (*blocks light*)
- Store inhibitor free chemicals under an inert atmosphere
- Designate an area for PF so they can all be tested and not “forgotten” in the back of a cabinet
- If stored in a refrigerator, do not store at temperatures near the compound’s melting/freezing point. There peroxides are likely condense into solids (freeze or begin crystalizing).

### Label:

- Dates: received, first opened, expiration, last tested
- Test results

### User Beware:

- Sources of contamination can promote peroxide formation.
  - Avoid metal sources e.g. metal spatulas and magnetic stir bars.<sup>5</sup>
  - Only dispense from original manufacturer containers. Don’t reuse containers.<sup>6</sup>
- Distillation/Evaporation
  1. Test for pf before distilling. Do not distill if > 100 ppm peroxides.
  2. Consider adding a nonvolatile oil such as mineral oil (ensures going to dryness is not possible) and a polymer sleeve (to connections to reduce friction).
  3. Stop distillations of pf when 20% of starting volume remains. Do not distill to dryness.
  4. Be cautious about “agitation” or shaking post distillation or freezing.
  5. Distillation removes inhibitors, replace it or add an inert gas.
- “Peroxide effect”- trace amounts of peroxide contaminants can change the orientation of an addition reaction<sup>7</sup>.



<sup>4</sup> Other inhibitors include hydroquinone, diphenylamine or other phenolic compounds. Note- Iron inhibits peroxides in diethyl ether but not other compounds.

<sup>5</sup> if possible use ceramic, teflon or wooden spatulas and stir bars.

<sup>6</sup> Never pour materials back into the reagent bottle, or containers that were used before, even if it was for the same compound. Especially important, if it is not possible to do a visual check of container integrity or early signs of peroxide precipitation.

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## Practices

- Set up a regular reminder to check for peroxides and verify sufficient inhibitor levels
- Avoid procedures which involve aeration, friction, or concentration.

## Incidents

- "A few years back, a bottle of methyl methacrylate exploded overnight on one of our storage shelves in Smith Hall. .... the only evidence that the bottle even existed was the 'puck' of polymer (image right) and a small section of the bottle that included the cap and neck about 95% of the glass simply disappeared. It must have been quite the blast!"
- Explosions at UC<sup>8</sup>: 1) rotovaping THF that had > 100 ppm 2) heating material that been distilled to 15 % of starting volume



## HOW TO DETECT THE FORMATION OF PEROXIDES



### CAUTION

- If crystals are visible on or in the container or lid,
  - If container has a metal screw cap , or glass stopper
  - If a Class A compound, past its expiration date
  - If a Class B or C has been open for more than two years and not tested
- Do NOT touch the container.

Call the Chemical Waste Program at (612) 626-1604 for assistance.

**Peroxide Test Strips**  
0-100ppm

**Peroxide Test Strip**  
1. Dip the Test strip into the solution to be tested for one second and shake off excess liquid.  
2. After 10 seconds compare with the color scale.

ppm  
0 1 3 10 50 100

Indigo® Instruments  
Part #: 33815-P100

For a qualitative check, colorimetric tests using potassium iodide may be used. Several methods are outlined in Prudent Practices 6.G.3.2

Peroxide Detection Commercial test strips<sup>9</sup>. Follow manufacturer testing instructions and compare the color promptly. It will continue to develop and must be read at the specified time.

Peroxide Concentration	Response
< 80 ppm	Solution is okay for use
80 ppm to 400 ppm	Dispose of as Hazardous Waste. Do not continue to use.
> 400 ppm	Call the Chemical Waste Program, they may need to call the Bomb Squad

<sup>7</sup> If peroxides are present, an anti- Markovnikov addition will occur instead of a planned Markovnikov addition See Clark.

<sup>8</sup> <https://www.ehs.uci.edu/salerts/AlcoholTosylationExplosion.pdf>, <https://www.ehs.uci.edu/salerts/AlcoholTosylationExplosion.pdf>

<sup>9</sup> The 0-100 ppm range works well and typically includes ~ 50/vial for around \$30. Image from Indigo Instruments. Commercial test strips have test ranges of 0.5 to 50 ppm or 3 -100 ppm, if the peroxide concentration is greater than the range of the strip, perform a serial dilution.

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## Inactivating peroxides

Removing peroxides is not recommended. Besides the risk of the peroxides themselves, the removal techniques often employ heat, concentration or additional hazardous reagents making the process riskier than simply disposing and purchasing new reagent<sup>10</sup>.

