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Safety and Health

Management of Peroxide-Forming Chemicals

This guideline outlines proper handling, use, and disposal of peroxide-forming chemicals at Marshall University to prevent unsafe conditions and potential explosions.

Peroxide-forming chemicals are compounds that may react with oxygen, even in low concentrations and at temperatures often not considered hazardous. Peroxidation is a hazard affecting primarily liquid peroxide formers and finely divided solids.

The risk of peroxide formation exists when the compound is exposed to oxygen. This occurs when the container is opened for the first time and is accelerated if containers are not properly sealed. Peroxidation occurs more rapidly at elevated temperatures and pressures. Refrigeration and freezing can cause peroxides to precipitate. Blanketing peroxide formers with an inert gas reduces the opportunity for oxygen to reach the compound during storage, but must be done in accordance with MSDS requirements.

Inorganic peroxides are generally stable, but some can be hazardous. They may generate peroxides in the presence of organic compounds, or can react violently in the presence of water.

Organic peroxides are carbon-based chemicals that contain the characteristic peroxide (-O-O-) bond. Many organic peroxides are shock, heat, or friction sensitive. Some peroxides quickly build up to high levels making them very explosive, while others are only explosive after concentration (e.g. after distillation). Although there is no specific rule nor mandate on what level of peroxides pose a significant hazard, at Marshall University any peroxide formation below 10 ppm is acceptable for retaining the chemical.

Peroxide levels detected at or above 10 ppm require immediate disposal as a hazardous waste. Submit an Unwanted Chemical Pickup Request. The form is available on the Environmental Health & Safety web site: http://www.marshall.edu/safety/chemical. If crystals are observed on the container of a peroxide former do not move it.

Container Labeling

In addition to the original manufacture label or secondary label, the containers of all peroxide-forming chemicals must be labeled with the following information. A label template is available on Safety & Health web site.

- **WARNING PEROXIDE FORMER or POTENTIALLY EXPLOSIVE PEROXIDE**
- Date of purchase
- Date container is first opened
- Required discard date based on the Disposal Requirements below
- Date and Results of all testing done to determine peroxide concentration

Storage and Handling

In order to safely manage chemicals that have the potential for forming heat and shock sensitive peroxides the following must be followed:

- Substitute non-hazardous chemicals whenever possible.
- Order the smallest possible amount for your needs, amount that can be used before disposal timeline.
- Purchase chemicals with inhibitors added when applicable. Inhibitors are depleted over time and must be replenished periodically.
- Store in original containers, when not possible use dark or amber-colored glass bottles with plastic caps. Do not use glass containers with a metal screw cap or glass stopper.
- Use metal cans when storing diethyl ethers. Iron in container inhibits the formation of peroxides.
- Plastic squeeze bottles may be used for small quantities of materials for immediate use, such as 2-propanol, but must be labeled.
- Dispense quantities only as needed.
- Never return unused material to stock container.
- Containers must be well-sealed, and stored away from light at cool temperatures.
- Do not refrigerate or freeze as this may cause peroxides to precipitate, unless directed to per label instructions.
- Provide secondary containment for all liquid storage.
- Never use a metal spatula, use ceramic or plastic instead.
- Follow lab procedures for personal protective equipment and hygiene. Avoid ingestion, inhalation or skin contact.
- Avoid friction, grinding, and any form of impact during handling or transport.
- Do not move or open older containers of peroxidizable chemicals, or containers of unknown age or history. Contact Environmental Health & Safety for disposal.
- Any peroxide-forming chemical with visible discoloration, crystallization or liquid stratification should be treated as potentially explosive. Contact Environmental Health & Safety for disposal.
- Older steel containers that have visible rust may be extremely dangerous.
- Distillation of any peroxide former should not be attempted unless the material has been tested for the presence of peroxide. Uninhibited Class C chemicals should not be distilled.
- Procedures which result in evaporation or extensive exposure to air or oxygen should be avoided unless chemical is first tested for peroxide levels and determined to be safe.
- Peroxide-forming chemicals must be labeled and dated when received. If the material is to be kept longer than the recommended storage time, the material must be tested for peroxides, and the test date and results attached to the container. If the peroxide concentration reaches 10 ppm the material must be disposed at hazardous waste.
- Store all chemicals away from other incompatible chemicals. Most peroxide formers are flammable. More information about storage compatibility is available on the Safety and Health web site.
- If the chemical is a flammable and requires refrigerated storage, an explosion-proof refrigerator is required.

