PEROXIDE FORMING CHEMICALS:
Managing, Retention, and Storage

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HAZARDS OF PEROXIDES

A wide variety of organic compounds spontaneously form peroxides by a free radical reaction of the hydrocarbon with molecular oxygen. Under normal storage conditions, formed peroxides can accumulate in the chemical container and may explode when subjected to heat, friction or mechanical shock. For this reason, it is imperative that laboratories learn to recognize and safely handle peroxide-forming compounds.

PRACTICES FOR CONTROL OF PEROXIDE FORMING MATERIALS

Purchase

Ideally, purchases of peroxide-forming chemicals should be restricted to ensure that these chemicals are used up completely before they can become peroxidized. This requires careful experiment planning. Researchers should purchase no more material than is needed to complete an experiment within the chemical's safe shelf life.

Labeling and Shelf-Life Limitation

Peroxides tend to form in materials as a function of age. Therefore, it is imperative that researchers are keenly aware of the age of their peroxide-forming chemicals. Researchers must date each container upon arrival in the laboratory. Containers must be dated again when opened for the first time. An appropriate expiration date based on what type of peroxide susceptible chemical the item is should also be on the label. Track dates and dispose of items through VEHS prior to expiration.

Storage

Peroxide-forming chemicals shall be stored in sealed, air-impermeable, light-resistant containers and should be kept away from light (light can initiate peroxide formation). Peroxide-forming chemicals should be stored in their original manufacturer's container whenever possible. This is very important in the case of diethyl ether because the iron in the steel containers that the material is shipped in acts as a peroxide inhibitor.

Inhibitors

Many methods can be used to stabilize or inhibit the peroxidation of susceptible chemicals. If it does not interfere with the use of the chemical and if available, peroxide-forming chemicals shall be ordered with inhibitor added and peroxide scavengers (inhibitors) shall be added in small quantities to items that have been redistilled. Contact VEHS at 322-2057 if the peroxide scavenger interferes with the use of the susceptible chemical.

Management and disposal of old containers

Older containers of peroxide-forming chemicals, or containers of unknown age or history, must be handled very carefully and should never be opened by researchers. Any peroxide-forming chemical with visible discoloration, crystallization or liquid stratification should be treated as potentially explosive. Older steel containers that have visible rust may also be extremely dangerous. If any of these conditions are observed on a peroxide-forming chemical container or if the origin and age are unknown, do not attempt to move or open the container. Contact VEHS at 2-2057 to have the container inspected and if necessary disposed of properly.

Safe Distillation of Peroxide Forming Chemicals

Eliminate the peroxides with a chemical reducing agent or pass the solvent through activated alumina.
Adding mineral oil to the distillation pot has the combined effect of "cushioning" any bumping, maintaining dilution, and serving as a viscous reaction moderator in case the peroxides begin to decompose. Carefully monitor the distillation process to ensure that it does not dry out completely, and then overheat. Distillation can concentrate peroxides, especially if taken to a dry state. Peroxides will be present mainly in the still bottoms.

Small pieces of sodium metal can be added to the distillation vessel to reduce peroxides. Use benzophenone as an indicator for the presence of sodium metal (benzophenone in the presence of sodium metal forms a radical with a deep-blue color). When the blue color disappears, add more sodium metal to the vessel.

CLASSIFICATION OF PEROXIDE FORMING MATERIALS

Chemicals that form peroxides are classified into four classes:

Class A: ***Peroxide Hazard on Storage – Without Concentration***
These chemicals can form peroxides that are difficult to detect and eliminate. Label these items with a date of receipt and date of opening and dispose of these items 3 months after opening or 12 months if unopened.

Class B: ***Hazard Due to Peroxide Concentration***
These chemicals can undergo explosive polymerization initiated by dissolved oxygen. Label these items with a date of receipt and date of opening and dispose of these items 6 months after opening or 12 months if unopened. When alcohols listed are used for purposes that do not involve heating, chemical reaction, bulk evaporation or other activities that may stress the peroxidizable material, it is not necessary to track and test these containers for peroxidation.

Class C: ***Auto Polymerize as a Result of Peroxide Accumulation***
These chemicals may explode when relatively small quantities of peroxides are formed. These items normally have an inhibitor (scavenger) added to the substance by the manufacturer in order to prevent peroxides from forming. This inhibitor can be removed if it interferes with the use of the chemical or the chemical is redistilled in the lab. If a lab procedure requires the use of an uninhibited item in this Class, please contact VEHS at 322-2057. Label these items with a date of receipt and date of opening and dispose of inhibited items after 12 months and *uninhibited items within 24 hours of use*.

Class D: ***May Form Peroxides***
These chemicals have the potential to form peroxides with varying conditions of use but are normally stable. Consult the manufacturer's MSDS to determine when peroxide formation is expected and label accordingly

Common chemicals that form explosive levels of peroxides (this list is not inclusive)

Class A: ***Peroxide Hazard on Storage – Without Concentration*** [a]

Butadiene[c]	Chloroprene[d]	Methacrylate
Vinylidene chloride	Tetrafluoroethylene	Divinyl acetylene