## Disposal

All peroxide formers should be disposed of as hazardous waste. Check peroxide levels. Materials with concentrations < 400 ppm can be disposed following standard waste procedures.

- Indicate the peroxide concentration on the request form.
- Don't mix peroxide containing solvents with other waste streams. As always, keep closed and dispose of promptly.
- Add a dash of additional inhibitor prior to disposal, if you have it

## FOR FURTHER INFORMATION

If you have any concerns regarding the stability or testing of a chemical, contact the Chemical Waste Program at (612) 626-1604. Testing is available upon request.

## References:

- [Those pesky peroxides, Dawn Mason, doi:10.1016/j.jchas.2013.12.011](https://doi.org/10.1016/j.jchas.2013.12.011)
- The National Research Council's (NRC) [Prudent Practices in the Laboratory: Handling and Management of Chemical Hazards](#) (2011),
  - Azo, Peroxides and Peroxidizables, pg 72-73
  - Organic Peroxides pg 133
  - Peroxidizables pg 134-135
- Jackson, H. L., W. B McCormack, C. S. Rondestvedt, K. C. Smeltx, and I.E. Viele. 1970 Control of peroxidizable compounds. *Journal of Chemical Education* 47(3):A175
- Kelly, R. J. 1996. Review of safety guidelines for peroxidizable organic chemicals. *Journal of Chemical Health and Safety* 3(5):28-36
- Laboratory Safety for Chemistry Students by Robert Hill & David Finster, Chapter 5 Peroxides- Potentially Explosive Hazards.
- Clark, D.E., Peroxides and Peroxide - Forming Compounds, *Chemical Health and Safety*, 2001, 8 (5), 12-21. - See more <https://www.bnl.gov/esh/cms/pdf/peroxides.pdf>

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<sup>10</sup> Experienced chemists can review the techniques (passing through activated alumina, shaking with sulfate reagent, or standing over molecular sieves) outlined in Kelly's Review and the 1995 edition of Prudent Practices.  
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## Alphabetical List of Peroxidizable Compounds. (Available as Excel file with CAS#, DDC and source)

