

DANGER: PEROXIDIZABLE CHEMICALS

By Thomas K. Wray

Many organic chemicals used in laboratory solutions and reagents can form potentially deadly peroxides - powerful oxidizing agents containing active oxygen in their molecular structures. Even otherwise safe substances can dry out over time and form peroxide crystals, which can be extremely shock sensitive and have been known to cause explosions. Generally, the more volatile a compound, the greater its potential hazard, because evaporation significantly can increase peroxide concentration.

The most widely used reference for peroxidizable compounds is an article written by H. L. Jackson, W. B. McCormack, C. S. Rondestvedt, K. D. Smeltz and L. E. Viele that appeared in the March 1970 issue of the *Journal of Chemical Education* (pp. A175-A188). This excellent work forms the basis for much of today's laboratory practice involving these materials.

Also available is the *Handbook of Reactive Chemical Hazards* by Leslie Bretherick, which includes information about the reactive properties of several chemicals but is not a comprehensive study of peroxidizable materials. The 1984 edition devotes four pages (151-154) to the identification of compounds susceptible to peroxide formation including a list of 70 chemicals that fit the criteria.

In an article appearing in the September 1988 issue of the *Journal of Chemical Education*, Gholam A. Mirafzal and Henry E. Baumgarten added a few entries to Bretherick's list.

They divide peroxidizable organic compounds into eight classes:

- Ethers and acetals
- Olefins (compounds with a single double bond) with hydrogen, chlorine or fluorine atoms attached, and terpenes and tetrahydronaphthalene;
- Dienes and vinyl acetylenes
- Vinyl monomers, including vinyl halides, acrylates, methacrylates and vinyl esters
- Ureas and amides
- Aldehydes
- Primary and secondary alcohols
- Ketones.

Compounds containing aldehyde or amine groups readily peroxidize, but the resulting products degrade easily and do not accumulate to dangerous levels. In a study conducted by Mirafzal and Baumgarten, alcohols and ketones, not more than 2 years old typically contained peroxide levels of less than 6 ppm. However, two aromatic alcohols - benzyl alcohol and phenyl ethanol - had measured levels of peroxide from 20 ppm to 100 ppm

Experts generally agree on three basic lists of compounds known to form peroxides (see table). These lists are meant to be inclusive rather than exclusive. List A includes compounds that form explosive peroxides even without concentration. List B includes examples of materials that are hazardous only when the peroxide level is concentrated, for example, by evaporation or distillation. List C contains examples of peroxidizable vinyl monomers, which, by themselves, are not particularly hazardous but may initiate exothermic polymerization of the bulk monomer. Uncontrolled polymerization can rupture a storage container, release toxic gases and initiate combustion.

Handling and Storage

As with most chemicals, peroxidizable compounds should be stored away from heat and light. Sunlight, in particular, accelerates peroxidation. Small metal cans are necessary for storing liquid materials from Lists A and B. Inerting the atmosphere in storage containers with nitrogen effectively inhibits Peroxide formation, although this is not recommended for inhibited vinyl monomers. Each opened container of peroxidizable materials should be resealed carefully to limit contact with atmospheric oxidants, particularly oxygen.

All chemicals used in the laboratory should be dated by the supplier, preferably with the manufacture date or, alternately, the packaging date. If a package is not dated by the supplier, it should be dated upon receipt by the user. This is especially important with peroxidizable compounds, because peroxide formation increases with age. An excellent source of information regarding the inventory and storage hazards of almost 600 commonly used chemicals is a 1994 document published by the U.S. Consumer Product Safety Commission titled *School Science Laboratories: A Guide to Some Hazardous Substances*. The commission's toll-free number is (800) 638-2772.

Peroxidizable Compounds

List A
Peroxide hazard
on storage

Isopropyl ether
Divinyl acetylene
Vinylidene chloride
Sodium amide
Potassium metal

**Store no longer than
three months**

List B
Peroxide hazard on concentration

Dimethyl ether
Tetrahydrofuran
Dioxane
Acetal
Ethylene glycol dimethyl ether
Methyl ether
Vinyl ethers
Dicyclopentadiene
Methyl acetylene
Diaceylene
Tetrahydronaphthalene
Cyclohexane
Diethylene glycol dimethyl ether (diglyme)

Store no longer than 12 month.

