

Many liquid organic compounds, a few solid and gaseous organic compounds and a few inorganic solids form peroxides upon storage. Most organic peroxides are sensitive to shock, heat or friction to varying degrees. These compounds form by the reaction of the chemical with oxygen allowed in the headspace of chemical containers once the container is opened for the first time. Peroxides form at varying rates depending upon the compound. Some peroxides quickly build up to an explosive level and some are only explosive on concentration, such as when a solvent is distilled. Although there is no agreement upon what level of peroxides present a significant hazard, several sources suggest that the "safe" range of peroxide formation is **100 ppm** or less. We recommend that all peroxide forming chemicals be tested at the end of the appropriate storage period (see below). If peroxides are detected at a level above 100 ppm, the material must be decontaminated with standard procedures for de-peroxidation or discarded as hazardous waste if the material cannot be drain disposed. Test strips for the detection of peroxides may be purchased from the Chemistry Department stock room in the basement of the Physical Science Building or lab supply houses. Several chemical methods for the detection of peroxides are also available.

### **General categories of compounds known to auto-oxidize to form peroxides:**

- Aldehydes
- Ketones (especially cyclic ketones)
- Ethers (especially cyclic and those containing primary and secondary alkyl groups)
- Compounds containing allylic hydrogens (e.g. alkenes, vinyl and vinylidene cmpds)
- Compounds that contain Benzylic hydrogens
- Compounds containing a tertiary C-H group (e.g., decalin and 2,5-dimethylhexane)
- Alkali metals and alkali metal amides

### **Control and Safe Use of Peroxide Formers**

#### **Peroxide formation may be controlled by the following methods:**

- Date all incoming containers of peroxide formers when received and again when opened. Many chemical companies now routinely print an expiration date on containers of the worst peroxide formers.
- Purchase the smallest possible container size for your needs.
- Store peroxide formers in sealed, air-impermeable containers such as dark amber glass with a tight-fitting cap.
- Iron inhibits the formation of peroxides in some materials, which is why diethyl ether and some other materials are purchased in metal cans. Ground glass stoppered bottles and plastic containers are not advisable, however, plastic squeeze bottles may be used for small quantities of some materials, such as 2-propanol, for immediate use.

## Peroxide Forming Chemicals



- Store peroxide formers in the dark.
- Inhibitors are added to some chemicals and the purchase of peroxide formers with added inhibitors is encouraged.
- Store peroxide formers, especially those in Table A below, 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.
- Avoid the distillation of peroxide formers without first testing for the existence of peroxides in the material. Most explosions with the use of peroxide formers occur when a material is distilled to dryness. Leave at least 10-20% bottoms. Stir such distillations with a mechanical stirrer or an inert gas. Air or an oxygen containing mixture should never be used for this purpose.

## Testing for Peroxides

**Routine testing done with commercial test strips, or using potassium iodide (100 mg/1 mL g. Acetic acid + 1 mL of solvent) show three categories of results:**

0-30 ppm: Little or no threat of violent reaction. Should be stabilized with hydroquinone, t-butyl catechol or ferrous sulfate. (KI test slightly yellow)

30-80 ppm: Expired or mismanaged compounds that **may** pose a threat to persons and structures. The available literature shows that attempts to stabilize these compounds may initiate exothermic reactions that may pose a threat to persons and structures. (KI test brilliant yellow)

Greater than 80 ppm: Expired or mismanaged compounds **that** pose a threat to persons and structures. (KI test brilliant yellow to red)

## Safe Storage Periods for Peroxide Formers

**Twelve-month storage limit:** Twelve-month test cycle will be completed unless the reagent is stabilized, such as, HPLC grade ethers. Special handling and accountability is required for uninhibited reagents. These compounds form peroxides with age. Exposure to air is necessary for peroxide formation. Light promotes peroxide formation in the presence of oxygen. Manage containers to minimize headspace or inert container contents. Do not attempt to test containers outside of safe storage limits. Concentration of peroxides by distillation or evaporation is typically necessary for explosivity. However, concentrations of peroxides that have caused crystallization or have phase separation are extremely dangerous:

Unopened chemicals from manufacturer:	18 months
Opened containers:	
Chemicals in Class III.	3 months
Chemicals in Classes II and IV.	12 months

## Peroxide Forming Chemicals



Uninhibited chemicals in Class I.