Classes of Peroxide Formers

Class A	Class B	Class C
Forms explosive levels of peroxides without concentration	Forms explosive levels of peroxides on concentration	May autopolymerize as result of minor peroxide accumulation
Test for peroxides, or Dispose After (write actual disposal date on the container label):		
12 months after received or 3 months after first opened	12 months after received or 6 months after first opened	12 months after received or 24 hours – uninhibited chemical 12 months after first opening for inhibited chemicals
Butadiene [a] Chloroprene [a] Divinyl acetylene Isopropyl (diisopropyl) ether Potassium amide Potassium metal Sodium amide Tetrafluoroethylene [a] Vinylidene chloride	Acetal Acetaldehyde Benzyl alcohol 2-Butanol Cumene (isopropylbenzene) Cyclohexanol 2-Cyclohexen-1-ol Cyclohexene Decahydronaphthalene Diacetylene (butadiene) Dicyclopentadiene Diethyl ether (Ethyl ether) Diethylene glycol dimethyl ether Dioxanes Ethylene glycol dimethyl ether 4-Heptanol 2-Hexanol Isopropyl alcohol Methyl acetylene 3-Methyl-1-butanol Methylcyclopentane Methyl isobutyl ketone 4-Methyl-2-pentanol 2-Pentanol 4-Penten-1-ol 1-Phenylethanol 2-Phenylethanol 2-Propanol (IPA) Tetrahydrofuran Tetrahydronaphthalene Vinyl ethers Other secondary alcohols	Acrylic acid Acrylonitrile Butadiene [b] Chlorobutadiene Chloroprene [b] Chlorotrifluoroethylene Dibenzocyclopentadiene Indene Methyl methacrylate Styrene Tetrafluoroethylene [b] Vinyl acetate Vinyl acetylene Vinyl chloride Vinyl pyridine Vinyladiene chloride

a. When stored as a liquid monomer.

b. When stored in liquid form, these chemicals form explosive levels of peroxides without concentration. They may also be stored as a gas in a cylinder, and may autopolymerize as a result of peroxide accumulation.

