Storage and Handling of Potentially Explosive Chemicals (Peroxide Forming and Shock Sensitive Chemicals)

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Peroxide Forming Chemicals

Certain organic solvents and materials are susceptible to react with oxygen in the air to form unstable peroxides. Peroxides can accumulate in the chemical and may explode when subjected to heat, friction or mechanical shock. The risk is increased when a peroxide forming chemical is concentrated by distillation or evaporation. Unless these materials are properly handled, they can pose a serious safety hazard to users and a difficult disposal problem to the UH Manoa Environmental Health and Safety Office (EHSO).

General Precautions for Storage and Handling of Peroxide Forming Chemicals:

- > Minimize the quantity of peroxides and peroxide forming chemicals in the lab.
- Purchase peroxide forming chemicals containing an inhibitor such as butylated hydroxytoluene (BHT).
- Know the properties and hazards of all chemicals you are using through adequate research and study, including reading labels and Safety Data Sheets.
- Upon receiving a new peroxide former, label the container with the Date Received, Date Opened, Expiration Date, and Testing Dates.
- Maintain the laboratory's chemical inventory and document and track the testing results and expiration dates of peroxide forming chemicals in the lab.
- Set up reminders for testing and when containers should be submitted to EHSO for disposal (see section: *Classes of Peroxide Forming Chemicals*).
- Segregate these compounds from incompatible materials; store away from ignition sources, and protect from flame, sources of heat, and static electricity.
- Test for peroxides before any distillation or purification of peroxide forming chemicals; Do not dry peroxide forming solvents through distillation. Storage over 3 Å molecular sieves will safely remove residual water.
- Develop written Standard Operating Procedures for lab experiments and processes using peroxide forming chemicals.
- Use extreme caution before concentrating or purifying peroxide forming chemicals as most incidents occur during these processes.
- Utilize laboratory chemical fume hoods for transfers, manipulations, and experiments involving peroxide forming chemicals.
- Wear proper personal protective equipment, including safety eyewear and face shields, when working with peroxide forming chemicals.

- Minimize peroxide formation in ethers by storing in tightly sealed containers in a cool place in the absence of light.
- Do not open or move peroxide forming chemical containers and contact EHSO at 808-956-8660 immediately if you observe any of the following.:
 - Clear liquid containing suspended wisp-like structures
 - o Crystals or solids in the liquid or around the cap
 - Layering or discoloration; cloudiness
 - o Gross contamination
 - o Lid looks dented or popped off
 - Bottle stored near heat or sunlight

Submitting Peroxide Forming Chemicals as Waste to EHSO:

- Although having peroxide levels at <25 ppm is safe to use, a waste that tests positive for peroxide formation at >10 ppm cannot be accepted for transport and therefore will not be accepted by EHSO at this level.
- Any waste containing peroxides must be reduced to less than 10 ppm, and the resultant material inhibited to prevent future formation of peroxides. Documentation of how peroxides were reduced must be confirmed in writing.
- Peroxide testing dates and results must be documented in order to be approved and accepted by EHSO as waste. Peroxide testing must be done within 7 days of submitting the chemical to EHSO for approval and pick-up.

Classes of Peroxide Forming Chemicals:

Class A: Chemicals that form explosive levels of peroxides without concentration. These are the most hazardous and can form explosive peroxide levels even if not opened.

Divinyl Acetylene (DVA)	
Potassium Metal	
Butadiene*	

Isopropyl Ether Sodium Amide Chloroprene* Potassium Amide Vinylidene Chloride Tetrafluoroethylene*

*When stored as a liquid monomer

Note: Solids such as sodium amide and potassium metal cannot be tested and should only be stored in a glove box or in sealed ampules.

<u>STORAGE PERIOD</u>: Unopened – 6 months maximum or at expiration date, whichever comes first. Test liquids for peroxides before using or discard within 3 months. (If no inhibitor, discard after one use). Do not test solids – discard within 3 months. If stored under nitrogen or argon in sealed glass ampules or in a glove box, storage periods may be extended.

Class B: Chemicals that form explosive levels of solid peroxides either through spontaneous crystallization or when concentrated through distillation, evaporation or exposure to air after opening.

Acetal
Cyclohexene
Dicyclopentadiene
Ethyl Vinyl Ether
Methyl Acetylene (gas)
Tetrahydrofuran
Vinyl Ethers

Acetaldehyde Cyclopentene Diethyl Ether Furan Methylcyclopentane Tetrahydronaphthalene Cumene Diacetylene (gas) Dioxane Glyme (ethylene glycol dimethyl ether) Methyl Isobutyl Ketone Tetrahydropyran

STORAGE PERIOD:

Unopened containers – 1 year maximum or at expiration date, whichever comes first. If unopened, do not open to test; discard at expiration date.

Opened containers – test initially and quarterly for peroxides. Discard at 12 months after opening or at the manufacturer's expiration date (whichever comes first) if no peroxides are detected. Dispose immediately upon any positive test for peroxides. Test all ethers upon opening.

If stored in unopened septum-sealed bottles or under nitrogen in a glove box, storage periods may be extended up to 3 years.