List C
Peroxide initiation of
polymerization

Methyl methacrylate
Styrene
Acrylic acid
Acrylonitrile
Butadiene
Vinylidene chloride
Tetrafluoroethylene
Chlorofluoroethylene
Vinyl acetylene
Vinyl acetate
Vinyl chloride
Vinyl pyridine
Chloroprene

**Store no longer than 12
months**

Chemicals that form hazardous levels of peroxides when stored, such as those in List A, should be evaluated at least every three months after opening. If peroxide is present, the material should be treated or disposed immediately. Materials in Lists B and C should not be stored more than 12 months. They also should be tested for peroxide formation before use. If peroxides are found, they should be removed by a suitable method before the compounds are used. Laboratory work only should be conducted with inhibited vinyl monomers to prevent uncontrolled polymerization. Certain solid peroxidizable compounds and some with very high boiling points (greater than 300 degrees Celsius), such as surfactants and plasticizers containing polyether groups, may be exempt from these storage recommendations.

Peroxide Detection

Two peroxide detection methods exist. The first involves the use of potassium iodide solution. The most consistent test reported by both Jackson and Mirafzal involves a non-acidified aqueous solution of potassium iodide, where 1 milliliter of test sample is added to 1 millimeter of 20-percent-by-weight aqueous potassium iodide in a small test tube. After vigorous shaking, the sample is observed. A pale yellow color indicates a low level of peroxide, while a brownish-red color indicates high peroxide content. No color change indicates the sample is peroxide free.

The second test method involves peroxide test paper. There are at least two commercially available peroxide test strips. These are simple to use but require slightly different test protocols, depending on the nature of the sample. Peroxide test strips must be protected from moisture, which will invalidate test results.

Before using materials from List A or B, a visual check should be done for crystalline solids on the outside of the container lid. If crystals are observed, they should be tested carefully with peroxide paper. If test results are positive, the container should not be opened.

Peroxide Removal

Peroxide impurities in water-soluble samples can be removed easily by shaking them with a concentrated solution of a ferrous salt. A saturated solution can be prepared by mixing 60 grains of ferrous sulfate 6 millimeters of concentrated sulfuric acid and 110 milliliters of distilled water. In tests conducted by Mirafzal, this method removed the highest concentration of peroxides. It was found to be a simple, fast and efficient method for removing peroxides from all water-immiscible samples. It may be necessary to discard the aqueous layer and repeat the process to ensure complete removal. The organic layer should be dried using an appropriate desiccant, such as magnesium sulfate, and the dried sample should be tested prior to use.

Many peroxides can be removed easily by passing the peroxidized solvent through a column of ordinary activated alumina. Tests conducted by Mirafzal indicated it generally is possible to remove up to 10 ppm of peroxide by passage through a relatively short column - 20 grams - of activated alumina. This method works well with all classes of compounds but frequently is slower and more expensive than using a concentration solution of a ferrous salt. Peroxide material remaining on the column was removed by passing a saturated solution of either ferrous sulfate or potassium iodide through the alumina.

Type "A" Peroxidizable Chemical Inventory

When a Type "A" Peroxidizable Chemical is received, enter the date in the "Received" column and the "Dispose by" date (**3 months after receiving**), in appropriate columns. When the chemical is disposed of, check the "Disposed" column. Periodically review the list to ensure chemicals are disposed of in a timely manner.

[illegible]

Type "A" Peroxidizable Chemicals	
	Divinyl acetylene
	Isopropyl ether
	Potassium metal
	Sodium amide
	Vinylidene chloride

- * Type A chemicals form explosive peroxides even without concentration. These should be stored away from heat and light. Sunlight accelerates peroxidation. Small metal cans are necessary for storing liquid materials.
- * Inerting the atmosphere in storage containers with nitrogen effectively inhibits peroxide formation, although this is not recommended for inhibited vinyl monomers.
- * Each opened container of peroxidizable materials should be re-sealed carefully to limit contact with atmospheric oxidants, particularly oxygen
- * Chemicals that form hazardous levels of peroxides when stored, such as Type "A" chemicals, should be evaluated at least every three months after opening. If peroxide is present, the material should be treated or disposed immediately.
- * If peroxides are found, they should be removed by a suitable method before the compounds are used.
- * Laboratory work only should be conducted with inhibited vinyl monomers to prevent uncontrolled polymerization.
- * Certain solid peroxidizable compounds and some with very high boiling points (greater than 300 degrees Celsius), such as surfactants and plasticizers containing polyether groups, may be exempt from these storage recommendations.
- * Before using materials, a visual check should be done for crystalline solids on the outside of the container lid. If crystals are observed, they should be tested carefully with peroxide paper.
- * If test results are positive, the container should not be opened.
- * Peroxide impurities in water-soluble samples can be removed easily by shaking them with a concentration solution of a ferrous salt.
- * A saturated solution can be prepared by mixing 60 grams of ferrous sulfate, 6 milliliters of concentrated sulfuric acid and 110 milliliters of distilled water.
- * It may be necessary to discard the aqueous layer and repeat the process to ensure complete removal.
- * The organic layer should be dried using an appropriate desiccant, such as magnesium sulfate, and the dried sample should be tested prior to use.