Class D		
Chemicals that may form peroxides		
Consult MSDS to determine when peroxide formation is expected and label and store accordingly. Do not use and immediately dispose if peroxide crystals are observed.		
Acrolein	Cyclooctene	4,5-Hexadien-2-yn-1-ol
Allyl ether	Cyclopropyl methyl ether	n-Hexyl ether
Allyl ethyl ether	Diallyl ether	o,p-Iodophenetole
p-(n-Amyloxy) benzoyl chloride	p-Di-n-butoxybenzene	Isoamyl benzyl ether
n-Amyl ether	1,2-Didenzyloxyethane	Isoamyl ether
Benzyl n-butyl ether	p-Dibenzyloxybenzene	Isobutyl vinyl ether
Benzyl ether	1, 2-Dichloroethyl ethyl ether	lsophorone
Benzyl ethyl ether	2,4-Dichlorophenetole	b-Isopropoxypropiontrile
Benzyl methyl ether	Diethoxymethane	Isopropyl-2,4,5-trichlorophenoxyacetate
Benzyl-1-napthyl ether	2,2-Diethoxypropane	Limonene
1,2-Bis(2-chloroethoxyl) ethane	Diethyl acetal	1,5-p-Methadiene
Bis(2-chloroethyl) ether	Diethyl ethoxymethylenemalonate	Methyl-p-(n-amyloxy) benzoate
Bis(2-ethoxyethyl) adipate	Diethyl fumarate	4-Methyl-2-pentanone
Bis(2-ethoxyethyl) ether	Diethylketene	n-Methylphenetole
Bis(2-(methoxyethoxy)ethyl) ether	m,o,p-Diethoxybenzene	2-Methyltetrahydrofuran
Bis(2-methoxyethyl) carbonate	1,2-Diethoxyethane	3-Methoxy- l-butyl acetate
Bis(2-methoxyethyl) ether	Dimethoxymethane	2-Methoxyethanol
Bis(2-methoxyethyl) phthalate	1,1-Dimethoxyethane	3-Methoxyethyl acetate
Bis(2-methoxymethyl) adipate	Dimethoxyketene	2-Methoxyethyl vinyl ether
Bis(2-n-butoxyethyl) phthalate	3,3-Dimethoxpropene	Methoxy-1,3,5,7-cyclooctateraene
Bis(2-phenoxyethyl) ether	2,4-Dinitrophenetole	b-Methoxypropionitrile
Bis(4-chlorobutyl) ether	1,3-Dioxepane	m-Nitrophenetole
Bis(chloromethyl) ether	Di(1-propynyl) ether	1-Octene
2-Bromomethyl ethyl ether	Di(2-propynyl) ether	Oxybis(2-ethyl acetate)
3-Bromophenetole	Di-n-propoxymethane	Oxybis(2-ethyl benzoate)
o-Bromophenetole	1,2-Epoxy-3-isopropoxypropane	b,b-Oxdipropionitrile
p-Bromophenetole	1,2-Epoxy-3-phenoxpropane	1 -Pentene
3-Bromopropyl phenyl ether	p-Ethoxyacetophenone	Phenoxyacetyl chloride
1,3-Butadiyne	1-(2-Ethoxyethoxy) ethyl acetate	a-Phenoxypropionyl chloride
1-Buten-3-yne	2-Ethoxyethyl acetate	Phenyl-o-propyl ether
t-Butyl ethyl ether	(2-Ethoxyethyl)-a-benzoyl benzoate	p-Phenylphenetone
t-Butyl methyl ether	1-Ethoxynaphthalene	n-Propyl isopropyl ether
n-Butyl phenyl ether	o,p-Ethoxyphenyl isocyanate	Sodium 8,11,14-eicosatetraenoate
n-Butyl vinyl ether	1-Ethyoxy-2-propyne	Sodium ethoxyacetylide
Chloroacetaldehyde diethylacetal	3-Ethoxypropionitrile	Tetrahydropyran
2-Chlorobutadiene	2-Ethylacrylaldehyde oxime	Triethylene glycol diacetate
1(2-Chlororethoxy)-2-phenoxyethane	2-Ethylbutanol	Triethylene glycol dipropionate
Chloroethylene	Ethyl-b-ethoxypropionate	1,3,3-Trimethoxypropene
Chloromethyl methyl ether	2-Ethylhexanal	l,l,2,3-Tetrachloro-l,3-butadiene
b-Chlorophenetole	Ethyl vinyl ether	4-Vinyl cyclohexene
o-Chlorophenetole	Furan	Vinylene carbonate
p-Chlorophenetole	2,5-Hexadiyn-1-ol	

Testing For Peroxides

The recommended way to test for peroxides is using peroxide detection dip strips, available from most lab equipment supply companies. One product that provides good test result gradations is the:

- EM Quant® Peroxide Test Strips 0.5-25 ppm, produced by EMD Chemicals, Inc., catalog no. 10011.

Note, test strips have a two (2) year expiration after the date of manufacture. Therefore, purchasing them directly from the manufacturer may result in obtaining a fresher product. Other manufacturers offering a 0.5-25 ppm test strip are equally viable options, this product was listed as an example.

If the test strip indicates a concentration above 10 ppm, the chemical cannot be used and must be promptly disposed through Safety and Health. Submit an Unwanted Chemical Pickup Request form, available on the Safety and Health web site: www.marshall.edu/safety/chemical.

If test shows peroxides are not present, the discard date can be extended the length of new product for that class, either 3, 6, or 12 months. The test date, results of test, and new disposal date must be marked on the label.

Chemicals that show the presence of peroxides below 10 ppm can be used but should not be concentrated. Write the test date, results of test and "DO NOT DISTILL or CONCENTRATE" on the label. Retest after 3 months.

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