Chemical, Class		Chemical, Class		Chemical, Class		Chemical, Class	
Butadiene,	C	a-Phenoxypropionyl chloride	D	Ethyl vinyl ether	D	tetrahydrofuran,	B
(2-Ethoxyethyl)-a-benzoyl benzoate	D	b,b-Oxydipropionitrile	D	Ethyl-b-ethoxypropionate	D	tetrahydronaphthalene,	B
1-(2-Chloroethoxy)-2-phenoxyethane	D	b-Chlorophenetole	D	ethylene glycol dimethyl ether (glyme),	B	Tetrahydropyran	D
1-(2-Ethoxyethoxy)ethyl acetate	D	benzyl alcohol	B	ethylene glycol ether acetates,	B	Triethylene glycol diacetate	D
1,1,2,3-Tetrachloro-1,3-butadiene	D	Benzyl ether	D	Ethylene glycol monoethers (cellosolves),	B	Triethylene glycol dipropionate	D
1,1-Dimethoxyethane	D	benzyl ethyl ether	D	Furan	D	Vinyl acetate,	C
1,2-Bis(2-chloroethoxy)ethane	D	benzyl methyl ether	D	fulan,	B	Vinyl acetylene	C
1,2-bis(2-chloroethoxy)ethyl ether	D	Benzyl n-butyl ether	D	Isoamyl benzyl ether	D	Vinyl chloride,	C
1,2-Dibenzoyloxyethane	D	Benzyl-1-naphthyl ether	D	Isoamyl ether	D	vinyl ethers	B
1,2-Dichloroethyl ethyl ether	D	beta-Bromophenetole	D	Isobutyl vinyl ether	D	Vinyl pyridine.	C
1,2-Diethoxyethane	D	bis(2-(methoxyethoxy)ethyl) ether	D	Isophorone	D	Vinyldiene chloride	C
1,2-Epoxy-3-isopropoxypropane	D	bis(2-chloroethyl) ether	D	Isopropyl ether	A	Vinylene carbonate	D
1,2-Epoxy-3-phenoxypropane	D	Bis(2-chloroethyl) ether	D	Isopropyl-2,4,5-trichlorophenoxy acetate	D	Vinylidene Chloride	A
1,3,3-Trimethoxypropene	D	Bis(2-ethoxyethyl) adipate	D	m,o,p-Diethoxybenzene	D		
1-Ethoxy-2-propyne	D	Bis(2-ethoxyethyl)ether	D	Methoxy-1,3,5,7-cyclooctatetraene	D		
1-Ethoxynaphthalene	D	Bis(2-methoxyethyl) carbonate	D	methyl acetylene,	B		
1-Octene	D	Bis(2-methoxyethyl) ether	D	methyl cyclopentane,	B		
1-Pentene	D	Bis(2-methoxyethyl) phthalate	D	methyl isobutyl ketone,	B		
1-phenylethanol	B	Bis(2-methoxymethyl) adipate	D	Methyl methacrylate ,	C		
2,2-Diethoxypropane	D	Bis(2-n-butoxyethyl) phthalate	D	m-Nitrophenetole	D		
2,4-Dichlorophenetole	D	Bis(2-phenoxyethyl) ether	D	n(n-amyloxy)benzoyl chloride	D		
2,5-Hexadiyn-1-ol	D	Bis(4-chlorobutyl) ether	D	n-amyl ether	D		
2-Bromomethyl ethyl ether	D	Bis(chloromethyl) ether	D	n-Amyl ether	D		
2-butanol	B	b-Isopropoxypropionitrile	D	n-Butyl phenyl ether	D		
2-Chlorobutadiene	D	b-Methoxypropionitrile	D	n-Butyl vinyl ether	D		
2-cylcohexen-1-ol	B	Butadiene	A	n-Hexyl ether	D		
2-Ethoxyethyl acetate	D	Chloroacetaldehyde diethylacetal	D	n-Methylphenetole	D		
2-Ethylacrylaldehyde oxime	D	Chlorobutadiene	C	n-Propyl ether	D		
2-Ethylbutanol	D	Chlorobutadiene (chloroprene),	A	n-Propyl isopropyl ether	D		
2-Ethylhexanal	D	Chloroethylene	D	o,p-Ethoxyphenyl isocyanate	D		
2-hexanol	G	Chlorofluoroethylene	B	o,p-Iodophenetole	D		
2-Methoxyethanol	D	Chloromethyl methyl ether	D	o-Bromophenetole	D		
2-Methoxyethyl vinyl ether	D	Chloroprene	C	o-Chorophenetole	D		
2-Methyltetrahydrofuran	D	Chlorotrifluoroethylene,	C	other secondary alcohols	B		
2-pentanol	B	Cumene,	B	Oxybis(2-ethyl acetate)	D		
2-phenylethanol	B	Cyclohexene,	B	Oxybis(2-ethyl benzoate)	D		
2-propanol	G	Cyclooctene	D	p-(n-Amyloxy)benzoyl chloride	D		
3-Bromopropyl phenyl ether	D	cyclopentene,	B	p-Bromophenetole	D		
3-Ethoxypropionitrile	D	Cyclopropyl methyl ether	D	p-Chlorophenetole	D		
3-Methoxy-1-butyl acetate	D	decahydronaphthalene(decalin)	B	other secondary alcohols	B		
3-Methoxyethyl acetate	D	Di(1-propynl) ether	D	p-Dibenzoyloxybenzene	D		
3-methyl-1-butanol (isoamyl alcohol)	B	Di(2-propynl) ether	D	p-Di-n-butoxybenzene	D		
4,5-Hexadien-2-yn-1-ol	D	diacetylene(butadiyne)	B	p-Ethoxyacetophenone	D		
4-heptanol	B	Diallyl ether	D	Phenoxyacetyl chloride	D		
4-methyl-2-pentanol	B	dicyclopentadiene	B	Phenyl-o-propyl ether	D		
4-penten-1-ol	B	Diethoxymethane	D	Potassium amide	A		
4-Vinyl cyclohexene	D	Diethyl acetal	D	Potassium Metal	A		
Acetal	B	diethyl ether,	B	p-Phenylphenetone	D		
acetaldehyde	B	Diethyl ethoxymethylenemalonate	D	Sodium 8-11-14-eicosatetraenoate	D		
Acrolein	D	Diethyl fumarate	D	Sodium amide	A		
Acrylic Acid,	C	diethylene glycol dimethyl ether	B	Sodium ethoxyacetylde	D		
acrylonitrile	C	Diethylketene	D	Stryene,	C		
Allyl ether	D	Dimethoxymethane	D	tert-Butyl methyl ether	D		
allyl ethyl ether	D	Di-n-propoxymethane	D	Tetrafluoroethylene	A		
Allyl phenyl ether	D	Divinyl acetylene	A	Tetrafluoroethylene	C		