Peroxide Formation in Chemicals

SafetyNet #: 23

There is a great deal of uncertainty regarding the hazards and safe handling of peroxidizable organic chemicals. No definitive data are available about the concentration at which these peroxides pose a hazard. Some common chemicals (e.g., isopropyl alcohol\textsuperscript{1}) are known to form potentially explosive concentrations of peroxides, but are rarely included as part of peroxide safety programs. Several common peroxide detection methods may not detect all types of unstable peroxides. Similarly, some common deperoxidation procedures may not remove all types of unstable peroxides. Recommended administrative controls (e.g., shelf life restrictions) vary widely. There are no specific Federal OSHA regulations that pertain to the handling of peroxidizable organic chemicals, the various classes of peroxide formers, hazardous levels of peroxides, or methods for control, detection and removal of peroxides.

A wide variety of organic compounds spontaneously form peroxides by a free-radical reaction with molecular oxygen in a process of auto-peroxidation. Although ethers are the most notorious in this regard, many other moieties are susceptible to the same process. Table 1 \textsuperscript{1} lists these moieties, numbered 1 to 14 from most likely to least likely to form peroxides.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|}
\hline
\textbf{Chemical Type} & \textbf{Possible Peroxide Formers} &\textbf{Notes} \\
\hline
1. Alcohols & Methanol, ethanol, and others & \\
2. Aldehydes & Formaldehyde, acetaldehyde & \\
3. Ketones & Acetone, methyl ethyl ketone, and others & \\
4. Ethers & Diethyl ether, tetrahydrofuran, and others & \\
5. Amines & Ethylamine, dimethylamine & \\
6. Carboxylic acids & Acetic acid, propionic acid & \\
7. Heterocyclic compounds & Pyridine, benzimidazole, and others & \\
8. Thiols & Methanethiol, ethanethiol & \\
9. Nitriles & Acetonitrile, propionitrile & \\
10. Haloalkanes & Chloroform, bromoform & \\
11. Carboxylic acids & Formic acid, acetic acid & \\
\hline
\end{tabular}
\caption{Possible Peroxide Formers}
\end{table}

Peroxides may explode when concentrated by evaporation or distillation, combined with compounds that create a detonable mixture, or when disturbed by heat, shock or friction.

To minimize the hazard of peroxide formation, meticulously observe the following safety guidelines:

- Any peroxidizable chemical with visible discoloration, crystallization, multiple
layers, or liquid stratification should be treated as potentially explosive. Call EH&S for immediate assistance.

- Label all containers of peroxide-forming chemicals with the date the chemical was received and the date the container was opened. The label shown below may be used for this purpose.

![Label for Peroxide-Forming Chemicals]

- **Always** store flammable materials that require reduced temperature storage in a refrigerator approved for flammable storage ("Lab-Safe"). However, refrigeration does not inhibit peroxide formation and may actually increase peroxide formation.

- Use or discard containers by the manufacturer's expiration date, if the expiration date is available. If there is no expiration date stamped on the container, discard according to the schedule in Tables 2, 3, and 4.

- Keep an inventory of peroxide-forming chemicals in the laboratory. NEVER purchase large containers of peroxide-forming chemicals if the quantity exceeds your actual need within the three- or twelve-month expiration period.

- **Never** distill potential peroxide-forming chemicals to dryness. Always leave a minimum of 20% still bottoms. When possible, adding a non-volatile organic compound (such as mineral oil) can dilute the peroxides remaining after distillation. When preparing to distill or evaporate compounds listed in the tables, always test for peroxides first, as described in reference 2.

- **Never** attempt to force open a rusted or stuck cap on a container of a peroxide-forming chemical.

- **Never** scrape or scrub glassware or containers that have been used with peroxide-forming compounds if you see an oily or crusty residue.

Listed in Table 2 are chemicals that form potentially explosive peroxides without concentration. These materials may spontaneously form peroxides that will make the materials shock- or heat-sensitive "on the shelf," that is, without any further concentration through evaporation or distillation. Table 2 chemicals have a 3-month storage limit. Store under nitrogen, if practical.

