



EH&S Guidance Document:

Peroxide Formers



Peroxide forming chemicals are a group of chemicals that can form shock-sensitive explosive peroxide crystals when exposed to atmospheric oxygen. A peroxide is a chemical that contains a peroxy (O-O) unit with the chemical formula of O_2^{2-} . These crystals form over time, and can develop within the container itself, around the opening of the lid, or even unseen between the lid and the threads of the bottle. These crystals can explode if subjected to mechanical shock, intense light, rapid changes in temperature, or heat. General categories of peroxide forming chemicals include Aldehydes, Ketones, Ethers, Alkenes and Alkali metals. Some of these chemicals come with inhibitors added (e.g. BHT) to help prevent peroxide formation, but formation can still occur over time. Commonly used peroxide formers include diethyl ether, tetrahydrofuran (THF), and cyclohexene.

The following requirements must be followed to prevent hazardous conditions from arising and ensure safe handling of these materials:

- 1) Containers of peroxide forming chemicals are required to be labeled with the dates that they are received, the date opened, their expiration date, and any peroxide test that has been performed. Most potential peroxide forming chemicals have a shelf life of 12 months once opened and 18 months if unopened, unless noted otherwise. See Appendix 1 for a container label you can use.
- 2) Once opened, potential peroxide forming chemicals should be periodically tested for the formation of peroxides. Always visually check for crystal formation before handling the container. Do not test or treat any peroxide forming chemical if there are any visible crystals, or a precipitate or oily viscous layer is present. Testing methods are described below in Section I.
- 3) Only purchase peroxide forming chemicals in quantities that will allow them to be completely used before they would expire or would have to be tested for formation of peroxides. If possible, purchase peroxide formers that come with an inhibitor added (e.g. THF inhibited with BHT).
- 4) Potential peroxide forming chemicals that are past their expiration dates or their safe shelf lives automatically become hazardous waste and are required to be disposed through EH&S, unless they have been documented as tested for safe levels of peroxides and inhibited.

If there is any question to the age or state of a peroxide forming chemical, contact EH&S for assistance or immediately dispose of it as hazardous waste through EH&S.



I. PEROXIDE TESTING METHODS

A variety of methods are available to test for the presence of peroxides in organic solvents, with the three most common tests described below. Presently, peroxide levels up to 30 ppm is widely used as the threshold for safe usage, and chemicals between 30-80 ppm should not be distilled or concentrated. Over 80 ppm means the container should avoid being handled and get disposed of through EH&S immediately. Document on the bottle itself every peroxide test and the results in order to ensure hazard communication to future users.

Visual Testing Method

If a bottle is potentially very old or expired, do not handle the bottle to inspect it. Pay special attention to the neck/opening of the bottle as this is where evaporation and concentration can occur. If there are visible crystals in or around the bottle, visible precipitate, or an oily viscous layer present in the material, these are visual indicators of dangerously high peroxide levels.

There is a chance that crystals have developed between the bottle's lid and the threads, so always apply caution opening these bottles even if no crystals are seen. Wispy like structures floating in a clear liquid suspension can also signify contamination.

Immediately contact the EH&S department to properly dispose of any bottle that shows signs of contamination or crystal formation.



Peroxide crystallization under bottle cap and around the neck



Peroxide crystallization developing within the bottle

Peroxide Testing Strips Method

We recommend using Quantofix® Peroxide Test Strips (Sigma-Aldrich Part # 37206) to test peroxide levels in organic solvents and aqueous solutions. In the presence of hydrogen peroxide, the test paper turns blue. Quantofix® Peroxide test sticks can also be used for the determination of peracetic acid and other organic and inorganic hydroperoxides. To test for hydroperoxides in organic solvents, the test zone is wetted with one drop of water after evaporation of the solvent. Compare results to product guidelines.

Interferences: In the pH range of 2-9, the accuracy of the determination is independent of the pH of the test solution. Buffer strongly acidic solutions with sodium acetate and adjust alkaline solutions to about pH 5-7 with citric acid. Falsely positive results can only be caused by strong oxidizing agents.

Iodide Indicator Method

Prepare a fresh solution of 100 mg of the sodium or potassium iodide crystals dissolved in 1.0 ml of glacial acetic acid. Add 1.0 ml of the solvent to the iodide solution. *(continued on next page)*



Iodide Indicator Method (cont.)

A yellow color indicates iodine formation via iodide oxidation by sample peroxide; a brown color indicates high concentration. A blank determination should be made particularly when color development is faint since iodide/acetic acid mixtures will, over time, turn a yellow-brown color due to air oxidation.

A more sensitive variation of the above method adds one drop of a saturated, aqueous starch solution to the sample solution. Starch and iodine form a bright blue complex that is more easily visualized than the yellow color generated by iodine alone. Dark blue solution color would be indicative of high peroxide concentrations.