24 hours

Inhibited chemicals in Class I.

12 months

**(Do not store under an inert atmosphere)**

### Removal of Peroxides or Destruction of Diacyl and Dialkyl Peroxides

Peroxides can be removed from a solvent by passing it through a column of basic activated alumina, by treating it with indicating Molecular Sieves<sup>®</sup>, or by reduction with ferrous sulfate. Although these procedures remove hydroperoxides, which are the principal hazardous contaminants of peroxide-forming solvents, they do not remove dialkyl peroxides, which may also be present in low concentrations. The following procedures are found in "Prudent Practices in the Laboratory": Handling and Disposal of Chemicals, 7.D.2.5.

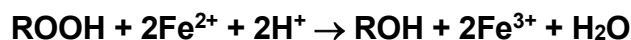
#### Removal of peroxides with alumina:

A 2 x 33 cm column filled with 80 g of 80-mesh basic activated alumina is usually sufficient to remove all peroxides from 100 to 400 mL of solvent, whether water-soluble or water-insoluble. After passage through the column, the solvent should be tested for peroxide content. Peroxides formed by air oxidation are usually decomposed by alumina, not merely absorbed on it. However, for safety it is best to slurry the wet alumina with a dilute acidic solution of ferrous sulfate before it is discarded.

#### Removal of peroxides with Molecular Sieves<sup>®</sup>:

Reflux 100 mL of solvent with 5 g of 4- to 8- mesh indicating activated 4A Molecular Sieves<sup>®</sup> for several hours under nitrogen. The sieves are separated from the solvent and require no further treatment because the peroxides are destroyed during their interaction with the sieves.

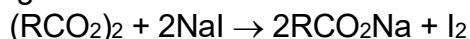
#### Removal of peroxides with ferrous sulfate:



A solution of 6 g of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , 6 mL of concentrated sulfuric acid, and 11 mL of water is stirred with 1L of water-insoluble solvent until the solvent no longer gives a positive test for peroxides. Usually only a few minutes are required.

#### Procedure for destruction of diacyl peroxides:

Diacyl peroxides can be destroyed by this reagent as well as by aqueous sodium hydrogen sulfite, sodium hydroxide, or ammonia. However, diacyl peroxides with low solubility in water, such as dibenzoyl peroxide, react very slowly. A better reagent is a solution of sodium iodide or potassium iodide in glacial acetic acid.



## Classes of Peroxides

**Class I:** Unsaturated materials, especially those of low molecular weight, may auto-polymerize violently and hazardously due to peroxide initiation. Test for peroxide formation or discard liquids after 6 months; discard gases after 1 year.

Acrylic acid <sup>b</sup>	Tetrafluoroethylene <sup>c</sup>
Acrylonitrile <sup>b</sup>	Vinyl acetate
Butadiene <sup>c</sup>	Vinyl acetylene
Chlorobutadiene (Chloroprene) <sup>c</sup>	Vinyl chloride
Chlorotrifluoroethylene	Vinyl pyridine
Methyl methacrylate <sup>b</sup>	Vinylidene chloride
Styrene	

**Class II:** The following chemicals are a peroxide hazard upon concentration (distillation / evaporation). A test for peroxide should be performed if concentration is intended or suspected. Test for peroxide formation or discard after 1 year.

