Title of SOP:	**Organic Peroxides and Peroxide Forming Compounds SOP**	
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PURPOSE:

This standard operating procedure (SOP) is intended to provide general guidance on how to safely work with organic peroxides and peroxide forming compounds. This SOP is generic in nature and only addresses safety issues specific to these materials. In some instances, several general use SOPs may be applicable for a specific chemical.

SCOPE:

Organic peroxides are a special class of compounds that have unusual stability problems, making them among the most hazardous substances normally handled in laboratories. In addition, certain laboratory chemicals can react with the oxygen in air to form peroxides. Some 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. The peroxide becomes concentrated because it is less volatile than the parent chemical is.

Manufacturers may add an inhibitor or stabilizer 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.

APPLICABILITY:

<u>Examples of organic peroxides and peroxide forming compounds include</u>:

Organic peroxides:

- Benzoyl peroxide
- Di-tert-butyl peroxide
- Cyclohexanone Peroxide
- Methyl Ethyl Ketone Peroxide

Peroxide formers:

Class A - Severe Peroxide Hazard **Spontaneously decompose and become explosive with exposure to air without concentration.**	**Class B - Concentration Hazard** **Require external energy for spontaneous decomposition. Form explosive peroxides when distilled, evaporated or otherwise concentrated.**		**Class C - Shock and Heat Sensitive** **Highly reactive and can auto-polymerize as a result of internal peroxide accumulation. The peroxides formed in these reactions are extremely shock- and heat-sensitive.**
Butadiene (liquid monomer)	Acetal	Furan	Acrylic acid
Chloroprene (liquid monomer)	Acetaldehyde	4-Heptanol	Acrylonitrile
Divinyl ether	Benzyl alcohol	2-Hexanol	Butadiene (gas)
Isopropyl ether	2-Butanol	Methylacetylene (gas)	Chlorobutadiene
Potassium amide	Cumene	3-Methyl-1-butanol	Chloroprene
Potassium metal	Cyclohexanol	Methyl cyclopentane	Chlorotrifluoroethylene (gas)
Sodium amide	Cyclohexene	Methyl isobutyl ketone	Methyl methacrylate
Tetrafluoroethylene (liquid monomer)	2-Cyclohexene-1-ol	4-Methyl-2-pentamol	Styrene
Viylidene chloride	Decahydronaphthalene (decalin)	2-Pentanol	Tetrafluoroethylene (gas)
	Diacetylene (butadine, gas)	4-Penten-1-ol	Vinyl acetate
	Dicyclopentadiene	1-Phenylethanol	Vinylacetylene (gas)
	Diethylene glycol dimethyl ether (diglyme)	Tetrahydrofuran (THF)	Vinyladiene chloride
	Diethyl ether (ether)	Tetrahydronaphthalene (tetralin)	Vinyl chloride (gas)
	Dioxanes	Vinyl ethers	Vinyl pyridine
	Ethylene glycol ether acetates (glyme)	Other Secondary alcohols	
Unopened container: discard or test for peroxide formation at 12 months from receiving or at manufacturer's expiration date whichever comes first. **Opened container:** test for peroxide formation quarterly.	**Unopened container:** discard or test for peroxide formation at 12 months from receiving date or at manufacturer's expiration date whichever comes first. **Opened container:** test for peroxide formation every 6 months. **Opened container used for distillation or evaporation:** test for peroxide formation immediately before distillation		

*Note: Some of the information in this SOP was adopted from Prudent Practices in the Laboratory, Handling and Management of Chemical Hazards, Updated Edition, National Research Council.

