

GUIDELINES FOR SAFE HANDLING OF PEROXIDE FORMING CHEMICALS

Safety Policy Manual Section 4.0 Policy No. LS 1.7





Certain chemical compounds can form explosive peroxides during use or storage. These chemicals can react with oxygen to create peroxides, compounds that can explode with impact, heat, or friction. Peroxide-forming compounds can be divided into hazard classes based on the method of reaction as described in the Tables below. Follow these guidelines for control and safe use of peroxide formers.

1. Purchase peroxide formers with inhibitors added by the manufacturer whenever possible.
2. Do not purchase large quantities of peroxide forming chemicals. Purchase the amount that you will use in a 12 month time period.
3. Date all peroxide formers upon receipt and again upon opening. Discard peroxide formers that have reached the manufacture expiration date. Discard peroxide formers 24 months after opening the containers or 24 months after receipt even if unopened. [Note that peroxide formers in the Table 1 list must be disposed of within 3 months after opening.]
4. DO NOT OPEN a container of peroxide forming chemical that has obvious crystal formation. Do not handle container or force open lid. Treat as potentially explosive material. Immediately call EH&S for assistance.
5. Store peroxide formers (especially those in Table 1) under nitrogen or other inert gas, or keep and use them in an inert atmosphere chamber. Note: Some inhibitors actually need small amounts of oxygen to prevent peroxide formation and it is recommended that inhibited chemicals are not stored under an inert atmosphere.
6. Store peroxide formers in sealed, air-impermeable containers such as dark amber glass with a tight-fitting cap. DO NOT store these chemicals in open, partially empty, or transparent containers as these conditions promote formation of peroxides.
7. Avoid the distillation of peroxide formers without first testing for the existence of peroxides in the material. Most explosions with the use of peroxide formers occur when a material is distilled to dryness. Leave at least 10-20% bottoms. Stir such distillations with a mechanical stirrer or a bubbling inert gas. Air or an oxygen containing mixture should never be used for bubbling or for stirring.

TABLE 1: Severe Peroxide Hazard: Chemicals that can spontaneously decompose, becoming explosive after exposure to air without concentration. These chemicals must be stabilized or decontaminated and discarded within 3 months of opening.

Isopropyl ether Potassium amide Divinylacetylene
Potassium metal Sodium amide (sodamide) Vinylidene chloride
Butadiene (liquid monomer) Chloroprene (liquid monomer) Tetrafluoroethylene
(liquid monomer)



TABLE 2: Concentration Hazard: These chemicals require external energy for spontaneous decomposition, forming explosive peroxides when distilled, evaporated or otherwise concentrated. Chemicals should be inventoried at least annually to ensure proper safety/stability. Test (such as strip test) subject chemicals at least annually. Discard chemicals that have; reached the manufactures expiration date, or within 2 years of opening, or failed the appropriate test.

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

TABLE 3: Shock and Heat Sensitive: These chemicals are 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. Chemicals should be inventoried at least annually to ensure proper safety/stability. Test (such as strip test) subject chemicals at least annually. Discard chemicals that have; reached the manufactures expiration date, or within 2 years of opening, or failed the appropriate test.

Acrylic acid Chlorotrifluoroethylene
Vinyl acetate Acrylonitrile Methyl
methacrylate Vinylacetylene (gas)
Butadiene (gas) Styrene Vinyl
chloride (gas) Chloroprene
Tetrafluoroethylene (gas)
Vinylpyridine Vinyladiene chloride

Many other chemicals may also form peroxides under the right conditions. A list of such chemicals can be found on the EH&S website.

NOTE: These tables and the referenced list represent prominent organic and inorganic compounds that are able to form peroxides under the right conditions. The lists are not comprehensive. The investigator should refer to the SDS or other reference material, contact the chemical manufacturer, or contact EH&S to determine if the chemicals they are using are potential peroxide formers.