Acetal	Dioxane (p-dioxane)
Acetaldehyde	Ethylene glycol dimethyl ether (Glyme)
Acrolein	Furan
Alcohols (primary, secondary)	Grignard reagents (ether solvents)
Alcohols (allylic, benzylic)	4-Heptanol
Alkyl-substituted cycloaliphatics	2-Hexanol
Benzyl alcohol	Methyl acetylene
2-Butanol	3-Methyl-1-butanol
Cumene	Methyl cyclopentane
Cycloheptanone	Methyl isobutyl ketone (MIBK)
Cyclohexanol	4-Methyl-2-pentanol
Cyclohexanone	2-Pentanol
2-Cyclohexen-1-ol	4-Penten-1-ol
Cyclohexene	1-Phenylethanol
Cyclopentene	2-Phenylethanol
Cyclopentanone	2-Propanol
Decahydronaphthalene	Tetrahydrofuran
Diacetylene	Tetrahydronaphthalene
Dicyclopentadiene	Vinyl ethers
Diethylene glycol dimethyl ether (Diglyme)	
Diethyl ether	

## Peroxide Forming Chemicals



**Class III:** Peroxides derived from the following compounds may explode without concentration.

There will be a three (3) month storage limit for the following chemicals and these chemicals **Must be stabilized**, tested or discarded.

Organic cmpds:	Inorganic cmpds:
Butadiene <sup>a</sup>	Potassium metal
Chloroprene <sup>a</sup>	Potassium amide
Divinyl ether	Sodium amide (Sodamide)
Divinyl acetylene	
Isopropyl ether	
Tetrafluoroethylene <sup>a</sup>	
Vinylidene chloride (1,1-DCE)	

**Class IV:** Chemicals that may form peroxides but cannot clearly be placed in Classes I, II, or III.

Acrolein	<i>B</i> -Bromophenetole
Allyl ether <sup>d</sup>	<i>o</i> -Bromophenetole
Allyl ethyl ether	<i>p</i> -Bromophenetole
Allyl phenyl ether	3-Bromopropyl phenyl ether
<i>p</i> -( <i>n</i> -Amyloxy)benzoyl chloride	1,3-Butadiyne
<i>n</i> -Amyl ether	Buten-3-yne
Benzyl <i>n</i> -butyl ether <sup>d</sup>	<i>tert</i> --Butyl ethyl ether
Benxyl ether <sup>d</sup>	<i>tert</i> -Butyl methyl ether
Benzyl ethyl ether <sup>d</sup>	<i>n</i> -Butyl phenyl ether
Benzyl methyl ether	<i>n</i> -Butyl vinyl ether
Benzyl 1-naphthyl ether <sup>d</sup>	Chloroacetaldehyde diethylacetal <sup>d</sup>
1,2-Bis(2-chloroethoxy) -ethane	2-Chlorobutadiene
Bis(2 ethoxyethyl)ether	1-(2-Chloroethoxy)-2-phenoxyethane
Bis(2(methoxyethoxy)-ethyl) ether	Chloroethylene
Bis(2-chloroethyl) ether	Chloromethyl methyl ether <sup>e</sup>
Bis(2-ethoxyethyl) adipate	<i>B</i> -Chlorophenetole
Bis(2-ethoxyethyl) phthalate	<i>o</i> -Chlorophenetole
Bis(2-methoxyethyl) carbonate	<i>p</i> -Chlorophenetole
Bis(2-methoxyethyl) ether	Cyclooctene <sup>d</sup>
Bis(2-methoxyethyl) phthalate	Cyclopropyl methyl ether
Bis(2-methoxymethyl) adipate	Diallyl ether <sup>d</sup>
Bis(2- <i>n</i> -butoxyethyl) phthalate	<i>p</i> -Di- <i>n</i> -butoxybenzene
Bis(2-phenoxyethyl) ether	1,2-Dibenzoyloxyethane <sup>d</sup>
Bis(4-chlorobutyl) ether	<i>p</i> -Dibenzoyloxybenzene <sup>d</sup>
Bis(chloromethyl) ether <sup>e</sup>	1,2-Dichloroethyl ethyl ether
2-Bromomethyl ethyl ether	2,4-Dichlorophenetole

