

## Peroxide-Forming Chemicals

### Introduction

Peroxide-forming chemicals are among the most hazardous substances commonly handled in laboratories. Several commonly used solvents (e.g., diethyl ether, tetrahydrofuran, dioxane, etc.) can form explosive peroxides through a relatively slow oxidation process in the presence of air and light. Since most peroxide-forming chemicals are packaged in atmospheres containing air, even unopened bottles can produce peroxides. Refrigeration does not eliminate peroxide formation and stabilizers only slow down formation.

Peroxide formation becomes evident when crystalline solids are observed in the liquid itself or around the bottle's cap. Some peroxide-forming chemicals produce solutions that appear cloudy. Once peroxides have formed, they can detonate when combined with other compounds or when disturbed by unusual heat, mechanical shock, impact, or friction. Visual inspection is the safest way to determine peroxide formation. If you suspect the presence of peroxides, contact EHS at 860-486-3613.

### Peroxide-Former Categories

There are four categories of peroxide-forming chemicals. The following tables list examples of chemicals commonly found in labs, but these lists are not comprehensive. Safety Data Sheets (SDSs) must be reviewed to indicate whether chemicals being utilized in the laboratory can form explosive peroxides.

#### Category 1: Severe peroxide hazard without storage

These are chemicals that form explosive levels of peroxides without concentration. Severe peroxide hazard occurs after prolonged storage, especially after exposure to air.

*Label with the date of receipt and date of opening. Test for peroxide formation monthly and discard after 3 months.*

Butadiene	Isopropyl ether	Sodium amide
Chloroprene	Potassium amide	Tetrafluoroethylene
Divinyl acetylene	Potassium metal	Vinylidene chloride

### Category 2: Peroxide hazard due to concentration

These are chemicals that form explosive levels of peroxide on concentration (distillation or evaporation).

*Label with the date of receipt and date of opening. Test for peroxides 6 months after opening (if uninhibited) and dispose of within 12 months unless peroxide testing confirms no peroxides present.*

Acetal	Diacetylene	2-Hexanol
Acetaldehyde	Dicyclopentadiene	Methylacetylene
Benzyl alcohol	Diethylene glycol dimethyl ether (diglyme)	Methyl cyclopentane
2-Butanol	Diethyl ether	Methyl-isobutyl ketone
Cumene	Diethylene glycol	2-Pentanol
2-Cyclohexen-1-ol	Dimethyl ether	1-Phenylethanol
Cyclohexane	Dioxanes	Tetrahydrofuran
Cyclooctene	Ethylene glycol dimethyl ether (glyme)	Tetrahydronaphthalene
Cyclopentene	4-Heptanol	Vinyl ethers

### Category 3: Autopolymerize due to peroxide accumulation

These chemicals may explode when relatively small quantities of peroxides form. They normally have an inhibitor added by the manufacturer to prevent peroxide formation. Do not store in an inert atmosphere.

*Label with the date of receipt and date of opening. Dispose of inhibited chemicals after 12 months and uninhibited items within 24 hours of use.*

Acrylic acid	Chlorotrifluoroethylene	Vinylacetylene
Acrylonitrile	Methyl methacrylate	Vinyl chloride
Butadiene	Styrene	Vinyl pyridine
Chloroprene	Vinyl acetate	Tetrafluoroethylene

#### Category 4: May form peroxides

Normally stable but may form peroxides under certain conditions.

*Review the safety data sheet to determine under which conditions peroxide formation is expected and manage accordingly. Consult EHS if crystals are present.*

Acrolein	2-Ethylbutanol	1-Pentene
Benzyl ethyl ether	Ethyl vinyl ether	Phenoxyacetyl chloride
Benzyl methyl ether	n-Hexyl ether	Phenyl-o-propyl ether
Cyclooctene	Isoamyl ether	n-Propyl ether
p-Dibenzylxybenzene	Isobutyl vinyl ether	Tetrahydropyran
Diethyl fumarate	b-Isopropoxypropionitrile	Triethylene glycol diacetate
Diethyl acetal	2-Methoxyethanol	1,3,3-Trimethoxypropene
Dimethoxymethane	3-Methoxyethyl acetate	1,1,2,3-Tetrachloro-1,3-butadiene
Di(1-propyl) ether	b-Methoxypropionitrile	4-Vinyl cyclohexane
2-Ethoxyethyl acetate	1-Octene	Vinylene carbonate

#### **Safe Work Practices**

1. Read the safety data sheet (SDS) for each peroxide-former prior to use.
2. Visually check for crystalline solids before each use.
3. Order only the quantities needed. Many uninhibited peroxide-formers must be tested or discarded after 12 months.
4. Use older bottles before opening or ordering new ones.
5. Test for peroxides or discard bottles that have exceeded the manufacturer's expiration date. If the chemical has been tested, the test date must be written on the side of the bottle.
6. Label each bottle with the date received and the date the bottle was first opened.
7. Never distill peroxide-forming solvents unless they have been tested and known to be free of peroxides. Peroxide concentrated in the residue can pose a serious explosion hazard.

8. Peroxide test strips must be used to test for presence of peroxides.
9. **DO NOT TEST** peroxide-forming chemicals that are of unknown age or origin, if crystals or discolored solids are present, or if the liquid appears cloudy. Contact EHS for evaluation and disposal.
10. Always use peroxide-formers inside a chemical fume hood.
11. Reduce the sensitivity of peroxides to heat and shock by dilution with inert solvents.
12. Avoid using solutions of peroxides in volatile solvents. Solvent evaporation must be controlled to avoid dangerous concentration of the peroxide.
13. Do not allow peroxides to contact iron; compounds of iron, cobalt, or copper; metal oxide salts; acids; bases; or acetone.
14. Do not handle peroxides with metal spatulas or magnetic stirring blades that could leach iron. Teflon™, ceramic, or wooden spatulas and stirring blades are recommended.
15. Do not allow open flames or sources of heat, sparks, friction, grinding, or impact near peroxides.
16. Do not return unused peroxide-forming chemicals to the original container.

## Storage

1. Store in tightly sealed, opaque containers when not in use. Protect them from air, heat, moisture, light, or impurities.
2. Do not store liquid peroxides or solutions of peroxides at a temperature below the point where the peroxide freezes or precipitates.
3. Store away from incompatible materials such as strong oxidizing and reducing agents.
4. Store in a flammable or explosion-proof refrigerator if materials must be refrigerated.

## Resources

### *Sigma-Aldrich: Peroxide Forming Solvents*

<http://www.sigmaaldrich.com/chemistry/solvents/learning-center/peroxide-formation.html>