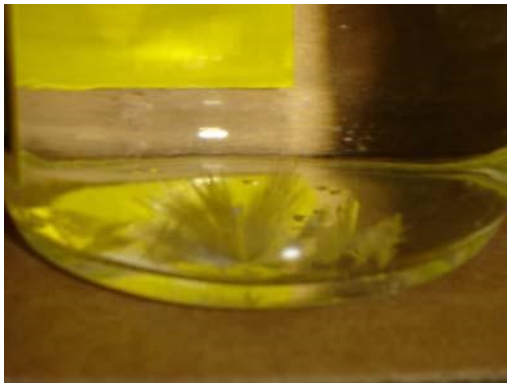
Peroxide-Forming Chemicals

Overview

Peroxide-forming chemicals are a class of compounds that have the ability to form shock-sensitive explosive peroxide crystals. Many of the organic solvents commonly used in laboratories have the potential to form explosive peroxide crystals. Diethyl ether and tetrahydrofuran are two of the more common peroxide-forming chemicals used today. Therefore, it is extremely important that this procedure be followed regarding the identification, handling, storage, and disposal of peroxide-forming chemicals.



Peroxide Formation

Under normal storage conditions the materials listed in this document have the potential to generate and accumulate peroxide crystal formations, which may violently detonate when subjected to thermal or mechanical shock. Peroxide-forming chemicals react with oxygen – even at low concentrations – to form peroxy compounds. The risk associated with peroxide formation increases if the peroxide crystallizes or becomes concentrated by evaporation or distillation. Factors that affect rate of peroxide formation include exposure to air, light and heat, moisture, and contamination from metals.

Manufacturers may add an inhibitor to peroxide forming chemicals to counter peroxide formation. For many peroxide-forming solvents, butylated hydroxy toluene (BHT) is commonly added. BHT 'scavenges' oxygen in the solvent and prevents it from reacting with the solvent to form peroxides. Over time, BHT or other inhibitor in the solvent can become exhausted allowing peroxides to form. Distilling the solvent can completely remove the BHT and make the solvent immediately susceptible to peroxide formation.

Peroxide crystals may form on the container plug or the threads of the lid and detonate when the lid is twisted. Do not open a liquid organic peroxide or peroxide-forming chemical if crystals or a precipitate are present.

Definition

A peroxide is a chemical that contains a peroxo (O-O) unit, one that has the chemical formula of O_2^{2-}. These are shock sensitive compounds, can explode if subject to mechanical shock, intense light, rapid changes in temperature, or heat.

Ideal Storage Conditions

Keep away from sources of ignition and store in a cool, dry place. Store in tightly closed containers and keep in a marked flammables area. Store protected from moisture, light and air. Containers should be dated when opened and tested periodically for the presence of peroxides. Do not exceed storage time limits.

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Condition of Material / Scenario Requiring Treatment

Peroxide formation may be present anywhere in the container, including the sides, bottom, exterior and threaded cap. Peroxide formation in PPM concentrations may not be visually observable and must be identified through the use of appropriate testing procedures. If any of the following conditions exist, the compound may be explosively unstable and will require stabilization prior to transportation.

1. Material appears to be degraded and or contaminated.
2. Material appears to be discolored.
3. Deterioration or distortion of storage container.
4. Gross contamination.
5. Thermal shock (sunlight).
6. Oxidation on exterior of container.
7. Age of material exceeds recommended storage time.

Hazard Analysis

Peroxides are less volatile than solvent and tend to concentrate in solution or in the container threads**.** Experiments have determined that a percentage of 0.008% (80 PPM) or greater is enough to initiate explosive decomposition**.** Peroxides are sensitive to heat, friction, and shock. Some peroxides may explode without being concentrated. (I.e. Isopropyl Ether)

Peroxide Forming Compound Evaluation Protocol

Upon discovering potential peroxide forming materials, do not remove from the storage location until a thorough evaluation of the material has been completed. Contact DEHS for assistance.

