



EAST TENNESSEE STATE UNIVERSITY

Facilities Management

Policy Number: 700.18

Title: Management of Peroxide Forming Chemicals Policy

Implementation Date: July 2011

Last Audited: December 18th, 2018

Last Revised: February 13th, 2017

Introduction

This guideline outlines proper handling, use, and disposal of peroxide-forming chemicals at East Tennessee State 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 SDS 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).

When a peroxide forming chemical is past expiry or has been classified as a waste please contact the Environmental Health & Safety Office at extension 9-6028, or submit a Chemical Pickup Request. The form is available on the Safety & Health web site: <http://healthsafety.etsu.edu/Safety/pickupform>.

IF CRYSTALS ARE OBSERVED ON OR IN THE CONTAINER OF A PEROXIDE FORMER, DO NOT MOVE AND CALL THE EHS OFFICE IMMEDIATELY

Container Labeling

In addition to the original manufacturer's label or secondary label, the containers of all peroxide-forming chemicals must be labeled with the following information:

- WARNING PEROXIDE FORMER or POTENTIALLY EXPLOSIVE PEROXIDE
- Date of purchase
- Date container is first opened
- Required discard date based on the Disposal Requirements below

Storage and Handling

In order to safely manage chemicals that have the potential for forming heat and shock sensitive peroxides, the following should 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 and Safety Office for disposal.
- Any peroxide-forming chemical with visible discoloration, crystallization or liquid stratification should be treated as potentially explosive. Contact Environmental Health and Safety office immediately 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.
- Store all chemicals away from other incompatible chemicals. Most peroxide formers are flammable.
- 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 12 months after received or 3 months after first opened | Test for peroxides or dispose after 12 months after received or 6 months after first opened | Test for peroxides or dispose after 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 | 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 |

| | | |
|--|--|--|
| | 1-Phenylethanol 2-Phenylethanol 2-Propanol (IPA) Tetrahydrofuran Tetrahydronaphthalene Vinyl ethers | |
|--|--|--|

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 SDS to determine when peroxide formation is expected and label and store accordingly. Do not use and immediately contact EHS Office for disposal 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-Dibenzoyloxybenzene | Isobutyl vinyl ether |
| Benzyl ether | 1, 2-Dichloroethyl ethyl ether | Isophorone |
| Benzyl ethyl ether | 2,4-Dichlorophenetole | b-Isopropoxypropionitrile |
| Benzyl methyl ether | Diethoxymethane | Isopropyl-2,4,5-trichlorophenoxyacetate |
| Benzyl-1-naphthyl 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-Dimethoxypropene | 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-phenoxypropane | 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-Ethoxy-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 | 1,1,2,3-Tetrachloro-1,3-butadiene |
| b-Chlorophenetole | Ethyl vinyl ether | 4-Vinyl cyclohexene |
| o-Chlorophenetole | Furan | Vinylene carbonate |

Contact Persons

Director of Environmental Health & Safety
Environmental Compliance Manager

Approved by: _____
William Brady Rasnick, Jr., Associate Vice President, Facilities
Management

Date approved: _____

Audited: February 6th, 2017
December 18th, 2018

Revised: November 5th, 2013
February 13th, 2017