## Peroxide Forming Chemicals



### Class IV (con't)

Diethoxymethane <sup>d</sup>	Limonene
2,2-Diethoxypropane	1,5- <i>p</i> -Methadiene
Diethyl ethoxymethylene-malonate	Methyl <i>p</i> -( <i>n</i> -amyloxy)benzoate
Diethyl fumarate <sup>d</sup>	4-Methyl-2-pentanone
Diethyl acetal <sup>d</sup>	<i>n</i> -Methylphenetole
Diethylketene <sup>f</sup>	2-Methyltetra-hydrofuran
<i>m,o,p</i> -diethoxybenzene	3-Methoxy-1-butyl acetate
1,2-Diethoxyethane	2-Methoxy-ethanol
Dimethoxymethane <sup>d</sup>	3-Methoxyethyl acetate
1,1-Dimethoxyethane <sup>d</sup>	2-Methoxyethyl vinyl ether
Dimethylketene <sup>f</sup>	Methoxy-1,3,5,7-cyclooctatetraene
3,3-Dimethoxypropene	B-Methoxy-propionitrile
2,4-Dinitrophenetole	<i>m</i> -Nitro-phenetole
1,3-Dioxepane <sup>d</sup>	1-Octene
Di(1-propynyl)ether <sup>f</sup>	Oxybis(2-ethyl acetate)
Di(2-propynyl)ether	Oxybis(2-ethyl benzoate)
Di- <i>n</i> -propoxymethane <sup>d</sup>	<i>B,B</i> -oxydi-propionitrile
1,2-Epoxy-3-isopropoxypropane <sup>d</sup>	1-Pentene
1,2-Epoxy-3-phenoxypropane	Phenoxyacetyl chloride
<i>p</i> -Ethoxyacetho-phenone	<i>a</i> -Phenoxy-propionyl chloride
1-(2-Ethoxyethoxy)-ethyl acetate	Phenyl <i>o</i> -propyl ether
2-Ethoxyethyl acetate	<i>p</i> -Phenylphenetone
(2-Ethoxyethyl)- <i>o</i> -benzoyl benzoate	<i>n</i> -Propyl ether
1-Ethoxynaphthalene	<i>n</i> -Propyl isopropyl ether
<i>o,p</i> -Ethoxyphenyl isocyanate	Sodium 8,11,14-eicosa-tetraenoate
1-Ethoxy-2-propyne	Sodium ethoxyacetylde <sup>f</sup>
3-Ethoxypropionitrile	Tetrahydropyran
2-Ethylacrylaldehyde oxime	Triethylene glycol diacetate
2-Ethylbutanol	Triethylene glycol dipropionate
Ethyl <i>B</i> -ethoxy-propionate	1,3,3-Trimethoxy-propene <sup>d</sup>
2-Ethylhexanal	1,1,2,3-Tetrachloro-1,3-butadiene
Ethyl vinyl ether	4-Vinyl cyclohexene
2,5-Hexadiyn-1-ol	Vinylene carbonate
4,5-Hexadien-2-yn-1-ol	
<i>n</i> -Hexyl ether	
<i>o,p</i> -Iodophenetole	
Isoamyl benzyl ether <sup>d</sup>	
Isoamyl ether <sup>d</sup>	
Isobutyl vinyl ether	
Isophorone <sup>d</sup>	
<i>B</i> -Isopropoxy-propionitrile <sup>d</sup>	
Isopropyl 2,4,5-tri-chlorophenoxyacetate	

## Peroxide Forming Chemicals



### NOTES:

- <sup>a</sup> When stored as a liquid monomer.
- <sup>b</sup> Although these chemicals form peroxides, no explosions involving these monomers have been reported.
- <sup>c</sup> When stored in liquid form, these chemicals form explosive levels of peroxides without concentration. They may also be stored as a gas in gas cylinders. When stored as a gas, these chemicals may auto-polymerize as a result of peroxide accumulation.
- <sup>d</sup> These chemicals easily form peroxides and should probably be considered under Class II.
- <sup>e</sup> OSHA - regulated carcinogen.
- <sup>f</sup> Extremely reactive and unstable compound.

### References:

Prudent Practices in the Laboratory, National Research Council, 1995.

"Review of Safety Guidelines for Peroxidizable Organic Chemicals," Chemical Health and Safety, September/October 1996.