Class D - Potential Peroxide Forming Chemicals **May form peroxides but cannot be clearly categorized in Class A, B, or C.**		
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 chloride	p-Di-n-butoxybenzene	Isoamyl ether
n-Amyl ether	1,2-Dibenzyloxyethane	Isobutyl vinyl ether
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-chloroethoxyl)ethane	Diethyl ethoxymethylenemalonate	3-Methoxy-1-butyl acetate
Bis(2-ethoxyethyl)ether	Diethyl fumarate	2-Methoxyethanol
Bis(2-(methoxyethoxy)ethyl) ether	Diethyl acetal	2-Methoxyethyl acetate
Bis(2-chloroethyl) ether	Diethylketene	3-Methoxybutyl acetate
Bis(2-ethoxyethyl) adipate	Diethoxybenzene (m-,o-,p-)	2-Methoxyethyl vinyl ether
Bis(2-methoxyethyl) carbonate	1,2-Diethoxyethane	Methoxy-1,3,5,7-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	1-Ethoxynaphthalene	n-Propyl ether
tert-Butyl methyl ether	o,p-Ethoxyphenyl isocyanate	n-Propyl isopropyl ether
n-Butyl phenyl ether	1-Ethoxy-2-propyne	Sodium 8-11-14-eicosatetraenoate
n-Butyl vinyl ether	3-Ethoxypropionitrile	Sodium ethoxyacetylide
Chloroacetaldehyde diethylacetal	2-Ethylacrylaldehyde oxime	Tetrahydropyran
2-Chlorobutadiene	2-Ethylbutanol	Triethylene glycol diacetate
1-(2-Chloroethoxy)-2-phenoxyethane	Ethyl-b-ethoxypropionate	Triethylene glycol dipropionate
Chloroethylene	Ethylene glycol monomethyl ether	1,3,3-Trimethoxypropene
Chloromethyl methyl ether	2-Ethylhexanal	1,1,2,3-Tetrachloro-1,3-butadiene
beta-Chlorophenetole	Ethyl vinyl ether	4-Vinyl cyclohexene
o-Chlorophenol	2,5-Hexadiyn-1-ol	Vinylene carbonate

PROCEDURE:

Potential Hazards/Toxicity

As a class, organic peroxides are low powered explosives, however they are particularly hazardous because they are sensitive to heat, friction, impact, light, and other forms of accidental ignition, as well as to strong oxidizing and reducing agents. The unusual stability problems of this class of compounds make them a serious fire and explosion hazard. This class of compounds is also highly flammable.

In addition to the physical hazards, these compounds may also pose health hazards. They are irritating to eyes, skin and respiratory tract and their vapors may cause drowsiness and dizziness. Repeated skin exposures may cause dryness or cracking.

As the hazards may vary by compound, users must familiarize themselves with the specific hazards of the compounds they are working with, which can be found on the chemical's Safety Data Sheet (SDS). SDSs are available through MSDS Online.

Personal Protective Equipment (PPE)

The University's Laboratory Personal Protective Equipment Policy is currently under review.

Eye Protection

Safety glasses must be worn whenever handling organic peroxides or peroxide forming compounds. When there is the potential for splashes, goggles and/or a faceshield must be worn.

Hand Protection

Gloves must be worn when handling organic peroxides or peroxide forming compounds. Exam style nitrile gloves (minimum 4 mil thickness) are generally adequate for handling these compounds in laboratory settings when skin contact is unlikely. However, if skin contact is likely or larger amounts are being used, then a utility grade glove should be worn over the exam style nitrile. To ensure that the appropriate utility grade glove is selected, use the glove selection guide or contact EHS.

Skin and Body Protection

Long pants or clothing that covers the body to the ankles and closed-toe solid top shoes must be worn when handling these compounds. Lab coats must be worn. For organic peroxides or peroxide forming compounds that pose health hazards through dermal absorption, additional protective clothing (i.e., apron, protective sleeves) may be appropriate where chemical contact with the skin is likely.

Engineering Controls

Fume Hood

Fume hoods, or other locally exhausted ventilation, must be used whenever handling organic peroxides or peroxide forming compounds.

Storage/Handling

- Avoid friction, grinding, and all forms of impact near peroxides, especially solid peroxides. Do not use glass containers with screw caps or glass stoppers. Polyethylene containers with screw tops may be used.
- Store peroxides 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 peroxide freezes or precipitates because peroxides in these forms are extremely sensitive to shock and heat.
- Store all peroxidizable compounds 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.
- Do not use metal spatulas to handle peroxides 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.