Benzyl Alcohol 4-Heptanol 4-Methyl-2-Pentanol 1-Phenylethanol 2-Butanol 2-Hexanol 2-Pentanol 2-Phenylethanol Cyclohexanol 3-Methyl-1-butanol 4-Penten-1-ol 2-Propanol

Benzylic and secondary alcohols may only form dangerous concentrations of peroxides when dried through distillation over a reactive metal or metal hydride; always test before and after distillation or evaporation. Do not store near heat or sunlight. If not distilling, test annually. If no peroxides are detected, storage periods may be extended beyond 12 months.

Class C: Chemicals which are a hazard due to peroxide initiation of polymerization.

- Acrylic acid Chlorobutadiene Methyl methacrylate Vinyl acetate Vinyl pyridine
- Acrylonitrile Chloroprene Styrene Vinyl acetylene (gas)
- Butadiene Chlorotrifluoroethlyene (gas) Tetrafluoroethylene (gas) Vinyl chloride (gas)

<u>STORAGE PERIOD</u>: Unopened – 1 year maximum or at expiration date, whichever comes first. After opening, test quarterly for peroxides and discard within 12 months. If stored in unopened septum-sealed bottles or under nitrogen in a glove box, storage periods may be extended up to 3 years.

Class D: Chemicals that may form peroxides but cannot be clearly placed in Class A-C. Refer to the SDS and test peroxide levels quarterly upon opening.

Acrolein	p-Chlorophenetole	4,5-Hexadien-2-yn-1-ol
Allyl ether	Cyclooctene	n-Hexyl ether
Allyl ethyl ether	Cyclopropyl methyl ether	o.p-Iodophenetole
Allyl phenyl ether	Diallyl ether	Isoamyl benzyl ether
p-(n-Amyloxy)benzoyl	p-Di-n-butoxybenzene	Isoamyl ether
chloride		
n-Amyl ether	1,2-Dibenzyloxyethane	
Benzyl n-butyl ether	p-Dibenzyloxybenzene	Isophorone
Benzyl ether	1,2-Dichloroethyl ethyl ether	b-Isopropoxypropionitrile
Benzyl ethyl ether	2,4-Dichlorophenetole	Isopropyl-2,4,5-
		trichlorophenoxy acetate
Benzyl methyl ether	Diethoxymethane	n-Methylphenetole
Benzyl-1-naphthyl ether	2,2-Diethoxypropane	2-Methyltetrahydrofuran
1,2-Bis(2-	Diethyl	3-Methoxy-1-butyl acetate
chloroethoxyl)ethane	ethoxymethylenemalonate	
Bis (2-ethoxyethyl) ether	Diethyl fumarate	2-Methoxyethanol
Bis(2-(methoxyethoxy)ethyl)		2-Methoxyethyl acetate
ether		
Bis(2-chloroethyl) ether	Diethylketene	3-Methoxybutyl acetate
Bis(2-ethoxyethyl) adipate	Diethoxybenzene (m-,o-,p-)	2-Methoxyethyl vinyl ether
Bis(2-methoxyethyl)	1,2-Diethoxyethane	Methoxy-1,3,5,7-
carbonate		cyclooctatetraene
Bis(2-methoxyethyl) ether	Dimethoxymethane	b-Methoxypropionitrile

Bis(2-methoxyethyl) phthalate	1,1-Dimethoxyethane	m-Nitrophenetole
Bis(2-methoxymethyl) adipate	Di(1-propynl) ether	1-Octene
Bis(2-n-butoxyethyl) phthalate	Di(2-propynl) ether	Oxybis(2-ethyl acetate)
Bis(2-phenoxyethyl) ether	Di-n-propoxymethane	Oxybis(2-ethyl benzoate)
Bis(4-chlorobutyl) ether	1,2-Epoxy-3- isopropoxypropane	b,b-Oxydipropionitrile
Bis(chloromethyl) ether	1,2-Epoxy-3-phenoxypropane	1-Pentene
2-Bromomethyl ethyl ether	p-Ethoxyacetophenone	Phenoxyacetyl chloride
beta-Bromophenetole	1-(2-Ethoxyethoxy)ethyl acetate	a-Phenoxypropionyl chloride
o-Bromophenetole	2-Ethoxyethyl acetate	Phenyl-o-propyl ether
p-Bromophenetole	(2-Ethoxyethyl)-a-benzoyl benzoate	p-Phenylphenetone
3-Bromopropyl phenyl ether tert-Butyl methyl ether	1-Ethoxynaphthalene o,p-Ethoxyphenyl isocyanate	n-Propyl ether
n-Butyl phenyl ether	1-Ethoxy-2-propyne	Sodium 8-11-14-
		eicosatetraenoate
	3-Ethoxypropionitrile	Sodium ethoxyacetylide
Chloroacetaldehyde diethylacetal	2-Ethylacrylaldehyde oxime	2-Chlorobutadiene
1-(2-Chloroethoxy)-2- phenoxyethane	2-Ethylbutanol	Triethylene glycol diacetate
Chloroethylene	Ethyl-b-ethoxypropionate	Triethylene glycol dipropionate
Chloromethyl methyl ether	Ethylene glycol monomethyl ether	1,3,3-Trimethoxypropene
beta-Chlorophenetole	2-Ethylhexanal	1,1,2,3-Tetrachloro-1,3- butadiene
o-Chlorophenol		4-Vinyl cyclohexene
2,5-Hexadiyn-1-ol	Vinylene carbonate	1 1

*The peroxide formers listed here is not a comprehensive list. Please refer to the SDS for any material to inquire if it's a potential peroxide former.

