

University of Pittsburgh Safety Manual	EH&S Guideline Number: 04-006	
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SAFE HANDLING OF PEROXIDE FORMING CHEMICALS

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 3 month time period.
3. Date all peroxide formers upon receipt and again upon opening. Discard peroxide formers 6 months after opening the containers or 12 months after receipt even if unopened. [Note that peroxide formers in the Table 1 list must be disposed of within 3 months after opening.] If within the expiration time frame and no crystal formation is evident, these chemicals can be properly disposed through the University's bi-monthly waste pick-up.
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 (412-624-9505).
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 gases should never be used for bubble stirring peroxides.

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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 concentrated. Test for peroxides and discard these chemicals within 6 months of opening.

Acetal	Diethyl ether	Methyl isobutyl ketone
Acetaldehyde	Diethylene glycol dimethyl ether (diglyme)	4-Methyl-2-pentanol
Benzyl alcohol		2-Pentanol
2-Butanol	Dioxanes	4-Penten-1-ol
Cumene	Ethylene glycol dimethyl ether (glyme)	1-Phenylethanol
Cyclohexanol		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. NOTE: The liquid chemicals in this group should be tested for peroxides and discarded within 6 months of opening.

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.