Safety Review

Peroxide-forming chemicals

Including \textit{p}-Dioxane
Peroxides
R-OO-R

• Peroxide crystal may violently detonate when subjected to thermal or mechanical shock.

• Peroxide-forming chemicals react with oxygen to form peroxy compounds, even at low concentrations.

• Factors that affect the rate of peroxide formation include exposure to air, light, heat, moisture and contamination from metals.

• The risk associated with peroxide formation increases if the peroxide crystallizes or becomes concentrated by evaporation or distillation.
It is extremely important that certain steps be followed regarding the purchasing, handling, identification, storage and disposal of peroxide-forming chemicals.
Purchasing Peroxide-Forming Compounds

- When possible, purchase only peroxide-forming chemicals which contain a peroxide formation inhibitor (e.g., tetrahydrofuran or diethyl ether inhibited with butylated hydroxytoluene (BHT)) or metal can with inner coating.

- Only purchase quantities of peroxide-forming chemicals that you expect to use within expiration and disposal timeframes.
Handling Peroxide Forming Compounds

- **NEVER, UNDER ANY CIRCUMSTANCES,** touch or attempt to open container of a peroxide-forming liquid if there are whitish crystals around the cap and/or in the bottle.

- Labeling requirements
  - All bottles of peroxide-forming chemicals must have the **date received** marked on the container.
  - When the bottle is first opened, the container must be marked with the **date opened**.

- Do not distill, evaporate or concentrate a peroxide-forming chemical until you have first tested it for the presence of peroxides.
Identification of Peroxides

Method for Testing Organic Peroxides

Whatman Starch Iodide Test Paper
Left:  No peroxide present - White
Middle: Low concentration of peroxide - Yellow
Right: High concentration of peroxide - Blue
Storage of Peroxide Forming Compounds

• Do not store for long

• Do not store peroxide-forming chemicals in direct sunlight as light can accelerate the chemical reactions that form peroxides.

• Store peroxidizable substances at the lowest feasible temperature.
Disposal of Peroxide Forming Compounds

Peroxide-forming chemicals must be disposed within the timeframes specified in the table below regardless if the container is unopened, unless they have been tested and found free of peroxides.

There are four classes of peroxide-forming chemicals based upon the peroxide formation hazard:
- **Class A** – Severe Peroxide Hazard
- **Class B** – Concentration Hazard
- **Class C** – Shock and Heat Sensitive
- **Class D** – Potential Peroxide-Forming Chemicals

<table>
<thead>
<tr>
<th></th>
<th>Class A</th>
<th>Class B</th>
<th>Class C</th>
<th>Class D</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Date Opened</strong></td>
<td>3 months</td>
<td>6 months</td>
<td>6 months</td>
<td>Only if peroxide crystals are present.</td>
</tr>
<tr>
<td><strong>Date Received</strong></td>
<td>1 year</td>
<td>1 year</td>
<td>1 year</td>
<td></td>
</tr>
</tbody>
</table>
Class A – Severe Peroxide Hazard

Spontaneously decompose and become explosive with exposure to air without concentration.

- Butadiene (liquid monomer)
- Isopropyl ether
- Sodium amide (sodamide)
- Chloroprene (liquid monomer)
- Potassium amide
- Tetrafluoroethylene (liquid monomer)
- Divinyl acetylene
- Potassium metal
- Vinylidene chloride
Class B – Concentration Hazard

Require external energy for spontaneous decomposition. Form explosive peroxides when distilled, evaporated or otherwise concentrated.

- Acetal
- Diethylene glycol dimethyl ether (diglyme)
- 4-Methyl-2-pentanol
- Acetaldehyde
- Diethyl ether
- 2-Pentanol
- Benzyl alcohol
- Dioxanes
- 4-Penten-1-ol
- 2-Butanol
- Ethylene glycol dimethyl ether (glyme)
- 1-Phenylethanol
- Cumene
- Furan
- 2-Phenylethanol
- Cyclohexanol
- 4-Heptanol
- 2-Propanol
- Cyclohexene
- 2-Hexanol
- Tetrahydrofuran
- 2-Cyclohexen-1-ol
- Methylacetylene
- Tetrahydronaphthalene
- Decahydronaphthalene
- 3-Methyl-1-butanol
- Vinyl ethers
- Diacetylene
- Methylcyclopentane
- Other secondary alcohols
- Dicyclopentadiene
- Methyl isobutyl ketone
Class C – Shock and Heat Sensitive

Highly reactive and can auto-polymerize as a result of internal peroxide accumulation. The peroxides formed in these reactions are extremely shock and heat sensitive.

- Acrylic acid
- Methyl methacrylate
- Vinlyadiene chloride
- Acrylonitrile
- Styrene
- Vinylpyridine
- Butadiene (gas)
- Tetrafluoroethylene (gas)
- Vinyl chloride (gas)
- Chloroprene
- Vinyl acetate
- Chlorotrifluoroethylene
- Vinylacetylene (gas)
Class D – Potential Peroxide Forming Chemicals

May form peroxides but cannot be clearly categorized in Class A, B, or C.

Over 200 organic and inorganic compounds are capable of forming peroxides under the right conditions.
**p-dioxane**

**Stability**
Stable. Incompatible with oxidizing agents, oxygen, halogens, reducing agents, moisture. *Highly flammable* - note wide explosive range. *May form explosive peroxides* in storage (rate of formation increased by heating, evaporation or exposure to light).

**Toxicology**
Probable carcinogen. Toxic. *Harmful by inhalation, ingestion and through skin contact.* Irritant.

**Personal protection**
Safety glasses, gloves (impervious), good ventilation. Treat as a potential carcinogen.
First Aid Measures

Eye Contact:
Immediately flush eyes with running water for at least 15 minutes, keeping eyelids open. Get medical attention.

Skin Contact:
Wash with soap and water. Get medical attention if irritation develops.

Inhalation:
If inhaled, remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Get medical attention if symptoms appear.

Serious Inhalation:
Evacuate the victim to a safe area as soon as possible. Loosen tight clothing such as a collar, tie, belt or waistband. If breathing is difficult, administer oxygen. If the victim is not breathing, perform mouth-to-mouth resuscitation. Seek medical attention.

Ingestion:
Do NOT induce vomiting. Loosen tight clothing such as a collar, tie, belt or waistband. Get medical attention if symptoms appear.
Spills

Small Spill:
Dilute with water and mop up, or absorb with an inert dry material and place in an appropriate waste disposal container.

Large Spill:
Flammable liquid. Keep away from heat. Keep away from sources of ignition. Stop leak if without risk. Absorb with DRY earth, sand or other non-combustible material. Do not touch spilled material.
Things we need to do better to prevent accidents!!!!

• Label with date opened
• Check for peroxides
• Clean up after distillation