Table 2: Chemicals that form potentially explosive peroxides without concentration
- Butadiene$^b$
- Chloroprene$^c$
- Divinyl acetylene
- Isopropyl ether
- Tetrafluoroethylene$^b$
- Vinylidene chloride
  - a Materials other than those listed may form peroxides. Review the references and contact EH&S for further information. Applies only to pure materials.
  - b When stored as an inhibited liquid monomer.
  - c When stored as a liquid monomer.

Listed in Table 3 are chemicals that form potentially explosive peroxides on concentration. These materials form peroxide levels that make the parent container shock sensitive only when the parent liquid is evaporated, which effectively concentrates the peroxides. This group of peroxidizable chemicals has a propensity for exploding when used experimentally in operations such as distillations. Very volatile materials in Table 3, such as diethyl ether, may evaporate if stored without a cap, and the resulting concentrated, peroxidized material may be shock sensitive. Test chemicals in Groups 1 through 7 on Table 1 within 12 months of receipt, and discard or deperoxidize, if necessary. Test chemicals in Groups 8 through 14 on Table 1 within 12 months of opening, and discard or deperoxidize if necessary. Alcohol/water solutions do not form high concentrations of peroxides.

Table 3: Chemicals that form potentially explosive peroxides on concentration$^{a,d}$

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetal</td>
<td>Acetaldehyde</td>
</tr>
<tr>
<td>Benzyl alcohol</td>
<td>2-Butanol</td>
</tr>
<tr>
<td>Cyclohexanol</td>
<td>2-Cyclohexen-1-ol</td>
</tr>
<tr>
<td>Cumene</td>
<td>Decahydronaphthalene</td>
</tr>
<tr>
<td>Diacetylene</td>
<td>Dicyclopentadiene</td>
</tr>
<tr>
<td>Diethyl ether</td>
<td>Diethylene glycol dimethyl ether (Diglyme)</td>
</tr>
<tr>
<td>Dioxanes</td>
<td>Ethylene glycol dimethyl ether (Glyme)</td>
</tr>
<tr>
<td>4-Heptanol</td>
<td>Methyl acetylene</td>
</tr>
<tr>
<td>Methyl isobutyl ketone</td>
<td>3-Methyl-1-butanol</td>
</tr>
<tr>
<td>Methyl cyclopentane</td>
<td>2-Pentanol</td>
</tr>
<tr>
<td>4-Pentene-1-ol</td>
<td>1-Phenylethanol</td>
</tr>
<tr>
<td>2-Phenylethanol</td>
<td>2-Propanol (isopropanol, IPA)</td>
</tr>
<tr>
<td>Tetrahydrofuran</td>
<td>Tetrahydronaphthalene</td>
</tr>
<tr>
<td>Vinyl ethers</td>
<td>Other secondary alcohols</td>
</tr>
</tbody>
</table>

$^a$ Materials other than those listed may form peroxides. Review the references and contact EH&S for further information. Applies only to pure materials.
$^d$ WARNING! May become unstable if concentrated intentionally or accidentally by the user.

Listed in Table 4 are chemicals that autopolymerize. These chemicals may autopolymerize (and
thus explode) when relatively small quantities of peroxides are formed. Uninhibited chemicals to be stored for < 5 days. If inhibited, chemicals may be stored for 12 months. Avoid storing inhibited materials under inert gas as some inhibitors require a small amount of oxygen to work.

Table 4: Chemicals that autopolymerize

<table>
<thead>
<tr>
<th>Chemical</th>
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</tr>
</thead>
<tbody>
<tr>
<td>Acrylic acid</td>
<td>Acrylonitrile</td>
</tr>
<tr>
<td>Butadiene</td>
<td>Chloroprene</td>
</tr>
<tr>
<td>Chlorotrifluoroethylene</td>
<td>Methyl methacrylate</td>
</tr>
<tr>
<td>Styrene</td>
<td>Tetrafluoroethylene</td>
</tr>
<tr>
<td>Vinyl acetate</td>
<td>Vinyl acetylene</td>
</tr>
<tr>
<td>Vinyl chloride</td>
<td>Vinyl pyridine</td>
</tr>
</tbody>
</table>

*Materials other than those listed may form peroxides. Review the references and contact EH&S for further information. Applies only to pure materials.*

*When stored as a gas.*

Information is based on information contained in References 1 and 2.

References:


Contact

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More information

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