Yale *Environmental Health & Safety*

Safety Guidelines

PEROXIDE FORMING CHEMICALS

Many commonly used organic solvents can react with oxygen in air (autooxidation) to form unstable peroxides, which may explode upon impact, heat or friction. The peroxide formation varies depending on the molecular structure of the chemical. Some chemicals may continue to build peroxides to potentially dangerous levels, while others accumulate a relatively low equilibrium concentration of peroxides, which becomes dangerous only after being concentrated by evaporation or distillation. In these cases, the peroxide becomes concentrated because it is less volatile than the parent chemical.

It is important that users are familiar with how to identify these types of chemicals, what the hazards are and know how to properly handle and store them.

Classification of Peroxide Forming Chemicals

Class A: Severe Peroxide Hazard

Chemicals that form explosive levels of peroxides without concentration. Severe peroxide hazard after prolonged storage even if unopened.
Discard within 3 months of receipt, even if unopened.

Class B: Concentration Hazard

Chemicals that can form explosive peroxides when concentrated by evaporation, distillation, etc.
Test for peroxide formation at least every 6 months after opening. Dispose of after 12 months unless testing indicates no peroxides present.

Class C: Shock and Heat Sensitive

Chemicals which violently auto-polymerize after internal peroxide accumulation.
Test for peroxide formation at least every 6 months after opening. Dispose of after 12 months unless testing indicates no peroxides present.

Common Peroxide Forming Chemicals

Class A: Severe Peroxide Hazard	***Class B: Concentration Hazard***		***Class C: Shock and Heat Sensitive***
Butadiene[a]	Acetal	Furan	Butadiene[b]
Chloroprene[a]	Acetaldehyde	4-Heptanol	Chlorobutadiene
Divinyl acetylene	Benzyl alcohol	2-Hexanol	Chloroprene[b]
Isopropyl ether	2-Butanol Dioxanes	Methyl acetylene	Chlorotrifluoroethylene
Potassium amide	Chlorofluoroethylene	3-Methyl-1-butanol	Styrene
Potassium metal	Cumene (isopropylbenzene)	Methyl-isobutyl ketone	Tetrafluoroethylene[b]
Sodium amide	Cyclohexene	4-Methyl-2-pentanol	Vinyl acetate
Tetrafluoroethylene[a]	2-Cyclohexen-1-ol	2-Pentanol	Vinyl acetylene
Vinylidene chloride	-Cyclopentene	4-Penten-1-ol	Vinyl chloride
	Decahydronaphthalene (decal-in)	1-Phenylethanol	Vinyl pyridine
	Diacetylene (butadiyne)	2-Phenylethanol	Vinyldiene chloride
	Dicyclopentadiene	Tetrahydrofuran	
	Diethylene glycol dimethyl ether (diglyme)	Tetrahydronaphthalene	
	Diethyl ether	Vinyl ethers	
	Ethylene glycol ether acetates (cellosolves)	Other secondary alcohols	

[a] When stored as a liquid monomer. [b] Can form explosive levels of peroxides when stored as liquid. When stored as gas, these chemicals may autopolymerize as a result of peroxide accumulation.

For More Information

- Sigma Aldrich – Peroxide Forming Solvents Information Page
  https://ehs.yale.edu/sites/default/files/files/peroxide-formation-sigma.pdf

- NRC Prudent Practices in the Laboratory: Organic Peroxides and Peroxidizable Compounds (https://www.nap.edu/read/12654/chapter/7#133)

- Clark, Donald E. (2001). Peroxides and peroxide-forming compounds. *Chemical Health and Safety: American Chemical Society, September/October*, 12-22.
  https://ehs.yale.edu/sites/default/files/files/peroxide-formation-clark.pdf

You can also contact your EHS Safety Advisor for further information or to perform a risk assessment at 203-785-3550 or ehs@yale.edu.

PEROXIDE FORMING CHEMICALS

Proper Storage and Handling

Purchase peroxide forming chemicals (PFCs) with inhibitors added by the manufacturer, when possible.

Maintain the minimal practical inventory of PFCs.

Do not retain or store redistilled or otherwise unstabilized PFCs.

Store PFCs at the lowest possible temperature consistent with their solubility or freezing point to minimize the rate of decomposition. Do not store them at, or lower than, the temperature at which the chemical freezes or precipitates. Peroxides in these forms are extremely sensitive to shock and heat.

Store all peroxidizable chemicals in tightly closed, air-impermeable, light-resistant containers, away from light, heat, direct sunlight, sources of ignition, oxidizers and oxidizing agents. Storage under nitrogen may be advisable in some cases.

Avoid friction, grinding and all forms of impact near peroxides, especially solid peroxides. Do not use glass containers with screw caps or glass stoppers. Use polyethylene containers, screw caps or stoppers.

Do not use metal spatulas to handle PFCs because metal contamination can lead to explosive decomposition. Magnetic stirring bars can unintentionally introduce iron, which can initiate an explosive reaction of peroxides. Teflon, ceramic or wooden spatulas and stirring blades may be used if it is known that the material is not shock sensitive.

Test PFCs immediately prior to distillation or evaporation. It can be extremely dangerous to distill or significantly concentrate any uninhibited solvent in Classes A or B unless known to be free of peroxidation products.

Determine how the PFC will be stabilized after the procedure is completed if the procedure removed the inhibitor.

Do not reuse PFC containers. Triple rinse them with water and follow standard procedures for container disposal.

