PEROXIDE FORMING SOLVENTS

- Why do peroxide forming chemicals present a hazard?
- Steps to be taken to minimise the risk from the formation of peroxides
- List of organic species known to form peroxides

Why Do Peroxide Forming Chemicals Present a Hazard?

Some organic solvents present a danger because they have the potential to form high levels of peroxides in the presence of atmospheric oxygen. Spontaneous explosion can occur with some solvents and others become susceptible to explosion when the peroxide content is concentrated by evaporation of the solvent. The use of these solvents in rotary evaporators is hazardous but deposits of peroxides can also form in and around the bottle neck due to natural evaporation and the concentration of residues. High levels of peroxide can build up over time so aging solvents also presents a significant risk.

Steps to be taken to minimise the risk from the formation of peroxides

1) Store peroxide forming chemicals properly

Since peroxides are formed by an auto-oxidation process:
- **Always Keep Bottle Sealed** when not in use to prevent the free ingress of air.
- **Store in the Dark, Do Not Store in Sunlight** - the auto-oxidation reaction can be photo-initiated.
- **Store in a Cool Place**. The auto-oxidation process is faster at higher temperatures.

2) Wherever possible use peroxide forming chemicals that contain antioxidant and buy the minimum necessary for the work planned

Many peroxide forming chemicals can be supplied with stabilisers which prevent the build-up of dangerous levels of peroxides. In general, they can be used for most laboratory work, including use as solvents which can be removed by distillation or rotary evaporation. It is also important to avoid the purchase of large volumes (e.g. 2.5 litres) of peroxide forming chemicals which are not needed. **Buy only the minimum needed** even if the chemical is cheap.

3) Label bottles appropriately

As peroxides are formed by an auto-oxidation process, their concentration builds up with time. All peroxide forming chemicals will be labelled to indicate the date of receipt and a “use by” date on them (2 years after receipt). A label (see example below) will be attached to the bottle. **UNLABELLED BOTTLES MUST BE CONSIDERED POTENTIALLY UNSAFE AND BE DISPOSED OF AS HAZARDOUS WASTE.**
4) Do not use metallic spatulas or magnetic stirrers
Explosions may be initiated by the presence of iron. Ceramic, wood or compatible plastics e.g. teflon may be used instead.

**Warning! Peroxide Forming Chemical**

<table>
<thead>
<tr>
<th>Date of Receipt</th>
<th>Do Not Use After (no more than 2 years after receipt)</th>
</tr>
</thead>
<tbody>
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</table>

**Tested for Peroxide**

<table>
<thead>
<tr>
<th>Date</th>
<th>Level</th>
</tr>
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<tbody>
<tr>
<td></td>
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</table>

**Name of Owner**

Example of label to be added to peroxide forming chemicals

4) Check peroxide levels in peroxide forming chemicals
It is recommended that peroxide levels in the solvent are periodically checked to ensure that levels remain safe. It is possible to test for the presence of peroxides using chemical methods but, for convenience, rapid, inexpensive and user-friendly commercial test strips are available from suppliers of chemicals.

**Frequency of Peroxide Checks**
- *Inhibited Ethers and other peroxide forming chemicals*: it is recommended that these should be tested every 6 months
- *Uninhibited Ethers and other peroxide forming chemicals*: it is recommended that these are checked on opening, and every 3 or 6 months subsequently
- *For use in vacuum distillation / evaporation*: Check immediately prior to use

**Level of Peroxide Detected**

<table>
<thead>
<tr>
<th>0 to 30 mg/l</th>
<th>Acceptable for all routine lab work, including vacuum distillation and evaporation to dryness. Note however, that even with less than 30 ppm of peroxide, if a very large volume of ether is distilled to dryness then a noticeable level of peroxide could, potentially, still build up. Therefore, ensure that the quantity of ether being used is as small as is necessary</th>
</tr>
</thead>
<tbody>
<tr>
<td>Greater than 30 to 100 mg/l</td>
<td>Acceptable for all routine lab work <strong>EXCEPT</strong> vacuum distillation and evaporation to dryness. If the peroxide level is approaching 100 ppm then it should be considered for disposal. Label bottle as waste as normal and record the level of peroxide.</td>
</tr>
<tr>
<td>Greater than 100 mg/l</td>
<td><strong>DO NOT USE. Contact Departmental Safety Advisor as soon as possible.</strong> If the level of peroxide is greater than 100 mg/l then the peroxide test strip will either be darker blue than</td>
</tr>
</tbody>
</table>
List of organic species known to form peroxides
Certain species are more prone to peroxide formation than others (this list is for guidance only and is not exhaustive).

1) Severe Peroxide Hazard on Storage with Exposure to Air
**Check for peroxides every three months and dispose of after two years**
- Di-isopropyl Ether (isopropyl ether)
- Divinylacetylene (DVA)
- 1,1 dichloroethene (Vinylidene Chloride)

2) Peroxide Hazard on Concentration
**Check for peroxides every six months and dispose of after two years**
- Acetaldehyde diethyl acetal (acetal)
- Ethylene glycol dimethyl ether (glyme)
- Cumene (isopropylbenzene)
- Ethylene glycol ether acetates (ethanediol)
- Cyclohexene
- Cyclopentene
- Furan
- Decalin (decahydronaphthalene)
- Methylacetylene
- Diacetylene (butadiene)
- Methylcyclopentane
- Dicyclopentadiene
- Methyl isobutyl ketone
- Diethyl ether (ether)
- Tetrahydrofuran (THF)
- Diethylene glycol dimethyl ether (diglyme)
- Tetralin (tetrahydronaphthalene)
- Dioxane
- Vinyl ethers

3) Hazard of Rapid Polymerization Initiated by Internally Formed Peroxides
**Discard or test for peroxides 6 months after opening**
- Chloroprene (2-chloro-1,3-butadiene)
- Vinyl acetate
- Styrene
- Vinylpyridine