Use the chart below to determine testing results:

Iodide Test Color	Testing Strip Value	What to do
Slight Yellow	0-30 ppm	Stabilize with an inhibitor; Does not require disposal (hydroquinone, t-butyl catechol or ferrous sulfate; between 1 and 250 ppm or about 0.1 mg inhibitor/ Liter of solvent)
Bright Yellow	30-80 ppm	May pose a hazard if attempted to stabilize. Tag the container for EH&S Hazardous Waste pickup.
Dark Yellow/Red	> 80 ppm	DO NOT attempt to stabilize or handle the container further. Tag the container for EH&S Hazardous Waste pickup.

II. PROPER USE AND STORAGE OF PEROXIDE FORMERS

Usage and Personal Protective Equipment

- Wear properly rated gloves and eye protection whenever using peroxide forming chemicals.
- Peroxide formers should be used in a chemical fume hood with the sash as low as feasible.
- Do not evaporate containers that held peroxide forming compounds to dryness for reuse unless it is known that the chemical was peroxide-free.
- Avoid the distillation of peroxide formers without first testing for the existence of peroxides. Most explosions occur when a material is distilled to dryness. Leave at least 10-20% of solution in the still bottom. Stir such distillations with a mechanical stirrer or an inert gas.
- After each use, carefully wipe clean the container neck, cap and threads before resealing.

Storage

- Store in a tightly closed container and keep in a flammable storage area. Keep away from sources of ignition. Store in a cool, dry place, protected from moisture, light and air.
- DO NOT store peroxide formers, such as diethyl ether, in a refrigerator or freezer unless it is officially rated for the storage of flammable solvents.
- Refrigeration does not prevent (and may not inhibit) peroxide formation. Peroxide forming compounds should not be stored at or lower than the temperature at which the peroxide freezes or precipitates, as this will make these compounds extremely sensitive to shock.



III. LIST OF COMMON PEROXIDE FORMING CHEMICALS

The rate of peroxide formation will depend 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. Peroxidizable compounds contain a reactive hydrogen atom that is 'activated' by adjacent structural components. The dangers of peroxide formation can be divided into three groups, A, B and C. As well, there are a number of chemical compounds that may form peroxides, but do not clearly fit into group A-C (Group D).

Group A

- 3 Month Storage Limit (Severe Peroxide Hazard)

- Chemicals that form explosive levels of peroxides without concentration.
- Severe peroxide hazard after prolonged storage, especially after exposure to air.
- All have been responsible for fatalities.
- Test before use, or discard after 3 months.

Butadiene*
Chloroprene*
Divinyl acetylene
Diisopropyl ether
Potassium metal
Potassium amide
Sodium amide (sodamide)
Tetrafluoroethylene*
Vinylidene chloride (1,1-DEC)

* Indicates a peroxide former when stored as a liquid monomer.

Group B

- 12 Month Storage Limit

- Chemicals that form a peroxide hazard on concentration.
- Test for peroxide formation before distillation or evaporation.
- Test before use, or discard after 12 months.

1-Phenylethanol
2-Cyclohexen-1-ol
2-Hexanol
2-Pentanol
2-Phenylethanol
3-Methyl-1-butanol
4-Heptanol
4-Methyl-2-pentanol
4-Penten-1-ol
1,4-Dioxane
Acetal
Acetaldehyde
Benzyl alcohol
Chlorofluoroethylene
Cumene
Cyclohexene
Cyclopentene
Decalin
Diacetylene
Dicyclopentadiene
Diethyl ether
Diglyme
Dimethoxyethane
Furan
Isopropanol
Methyl-isobutyl ketone
Propyne
sec-Butanol
Tetrahydrofuran
Tetralin
Vinyl ethers
Other secondary alcohols

Group C

- 12 Month Storage Limit

- Chemicals that may autopolymerize as a result of peroxide accumulation
- The peroxide-forming potential increases for liquids of this group, especially for butadiene, chloroprene, and tetrafluoroethylene
- Test before use, or discard liquids after 6 months; discard gases after 1 year

Acrylic acid
Acrylonitrile
Butadiene**
Chlorobutadiene (Chloroprene)**
Chlorotrifluoroethylene
Methyl methacrylate
Styrene
Tetrafluoroethylene**
Vinyl acetate
Vinyl acetylene
Vinyl chloride
Vinyl pyridine
Vinylidene chloride

** Can form explosive levels of peroxides if stored as a liquid. When stored as a gas, peroxide accumulation may cause autopolymerization.