Discard containers of PFCs within the appropriate time frame (Class A: 3 months, Classes B&C: 12 months) or by the manufacturer’s expiration date, if listed on the container. Testing can extend the 12-month period for Class B & C PFCs, but they should not be stored past the manufacturer’s expiration dates. Class A PFCs must be disposed of after three months, even if unopened.
If any of the following are observed with a peroxide forming chemical container, do not move or open the container and immediately contact EHS for assistance:

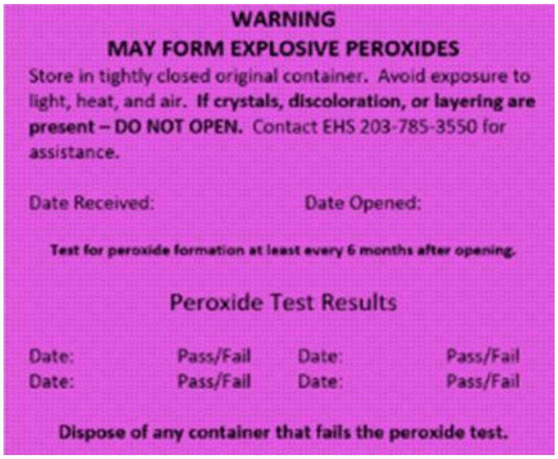
- Clear liquid containing suspended wisp-like structures
- Precipitated crystal formation appearing as chips, ice-like structures, or a solid mass
- Appearance of cloudiness
- Gross contamination

PEROXIDE FORMING CHEMICALS

Management Plan

All peroxide forming chemicals (PFCs) will be tracked through the University's chemical inventory system (EHS Integrator) as follows:

- Laboratories and departments which have their full inventories in EHS Integrator will continue to enter PFCs into the inventory system as they always have. Bar codes will be generated and placed on the PFC container as they are for all other chemicals.
- PFCs ordered by laboratories which do not use EHS Integrator for their chemical inventories will be entered into the inventory system by EHS and a bar code will be generated. This bar code will be provided to the laboratory to be affixed to the chemical container for tracking purposes.
- An expiration date for the PFC container will automatically be added in the chemical inventory system, based on PFC class and date of receipt.
- Each PFC container will also have the EHS supplied Warning label (pictured below) placed on it. Containers, which are either too small for this label or are stored in refrigerators or freezers, will be identified by a label with a bright pink "P" on it (also supplied by EHS). These containers must have a corresponding Warning label in the laboratory, to track receipt and open dates, as well as testing information.



WARNING

MAY FORM EXPLOSIVE PEROXIDES

Store in tightly closed original container. Avoid exposure to light, heat, and air. **If crystals, discoloration, or layering are present – DO NOT OPEN.** Contact EHS 203-785-3550 for assistance.

Date Received: Date Opened:

Test for peroxide formation at least every 6 months after opening.

Peroxide Test Results

Date:	Pass/Fail	Date:	Pass/Fail
Date:	Pass/Fail	Date:	Pass/Fail

Dispose of any container that fails the peroxide test.

The following information must be placed on the label by the laboratory staff:

- The receipt and opening date
- The date and result any time a test is conducted to detect the presence of peroxides

PEROXIDE FORMING CHEMICALS

Testing PFCs

Laboratories must test Class B & C PFCs at least every six months after opening the container. Additionally, PFCs should be tested prior to distillation or evaporation. The testing must be performed using the QUANTOFIX® Peroxide 100 test strips. These test strips turn blue in the presence of peroxides. **Any blue color on the test strip indicates a positive test (FAIL). White is a negative test (PASS).**

Peroxide forming compounds which have a positive test must be disposed of through EHS. Submit a hazardous waste request through EHS Integrator and indicate on the hazardous waste tag that peroxides are present. Contact EHS with any questions (203-432-6545 or waste.requests@yale.edu).

Instructions

The following are instructions for using QUANTOFIX® Peroxide 100 test strips. More detailed information is included in the QUANTOFIX® test strips packaging.
Ensure appropriate storage of the test strips: Avoid exposing the strips to sunlight and moisture. Keep container cool and dry (storage temperature not above +30 °C). If correctly stored, the test strips may be used until the use-by-date printed on the packaging.
Remove only as many test strips as are required. Close the container immediately after removing a strip. Do not touch the test field.

QUANTOFIX® Peroxide 100 is also suitable for the detection of other organic and free inorganic hydrogen peroxides. When detecting hydroperoxides in organic solvents, moisten the test field with one drop of water after evaporation/drying of the solvent.

Instructions for use:

1. Dip the test strip into the test solution for one second.
2. Shake off excess liquid.
3. Wait five seconds.
4. Compare test field with the color scale. If hydrogen peroxide is present, the test field turns blue.
   Note: Per Yale guidelines, any blue result is a "fail" and the PFC must be disposed of through EHS.

Color changes after one minute do not represent a positive reaction.

Quality control:
For the control of the functions of the test strips one uses a hydrogen peroxide solution with a concentration of 3 mg/L. For this a control standard of 500 mg/L H_2O_2 is prepared, whereby 1.5 mL of the 30 % hydrogen peroxide solution is diluted with 1000 mL of distilled water. Then 3 mL of this standard control solution are diluted with 500 mL of distilled water (= 3 mg/L H_2O_2). Now control the test strips immediately. Should the results still be negative after a repeated control, then the remaining unused test strips should be properly disposed of. Also with a negative control, whereby the test strips are dipped into distilled water, there should be no blue coloration. The reasons for both failures can be, that the expiration date has passed, the tube was left open too long or improper storage, meaning not according to instructions.

Interferences:
If the sample solution has a pH value of 2–9, the reaction will take place without interferences. Strong acid solutions must be buffered with sodium acetate, and alkaline solutions with citric acid to a pH of 5–7. The presence of other strong oxidants will also lead to false positive results. The following ions interfere with the determination only when the concentrations below are exceeded:
3 mg/L: free chlorine (hypochlorite)
4 mg/L: bromine (Br2)