Peroxide Forming Chemical Labels and Test Strips

Peroxide forming chemical labels are available from EHSO or at the chemical stockroom in Bilger 116. Please place this label on any peroxide forming chemicals or even chemical mixtures (including waste) that may contain a peroxide forming chemical and record date received, date opened, and expiration date. Record required testing dates and results. A Peroxide Evaluation Form will need to be filled out prior to submitting as waste. Please contact 808-956-3198 or hazwaste@hawaii.edu for labels and/or the evaluation form.

	CAUTION!	
PEROXIDE	FORMING	CHEMICAL

Store tightly and avoid exposure to light, air or heat. Do not open if crystals or solids are visible inside or around the cap or if there is any discoloration or layering observed.

Date Received: Date Opened: Expiration Date:		_
Date Tested:	Results:	ppm

Peroxide test strips are available from the following sources:

- University of Hawaii at Manoa Chemistry Department Stockroom, Bilger 116; Phone 808-956-6021
- Hawaii Chemical and Scientific, 2363 N. King Street, Honolulu, HI 96819; Phone #808-841-4265
- Fisher Scientific, VWR International, various online vendors

Shock Sensitive and Potentially Explosive Chemicals

The following chemicals are known to be shock sensitive or potentially explosive and need to be handled with care. The shock sensitivity and explosive potential of those which are solids is increased if they become dry. This list is not all inclusive, but it is limited to those chemicals which may be present at the University of Hawaii. EHSO is not able to accept any explosives for waste disposal.

Benzoyl Peroxide	White, crystalline solid; requires 25-35%
	water
Dinitrophenyl hydrazine	Red crystalline solid, requires >30% water
Methyl Ethyl Ketone Peroxide	Colorless liquid; strong oxidizer
Nitroglycerin	Colorless liquid
Picramide (Trainitroaniline)	Yellow crystalline solid; requires >30% water
Picric acid (Trinitrophenol)	Yellow crystalline solid; requires >30% water;
	incompatible with metals, oxidizers or
	reducers
Picryl Chloride	White crystalline solid; requires >30% water;
	incompatible with oxidizers and inorganic
	nitrates
Picryl Sulfonic Acid (Trinitrobenzenesulfonic	Flammable solid, corrosive, requires >30%
acid)	water
Trinitroanisole (Methyl Picrate)	Yellow crystalline solid, highly explosive
Trinitrobenzene	Yellow crystalline solid; requires >30% water
Trinitrobenzoic Acid	Yellow crystalline solid; highly flammable and
	explosive
Urea Nitrate	Colorless crystalline solid; requires >10%
	water

Picric Acid and Di- and Tri- Nitro Compounds:

Picric Acid (2,4,6-trinitrophenol) is a common trinitro compound used in many laboratories. Picric acid is in wetted form, but if water evaporates, the substance becomes shock sensitive. Dry picric acid is highly explosive, especially if combined with metals such as copper, lead, zinc, and iron. It will also react with alkaline materials including plaster and concrete to form explosive materials

- Only purchase picric acid in solution.
- Label the container to show the date when it is first received and opened; and expiration date if available.
- Develop written Standard Operating Procedures for lab experiments and processes using these substances.
- > Maintain a log for regular inspection of container and usage.

- Dispose of bottle as hazardous waste to EHSO once expiration date has been reached or when no longer needed.
- Hydrate picric acid as needed with deionized water always keep wet with at least 30% water.
- Store container in an approved flammable safety cabinet
- Do not pour contents from these containers into a sink drain.
- Clean bottleneck, cap, and threads with a wet cloth before resealing.
- > Do not use a metal lid/cap; do not use metal spatulas.
- Use in a fume hood and wear appropriate PPE when working with picric acid. Review the SDS before working with this chemical.
- Do not open or move chemical container and contact EHSO at 808-956-8660 immediately if you observe any of the following.:
 - Crystals or solids inside the bottle or around the cap.
 - Picric acid has dried and contains less than 30% water.

Attention: According to the UHM Chemical Hygiene Plan, if your lab is using chemicals that fall into any of the hazard categories mentioned above for research, it is essential to account for their presence and safe use. Utilize the UH Safety Solutions Lab Hazard Assessment tool to document this information. Additionally, make sure to have written Standard Operating Procedures in place, along with risk reduction controls such as chemical fume hoods and appropriate personal protective equipment (PPE). Ensure that these procedures and controls are communicated to all lab personnel. If you have any questions about lab protocols involving these items, feel free to contact the UHM Lab Safety Program at labsafe@hawaii.edu.