Class B: ***Hazard Due to Peroxide Concentration***

Acetal	Diethyl ether	2-pentanol
Acetaldehyde	Diethylene glycol	4-penten-1-ol
Benzyl alcohol	Dimethyl ether	1-phenylethanol
Isopropyl ether	Dioxanes	2-phenylethanol
Cyclohexanol	Ethylene glycol dimethyl ether	2-propanol (isoproranol, "IPA")
2-cyclohexen-1-ol	4-heptanol	Tetrahydrofuran
Cumene	Methyl acetylene	Tetrahydronaphthalene
Decahydronaphthalene	Methyl isobutyl ketone	Vinyl ethers
Diacetylene	3-methyl-1 butanol	Other secondary alcohols
Dicyclopentadiene	Methyl cyclopentane	

Class C: ***Auto-Polymerize as a Result of Peroxide Accumulation***

Acrylic acid	Chlorotrifluoroethylene	Vinyl acetylene
Acrylonitrile	Methyl methacrylate	Vinyl chloride
Butadiene[e]	Stryene	Vinyl pyridine
2-butanol	Vinyl acetate	Tetrafluoroethylene[c]

Class D: ***Chemicals that may form peroxides but cannot be clearly placed in Class A-C***

Acrolein
Allyl ether
Allyl ethyl ether
Allyl phenyl ether
p-(n-Amyloxy)benzoyl chloride
n-Amyl ether
Benzyl n-butyl ether
Benzyl ether
Benzyl ethyl ether
Benzyl methyl ether
Benzyl-1-napthyl ether
1,2-Bis(2-chloroethoxyl)ethane
Bis(2-ethoxyethyl)ether
Bis(2-(methoxyethoxy)ethyl) ether
Bis(2-chloroethyl) ether
Bis(2-ethoxyethyl) adipate
Bis(2-methoxyethyl) carbonate
Bis(2-methoxyethyl) ether
Bis(2-methoxyethyl) phthalate
Bis(2-methoxymethyl) adipate
Bis(2-n-butoxyethyl) phthalate
Bis(2-phenoxyethyl) ether
Bis(4-chlorobutyl) ether
Bis(chloromethyl) ether
2-Bromomethyl ethyl ether
beta-Bromophenetole
o-Bromophenetole
p-Bromophenetole
3-Bromopropyl phenyl ether
tert-Butyl methyl ether
n-Butyl phenyl ether
n-Butyl vinyl ether
Chloroacetaldehyde diethylacetal
2-Chlorobutadiene
1-(2-Chloroethoxy)-2-phenoxyethane
Chloroethylene
Chloromethyl methyl ether
b-Chlorophenetole
o-Chorophenetole
p-Chlorophenetole
Cyclooctene
Cyclopropyl methyl ether
Diallyl ether
p-Di-n-butoxybenzene
1,2-Dibenzyloxyethane
p-Dibenzyloxybenzene
1,2-Dichloroethyl ethyl ether
2,4-Dichlorophenetole
Diethoxymethane
2,2-Diethoxypropane
Diethyl ethoxymethylenemalonate
Diethyl fumarate
Diethyl acetal
Diethylketene
m,o,p-Diethoxybenzene
1,2-Diethoxyethane
Dimethoxymethane
1,1-Dimethoxyethane
Di(1-propynl) ether
Di(2-propynl) ether
Di-n-propoxymethane
1,2-Epoxy-3-isopropoxypropane
1,2-Epoxy-3-phenoxypropane
p-Ethoxyacetophenone
1-(2-Ethoxyethoxy)ethyl acetate
2-Ethoxyethyl acetate
(2-Ethoxyethyl)-a-benzoyl benzoate
1-Ethoxynaphthalene
o,p-Ethoxyphenyl isocyanate
1-Ethoxy-2-propyne
3-Ethoxypropionitrile
2-Ethylacrylaldehyde oxime
2-Ethylbutanol
Ethyl-b-ethoxypropionate
2-Ethylhexanal
Ethyl vinyl ether
Furan
2,5-Hexadiyn-1-ol
4,5-Hexadien-2-yn-1-ol
n-Hexyl ether
o.p-Iodophenetole
Isoamyl benzyl ether
Isoamyl ether
Isobutyl vinyl ether
Isophorone
b-Isopropoxypropionitrile
Isopropyl-2,4,5-trichlorophenoxy acetate
n-Methylphenetole
2-Methyltetrahydrofuran
3-Methoxy-1-butyl acetate
2-Methoxyethanol
3-Methoxyethyl acetate
2-Methoxyethyl vinyl ether
Methoxy-1,3,5,7-cyclooctatetraene
b-Methoxypropionitrile
m-Nitrophenetole
1-Octene
Oxybis(2-ethyl acetate)
Oxybis(2-ethyl benzoate)
b,b-Oxydipropionitrile
1-Pentene
Phenoxyacetyl chloride
a-Phenoxypropionyl chloride
Phenyl-o-propyl ether
p-Phenylphenetone
n-Propyl ether
n-Propyl isopropyl ether
Sodium 8-11-14-eicosatetraenoate
Sodium ethoxyacetylide
Tetrahydropyran
Triethylene glycol diacetate
Triethylene glycol dipropionate
1,3,3-Trimethoxypropene
1,1,2,3-Tetrachloro-1,3-butadiene
4-Vinyl cyclohexene
Vinylene carbonate

[a] Store under nitrogen, if practical.

[b] WARNING! May become unstable if concentrated intentionally or accidentally by user.

[c] When stored as an inhibited liquid monomer.

[d] When stored as a liquid monomer.

[e] When stored as a gas.

R.J. Kelly, "Review of Safety Guidelines for peroxide-forming Organic Chemicals", *Chemical Health & Safety*, September/October 1996, pp 28-36.