

# Safe Use of Peroxide Forming Chemicals

## Introduction

Some organic and inorganic compounds are capable of reacting with atmospheric oxygen to form potentially explosive peroxides. This reaction of molecular oxygen and peroxidizable compounds is formed by a process called autoxidation or peroxidation. Formation of peroxides is accelerated by light and heat. Substances which have undergone peroxidation are sensitive to thermal and/or mechanical shock and may explode violently. All laboratory workers must learn to recognize and safely handle peroxidizable compounds. Peroxide forming substances include: aldehydes, ethers (especially cyclic ether), compounds containing benzylic hydrogen atoms, compounds containing the allylic structure (including most alkenes), vinyl and vinylidene compounds. See the tables below listing some chemicals that may form explosive peroxides.

## Safe Handling

Peroxides may explode when concentrated by evaporation or distillation, combined with compounds that create a detonable mixture, or when disturbed by heat, shock or friction.

To minimize the hazard of peroxide formation, meticulously observe the following safety guidelines:

- **Any peroxidizable chemical with visible discoloration, crystallization, multiple layers, or liquid stratification or any container with crystals on the lid should be treated as potentially explosive. Call Laboratory Safety at 2-4996 for immediate assistance.**
- Follow recommendations on MSDS sheets regarding proper monitoring and handling of chemical.
- Label all containers of peroxide-forming chemicals with the date the chemical was received and the date the container was opened. The label shown below may be used for this purpose. It is good laboratory practice to label all containers with the date it was opened.

### **WARNING-PEROXIDE FORMER**

This material will form explosive peroxides during storage and must not be kept for more than \_\_\_\_\_ months after opening.

Date Received \_\_\_\_\_

Date Opened \_\_\_\_\_

**TEST BEFORE USE-DO NOT USE IF POSITIVE**

- **Always** store flammable materials that require reduced temperature storage in a refrigerator approved for flammable storage. However, refrigeration does not inhibit peroxide formation and may actually increase peroxide formation.
- Use or discard containers by the manufacturer's expiration date, if the expiration date is available. If there is no expiration date stamped on the container, discard according to the schedule in Tables 1, 2, and 3.
- Keep an inventory of peroxide-forming chemicals in the laboratory. **Never** purchase large containers of peroxide-forming chemicals if the quantity exceeds your actual need within the three- or twelve-month expiration period.
- **Never** distill potential peroxide-forming chemicals to dryness. Always leave a **minimum** of 20% of solvent in the bottom of a still. When possible, adding a non-volatile organic compound (such as mineral oil) can dilute the peroxides remaining after distillation. When preparing to distill or evaporate compounds listed in the tables, always test for peroxides first, using a method as described in Testing.
- **Never** attempt to force open a rusted or stuck cap on a container of a peroxide-forming chemical.
- **Never** scrape or scrub glassware or containers that have been used with peroxide-forming compounds if you see an oily or crusty residue.

## TESTING

The following test procedures may be used on most organic solvents. However, there is not a suitable, simple test procedure for detection of peroxides in substances such as alkali metals, alkali metal alkoxides, amides, or organometallics. **Do not test or treat any peroxide forming chemicals if you are unsure of the age, if there are visible crystals, or a precipitate or oily viscous layer is present.**

- **Iodide Test:**  
Add 0.5-1.0 ml of the solvent to be tested to an equal volume of glacial acetic acid to which has been added about 0.1 g of sodium iodide or potassium iodide crystals. A yellow color indicates a low concentration of peroxide in the sample; a brown color indicates a high concentration. A blank determination should be made. Always prepare the iodide/acetic acid mixture at the time the test is made, because air oxidation slowly turns the blank to a brown color.
- **Ferrous Thiocyanate Test:**  
A drop of the solvent to be tested is mixed with a drop of sodium ferrous thiocyanate reagent which is prepared by dissolving 9 g of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  in 50 ml of 18% hydrochloric acid. Add 0.5-1.0 g granulated zinc followed by 5 g sodium thiocyanate. When the transient red color fades, add 12 g more of sodium thiocyanate and decant the liquid from the unused zinc into a clean stoppered bottle. Pink or red coloration indicates the presence of peroxides.
- **Peroxide Test Strips:**  
Test strips are commercially available from a number of vendors, including [Gallade Chemical](#) [Cat. No. 10081, (888) 830- 9092] or [Laboratory Safety Supply](#) [Cat. No. 1162, (800) 356-0783]. Follow the manufacturer's instructions for using the strips to ensure adequate colorimetric detection.