Type "B" Peroxidizable Chemical Inventory

When a Type "B" Peroxidizable Chemical is received, enter the date in the "Received" column and the "Dispose by" date (**12 months after receiving**), in appropriate columns. When the chemical is disposed of, check the "Disposed" column. Periodically review the list to ensure chemicals are disposed of in a timely manner.

[illegible]

Type "B" Peroxidizable Chemicals		
Acetal	Diethyl ether	Methyl acetylene
Cyclohexene	Diethylene glycol	Tetrahydrofuran
Diacetylene	Dioxane	Tetrahydronaphthal
Dicyclopentadiene	Ethylene glyco dimethyl	Vinyl ethers

- * Type "B" chemicals are hazardous only when the peroxide level is concentrated. These should be stored away from heat and light. Sunlight accelerates peroxidation. Small metal cans are necessary for storing liquid materials.
- * Inerting the atmosphere in storage containers with nitrogen effectively inhibits peroxide formation, although this is not recommended for inhibited vinyl monomers.
- * Each opened container of peroxidizable materials should be re-sealed carefully to limit contact with atmospheric oxidants, particularly oxygen
- * Type "B" chemicals should not be stored more than 12 months. They should be tested for peroxide formation before use.
- * If peroxides are found, they should be removed by a suitable method before the compounds are used.
- * Laboratory work only should be conducted with inhibited vinyl monomers to prevent uncontrolled polymerization.
- * Certain solid peroxidizable compounds and some with very high boiling points (greater than 300 degrees Celsius), such as surfactants and plasticizers containing polyether groups, may be exempt from these storage recommendations.
- * Before using materials, a visual check should be done for crystalline solids on the outside of the container lid. If crystals are observed, they should be tested carefully with peroxide paper.
- * If test results are positive, the container should not be opened.
- * Peroxide impurities in water-soluble samples can be removed easily by shaking them with a concentration solution of a ferrous salt.
- * A saturated solution can be prepared by mixing 60 grams of ferrous sulfate, 6 milliliters of concentrated sulfuric acid and 110 milliliters of distilled water.
- * It may be necessary to discard the aqueous layer and repeat the process to ensure complete removal.
- * The organic layer should be dried using an appropriate desiccant, such as magnesium sulfate, and the dried sample should be tested prior to use.

Type "C" Peroxidizable Chemical Inventory

When a Type "C" Peroxidizable Chemical is received, enter the date in the "Received" column and the "Dispose by" date **(12 months after receiving)**, in appropriate columns. When the chemical is disposed of, check the "Disposed" column. Periodically review the list to ensure chemicals are disposed of in a timely manner.

[illegible]

Type "C" Peroxidizable Chemicals		
Acrylic acid	Chloroprene	Vinyl acetate
Acrylonitrile	Styrene	Vinyl chloride
Butadiene	Tetrafluoroethylene	Vinyl pyridine
Chlorofluoroethylene	Vinyl acetylene	Vinylidene chloride

- * Type "C" Chemicals are peroxidizable vinyl monomers, which, by themselves, are not particularly hazardous but may initiate exothermic polymerization of the bulk monomer.
- * Uncontrolled polymerization can rupture a storage container, release toxic gases and initiate combustion
- * Type "C" chemicals should not be stored more than 12 months. They should be tested for peroxide formation before use.
- * If peroxides are found, they should be removed by a suitable method before the compounds are used.
- * Laboratory work only should be conducted with inhibited vinyl monomers to prevent uncontrolled polymerization.
- * Certain solid peroxidizable compounds and some with very high boiling points (greater than 300 degrees Celsius), such as surfactants and plasticizers containing polyether groups, may be exempt from these storage recommendations.
- * Peroxide impurities in water-soluble samples can be removed easily by shaking them with a concentration solution of a ferrous salt.
- * A saturated solution can be prepared by mixing 60 grams of ferrous sulfate, 6 milliliters of concentrated sulfuric acid and 110 milliliters of distilled water.
- * It may be necessary to discard the aqueous layer and repeat the process to ensure complete removal.
- * The organic layer should be dried using an appropriate desiccant, such as magnesium sulfate, and the dried sample should be tested prior to use.