

Compounds That Form Peroxides

Some compounds tend to form peroxides upon exposure to air or during long term storage. These are often termed "peroxidizable" or "peroxide formers." The hazard associated with the formation of peroxides varies widely, as does the rate of peroxide formation. In some cases, the peroxides may initiate violent polymerization. In other cases, the presence of the peroxide may not present a hazard unless the material is evaporated to near dryness, when the peroxide is concentrated and may detonate. In other materials, detonation may occur even without concentration. Some peroxidizable compounds are listed in Table 1, taken from *Prudent Practices in the Laboratory: Handling and Disposal of Chemicals*. This is not an exhaustive list, but is useful in identifying common specific chemicals and groups of chemicals likely to form peroxides. Additionally, there is indication that more common groups of chemicals such as aldehydes, ketones, and alcohols form peroxides upon extended storage. The prolonged retention of these chemicals in academic and research labs dictates that caution should be exercised with them, especially when performing distillations or similar procedures.

Compounds classified as potential peroxide formers should be ordered in the smallest quantity feasible for the intended purpose and should be used or discarded within specific time limits (see Table 1). Incoming materials should be labeled as follows.

<p style="text-align: center;">Peroxidizable Compound</p> <p>Date received @MSU: _____</p> <p>Dispensed to: _____ BL _____</p> <p>Date opened: _____ by _____</p> <p>Discard or test within 12 months after opening!</p>

Centralized storage in the solvent room of the stockroom is recommended. Most of these compounds require storage in a flammable materials cabinet. Bottles should not be opened until use, unless required for testing of out-of-date material. In many cases, formation of peroxides may be inhibited by purging opened containers with nitrogen before resealing.

A central inventory should be maintained for peroxidizable compounds, with date of receipt and location of the material. This will allow tracking of containers of "expired" chemicals. Bottles past the recommended cutoff date should be tested for peroxides before *any* lab use is undertaken. If it is substantially past the cutoff date, or there is no date listed on the bottle, the bottle *should not be moved or opened*. The lab/safety/waste coordinator should be contacted to evaluate the hazard potential and to arrange for disposal. The lab/safety/waste coordinator will periodically check the level of peroxides on stockroom materials that are past the recommended use date. A single container from an individual lot may be opened for this purpose, and will be used to represent the entire lot. Once peroxides are detected in the opened container, it will be discarded and another container will be designated for testing.

Several analytical methods are available for determination of peroxides. Perhaps the simplest is the use of peroxide test strips, which are available in the chemistry stockroom. All peroxide formers that have been opened and tested should be labeled as follows.

<i>Peroxide Former</i>	
Chemical Name	
Date Received:	Date Opened:
Test Date:	Results:
Test Date:	Results:
Test Date:	Results:

If a positive peroxide test is obtained for any material, the lab/safety/waste coordinator should be consulted before proceeding with any use of the material. Although there are approved methods for removal of peroxides from solvents, these should not be attempted by anyone unfamiliar with the techniques and proper safety precautions.

Table 1. Classes of Chemicals That Can Form Peroxides Upon Aging

Class I: Unsaturated materials, especially those of low molecular weight, may polymerize violently and hazardously due to peroxide initiation. Store no longer than 12 months.

Acrylic acid	Tetrafluoroethylene
Acrylonitrile	Vinyl acetate
Butadiene	Vinyl acetylene
Chlorobutadiene (chloroprene)	Vinyl chloride
Chlorotrifluoroethylene	Vinyl pyridine
Methyl methacrylate	Vinylidene chloride
Styrene	

Class II: The following chemicals are a peroxide hazard upon concentration (distillation/evaporation). A test for peroxide should be performed if concentration is intended or suspected. Store no longer than 12 months.

Acetal	Dioxane (<i>p</i> -dioxane)
Cumene	Ethylene glycol dimethyl ether (glyme)
Cyclohexene	Furan
Cyclooctene	Methyl acetylene
Cyclopentene	Methyl cyclopentane
Diacetylene	Methyl- <i>i</i> -butyl ketone
Dicyclopentadiene	Tetrahydrofuran
Diethylene glycol dimethyl ether (diglyme)	Tetrahydronaphthalene
Diethyl ether	Vinyl ethers

Class III: Peroxides derived from the following compounds may explode without concentration. Store no longer than 3 months.

Organic	Inorganic
Divinyl ether	Potassium metal
Divinyl acetylene	Potassium amide
Isopropyl ether	Sodium amide (sodamide)
Vinylidene chloride	

NOTE: Lists are illustrative but not exhaustive.