## Some Chemicals That Form Peroxides.

Listed in Table 1 are chemicals that form potentially explosive peroxides without concentration. These materials may spontaneously form peroxides that will make the materials shock- and/or heat-sensitive "on the shelf," that is, without any further concentration through evaporation or distillation. Table 1 chemicals have a 3-month storage limit. Store under nitrogen, if practical.

**Table 1: Chemicals that form potentially explosive peroxides without concentration**

Acrylic acid	Tetrafluoroethylene
Acrylonitrile	Vinyl acetate
Butadiene	Vinyl acetylene
Chlorobutadiene(chloroprene)	Vinyl chloride
Chlorotrifluoroethylene	Vinyl pyridine
Methyl methacrylate	Vinylidene chloride
Styrene	Potassium amide
Isopropyl ether	Potassium metal
Sodium amide (sodamide)	Divinyl acetylene

Listed in Table 2 are chemicals that form potentially explosive peroxides on concentration. These materials form peroxide levels that make the parent container shock sensitive only when the parent liquid is evaporated, which effectively concentrates the peroxides. This group of peroxidizable chemicals has a propensity for exploding when used experimentally in operations such as distillations. Very volatile materials in Table 2, such as diethyl ether, may evaporate if stored without a cap, and the resulting concentrated, peroxidized material may be shock sensitive. Test for peroxides before each use. Discard after one year.

**Table 2: Chemicals that form potentially explosive peroxides on concentration**

Acetal	Acetaldehyde
Benzyl alcohol	2-Butanol
Cyclohexanol	2-Cyclohexen-1-ol
Cumene	Decahydronaphthalene
Diacetylene	Dicyclopentadiene
Diethyl ether	Diethylene glycol dimethyl ether (Diglyme)
Dioxanes	Ethylene glycol dimethyl ether (Glyme)
4-Heptanol	Methyl acetylene
Methy isobutyl ketone	3-Methyl-1-butanol
Methyl cyclopentane	2-Pentanol
4-Pentene-1-ol	1-Phenylethanol
2-Phenylethanol	2-Propanol (isopropanol, IPA)

Tetrahydrofuran	Tetrahydronaphthalene
Vinyl ethers	Other secondary alcohols
Methyl ethyl ketone	Cyclohexene
Cyclooctene	Furan
Cyclopentene	Diacetylene
Vinyl ethers	

Listed in Table 3 are chemicals that autopolymerize. These chemicals may autopolymerize (and thus explode) when relatively small quantities of peroxides are formed. Uninhibited chemicals should be stored for < 5 days. If inhibited, chemicals may be stored for 12 months. Avoid storing inhibited materials under inert gas as some inhibitors require a small amount of oxygen to work. Discard after one year.

**Table 3: Chemicals that autopolymerize**

Acrylic acid	Acrylonitrile
Butadiene <sup>e</sup>	Chloroprene
Chlorotrifluoroethylene	Methyl methacrylate
Styrene	Tetrafluoroethylene
Vinyl acetate	Vinyl acetylene
Vinyl chloride	Vinyl pyridine

The above list provides examples of peroxide-forming chemicals only and is not an inclusive list. Other chemicals are capable of forming peroxides. Consult applicable Material Safety Data Sheets for information on peroxide-forming potential of specific chemicals.

References:

Kelly, R. J. Chemical Health and Safety 1996, Sep/Oct, pp 28-36, "Review of Safety Guidelines for Peroxidizable Organic Chemicals"

From UC Davis Safety Net 23-Peroxide Formation in Chemicals and other sources.

National Research Council. *Prudent Practices in the Laboratory: Handling and Management of Chemical Hazards, Updated Version*. Washington, DC: The National Academies Press, 2011.