Group D

- 12 Month Storage Limit

- Chemicals that may form peroxides but cannot clearly be placed in Groups A–C
- Test for peroxide formation before use, or discard after 12 months


1-Ethoxy-2-propyne
1-Ethoxynaphthalene
1-Octene
1-Pentene
1-(2-Chloroethoxy)-2-phenoxyethane
1-(2-Ethoxyethoxy)-ethyl acetate
1,1-Dimethoxyethane
1,1,2,3-Tetrachloro-1,3-butadiene
1,2-Bis(2-chloroethoxy)-ethane
1,2-Dibenzoyloxyethane
1,2-Dichloroethyl ethyl ether
1,2-Diethoxyethane
1,2-Epoxy-3-isopropoxypropane
1,2-Epoxy-3-phenoxypropane
1,3-Butadiyne
1,3-Dioxepane
1,3,3-Trimethoxy-propene
1,5-p-Methadiene
2-Bromomethyl ethyl ether
2-Chlorobutadiene
2-Ethoxyethyl acetate
(2-Ethoxyethyl)-o-benzoyl benzoate
2-Ethylbutanol
2-Ethylhexanal
2-Methoxy-ethanol
2-Methyltetra-hydrofuran
2,2-Diethoxypropane
2,4-Dichlorophenetole
2,4-Dinitrophenetole
2,4,5-Tri-chlorophenoxyacetate
2,5-Hexadiyn-1-ol
3-Bromopropyl phenyl ether
3-Ethoxypropionitrile
2-Ethylacrylaldehyde oxime
3-Methoxy-1-butyl acetate
3,3-Dimethoxypropene


4-Methyl-2-pentanone
4-Vinyl cyclohexene
4,5-Hexadien-2-yn-1-ol
Acrolein
Allyl ether
Allyl ethyl ether
Allyl phenyl ether
Benzyl 1-naphthyl ether
Benzyl ether
Benzyl ethyl ether
Benzyl methyl ether
Benzyl n-butyl ether
Bis(2-chloroethyl) ether
Bis(2-ethoxyethyl) adipate
Bis(2-ethoxyethyl) ether
Bis(2-ethoxyethyl) phthalate
Bis(2-(methoxyethoxy)-ethyl) ether
Bis(2-methoxyethyl) carbonate
Bis(2-methoxyethyl) ether
Bis(2-methoxyethyl) phthalate
Bis(2-methoxymethyl) adipate
Bis(2-n-butoxyethyl) phthalate
Bis(2-phenoxyethyl) ether
Bis(4-chlorobutyl) ether
Bis(chloromethyl) ether
Buten-3-yne
Chloroacetaldehyde diethylacetal
Chloroethylene
Chloromethyl methyl ether
Cyclooctene
Cyclopropyl methyl ether
Di(1-propynyl)ether***
Di(2-propynyl)ether
Di-n-propoxymethane
Diallyl ether
Diethoxymethane
Diethyl acetal
Diethyl ethoxymethylene-malonate
Diethyl fumarate
Diethyketene***
Dimethoxymethane
Dimethylketene***
Ethyl vinyl ether
Ethyl β-ethoxy-propionate
Furan
Isoamyl benzyl ether
Isoamyl ether


Isobutyl vinyl ether
Isophorone
Limonene
m,o,p-Diethoxybenzene
m-Nitro-phenetole
Methoxy-1,3,5,7-cyclooctatetraene
Methyl p-(n-amlyoxy)benzoate
n-Amyl ether
n-Butyl phenyl ether
n-Butyl vinyl ether
n-Hexyl ether
n-Methylphenetole
n-Propyl ether
n-Propyl isopropyl ether
o-Bromophenetole
o-Chlorophenetol
o,p-Ethoxyphenyl isocyanate
o,p-Iodophenetole
Oxybis(2-ethyl acetate)
Oxybis(2-ethyl benzoate)
p-(n-Amyloxy)benzoyl chloride
p-Bromophenetole
p-Chlorophenetole
p-Di-n-butoxybenzene
p-Dibenzoyloxybenzene
p-Ethoxyacetho-phenone
p-Phenylphenetone
Phenoxyacetyl chloride
Phenyl o-propyl ether
Sodium 8,11,14-eicosa-tetraenoate
Sodium ethoxyacetylde***
tert-Butyl ethyl ether
Tetrahydropyran
Triethylene glycol diacetate
Triethylene glycol dipropionate
Vinylene carbonate
Vinylidene chloride
α-Phenoxy-propionyl chloride
β-Bromophenetole
β-Chlorophenetole
β-Isopropoxy-propionitrile
β-Methoxy-propionitrile
β,β-Oxydi-propionitrile


*** Extremely Reactive and unstable chemical.


APPENDIX 1: Labels (2" and 3" tall) to cut out and apply to containers of peroxide forming chemicals


 CAUTION SHOCK-SENSITIVE PEROXIDE FORMER	
Date Received <u> </u> / <u> </u> / <u> </u> Date Opened <u> </u> / <u> </u> / <u> </u> Date Expires <u> </u> / <u> </u> / <u> </u> <small>(12 months after opening)</small>	INHIBITOR ADDED? <input type="checkbox"/> YES <input type="checkbox"/> NO Type <u> </u>
Peroxide Testing Date <u> </u> Tester <u> </u> Peroxide Conc. <u> </u> Date <u> </u> Tester <u> </u> Peroxide Conc. <u> </u> Date <u> </u> Tester <u> </u> Peroxide Conc. <u> </u>	
<small>*IF PEROXIDE CONCENTRATION EXCEEDS 30ppm (0.003%), TAG FOR EH&S DISPOSAL*</small>	


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