DEHS staff will consider in its assessment to determine if the potential peroxide forming chemical can be safely transported from the lab or other work area to the University's designated permitted hazardous waste storage facility. Any material from the potential peroxide forming compound list can be approved for transportation and disposal if the following conditions exist:

- The container is unopened and the contents are unexpired
- The container has been opened and the contents are unexpired or there is no expiration date but the date of manufacture is present and the compound falls within the acceptance parameters on the Recommended Storage Time Limits Table.
- The inner container has been confirmed unopened (seal intact) full, contains an inhibitor, the contents are expired, but the container is less than 3 yrs old and none of the conditions exist.
- The compound is a solid peroxide former (potassium metal, potassium amide, sodium amide, or sodium ethoxyacetylide) **and** is not discolored and has not formed a crust on the surface.
- Lab personnel can confirm testing for peroxides with results of less than 8 ppm and the testing falls within the timeframes for the groups.

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Performing the Visual Inspection

Solvents stored in glass bottles can be visually inspected for peroxides. Bottles containing organic solvents are typically made of amber/brown glass, so a flashlight can be used to light the interior of the bottle.

During the inspection, you should look for two signs that is indicative that the material is contaminated:

1. Hard crystal formations in the form of ice like structures, crystals, solid masses or an obscure cloudy medium signify gross contamination.
2. Wisp like structures floating in a clear liquid suspension signify contamination.

Use caution when performing the inspection; peroxide formation may be present anywhere in the container:

- The bottom of the container
- The side of the container
- The threaded cap
- The outside of the container

Peroxide formation in ppm concentrations may not be visually observable and must be identified through appropriate testing procedures.

Employees should not open any containers that do not pass this evaluation without the proper training, engineering controls, and PPE. Consult DEHS for further guidance.

List of potential peroxide-forming chemicals on following page. List is not conclusive, personnel should review chemical safety data sheet (SDS) and other manufacturer safety information. Consult DEHS for assistance.

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Solvents and Recommended Storage Time Limits Table

Category I Materials- recommended shelf life is 3 months whether it is inhibited or uninhibited.

Chemical	*Synonym(s)*
Isopropyl Ether	*Diisopropyl Ether, Diisopropyl Oxide*
Diethyl Ketene	*2-Ethyl-1-butene-1-one*
Divinyl Ether	*Vinyl Ether, Divinyl Oxide*
Potassium Metal	*Potassium*
Potassium Amide	
Sodium Amide	*Sodamide*
Sodium Ethoxyacetylide	
Vinylidene Chloride	*1,1-Dichloroethylene, 1,1-Dichloroethane*

Category II Materials- recommended shelf life is 12 months if inhibited and 3 months if uninhibited.

Chemical	*Synonym(s)*
p-Dioxane	*1,4-Dioxane, Diethylene Dioxide*
Ethyl Ether	*Ether, Diethyl Ether, Ethoxyethane*
Tetrahydrofuran	*Butylene Oxide, Diethylene Oxide*
Acetal	*1,1-Diethoxyethane, Diethyl Acetal*
Acetaldehyde	*Ethanal, Ethyl Aldehyde*
Cumene	*Isopropyl Benzene*
Cyclohexene	*1,2,3,4-Tetrahydrobenzene*
Cyclopentene	
Diacetylene)	*Butadiyne*
Ethylene Glycol Dimethyl Ether	*1,2-Dimethoxy Ethane, Glyme, Monoglyme*
Furan	*Divinylene oxide*
Methyl Acetylene	*Allylene, Propyne*
Methyl Cyclopentane	
Tetrahydronapthalene	*Tetraline*
Vinyl Ethers	*Ethyl Vinyl Ether, Methyl Vinyl Ether*
Diethylene Glycol Dimethyl Ether	*Diglyme*

Category III Materials- recommended shelf life is 12 months if inhibited and 3 months if uninhibited. These are hazardous due to peroxide polymerization when stored as a liquid. The peroxide forming potential increases and should be considered as a peroxide hazard on storage.

Chemical	*Synonym(s)*
Chlorobutadiene	Chloroprene
Vinyl Acetate	
Vinyl Acetylene	Buten-3-yne
Vinyl Chloride	Chloroethylene, Ethylene Monochloride
Vinyl Pyridine	
Styrene	