

3.4.7 Peroxide Forming Materials

Peroxide forming materials are chemicals that react with air, moisture, or impurities to form peroxides. The tendency to form peroxides is greatly increased by evaporation or distillation. Peroxide forming materials can form shock sensitive peroxide crystals over time or upon exposure to air. Organic peroxides are extremely sensitive to shock, sparks, heat, friction, impact, and light. They are very unstable and some chemicals that can form them are commonly used in laboratories. The most common peroxide forming chemicals in use are diethyl ether and tetrahydrofuran (THF). Peroxide formation cannot be prevented once the chemical has been opened unless the chemical is maintained under an inert atmosphere (impractical). *For this reason, it is recommended that all peroxide formers be dated when received, and periodically evaluated using test strips to indicate peroxide formation. It is prudent practice to maintain only the inventory necessary to complete ongoing work. DO NOT STOCKPILE! The Safety Data Sheet is a good source for determining if a material is capable of forming peroxides.*

- Do not open the chemical container if peroxide formation is suspected. Visually inspect liquid peroxide forming materials for crystals or unusual viscosity before opening. Pay special attention to the area around the cap. Peroxides usually form upon evaporation, so they will most likely be formed on the threads under the cap.
- Date all peroxide forming materials with the date received, and the expected shelf life. Chemicals such as diisopropyl ether, divinyl acetylene, sodium amide, and vinylidene chloride should be discarded after three months. Chemicals such as dioxane, diethyl ether, and tetrahydrofuran should be disposed after one year.
- Store all peroxide forming materials away from heat, sunlight, and sources of ignition. Sunlight accelerates the formation of peroxides.
- Secure the lids and caps on these containers to discourage the evaporation and concentration of these chemicals.
- Never store these chemicals in glass containers with screw cap lids or glass stoppers. Friction and grinding must be avoided. Also, never store them in a clear glass bottle where they would be exposed to light.

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.

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.

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

Class III: Peroxides derived from the following compounds may explode without concentration.

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

NOTE: Lists are illustrative but not exhaustive.