- Do not allow these compounds to evaporate to near dryness unless absence of peroxides has been shown.
- Purchase peroxide formers with inhibitors added by the manufacturer when possible.
- If a peroxide-forming chemical or container is of unknown age or history, if crystals or solid masses are visibly present on or in the container or lid, or if the chemical shows discoloration, string-like formations, or liquid stratification, do not open the container. Contact EHS for assistance.
- For peroxide forming compounds, mark the receipt and opening date on the container and discard within the time frame listed in the table above (or by the manufacturer's expiration date, if listed on the container).
- Periodic testing to detect peroxides should be performed and recorded on previously opened material
- This label must be affixed to the storage container and routine maintenance must be implemented:

Label for Storage Cabinet:

Warning: May Form Explosive Peroxides Store in tightly closed original container. Avoid exposure to light, air and heat. If crystals, discoloration or layering is visible, do not move or open; contact EHS immediately. Check for peroxides each time before distilling or concentrating.				
Name of Chemical:				
Date Received:			Date Opened:	
Test or Dispose _____ months after receipt, or _____ months after opening				
Test Date:			Peroxides Y N	mg/l H_2O_2
Test Date:			Peroxides Y N	mg/l H_2O_2
Test Date:			Peroxides Y N	mg/l H_2O_2
Test Date:			Peroxides Y N	mg/l H_2O_2
Do not use chemical if >20 mg/l H_2O_2 peroxides are detected.				

Label for Bottle:

Date Received:		
Date Opened:		
Test Date:		mg/l H_2O_2
Test Date:		mg/l H_2O_2
Test Date:		mg/l H_2O_2
Test Date:		mg/l H_2O_2

Peroxide Detection

A variety of methods are available to test for the presence of peroxides in organic solvents. Peroxide test strips provide a simple and convenient mechanism for detection . If your lab needs some peroxide test strips (https://www.sigmaaldrich.com/catalog/product/mm/110011?lang=en&region=US), contact EHS or the Chemistry Stockroom. For volatile organic chemicals the test strip is immersed in the chemical for 1 second, then the tester blows slowly on the strip for 15-30 seconds or until the color stabilizes. Test strip color is compared with a colorimetric scale provided on the test kit bottle. Strips that offer a 0-25 mg/l H_2O_2 peroxide range are useful for determining if the material is below the control point of 20 mg/l H_2O_2. It is not necessary to start testing a stabilized peroxide forming agent until the bottle has been opened for the first time.

It is important to note that peroxide concentrations greater than 20 mg/l H_2O_2 are considered explosive and pose a significant issue for hazardous waste vendors being able to pick up the container.

If there are visible crystals, visible precipitate or an oily viscous layer present in the material, these are visual indicators of dangerous high peroxide levels, immediately contact EHS, to manage this hazardous situation and to dispose of this material.

Waste Disposal

Organic peroxides or peroxide forming compounds must be collected as hazardous waste. It is important to put in a work order as soon as you are ready to have your waste or expired chemicals picked up. If you are uncertain of the stability of a chemical/waste bottle, please contact EHS at your earliest convenience and do not open it.

Emergency Procedures

Fire Extinguishers

An ABC dry powder extinguisher is appropriate if there is a fire involving these compounds.

Eyewash/Safety Showers

An ANSI approved eyewash station that can provide quick drenching or flushing of the eyes must be immediately available within 10 seconds travel time for emergency use. An ANSI approved safety drench shower must also be available within 10 seconds travel time from where these compounds are used. Ensure the locations of the eyewashes and safety showers, and how to activate them, are known prior to an emergency.

First Aid Procedures

Life Threatening Emergency, After Hours, Weekends and Holidays

Call 911 or CPSO at 503-725-4404. Once it is safe to do so, report to EHS and HR (if an employee is injured)

Assess the extent of danger.

If you cannot assess the conditions of the environment well enough to be sure of your own safety, do not enter the area. If possible, help contaminated or injured persons. Obtain medical attention for the individual as soon as possible by calling 911 or CPSO at 503-725-4404. Provide a copy of the appropriate SDS and lab specific SOP to the emergency responders or physician, as needed.

If inhaled

Move to fresh air. If person is not breathing or unconscious, call 911 or CPSO at 503-725-5911. Report to EHS and HR when safe to do so.

In case of skin contact

Go to the nearest emergency shower if contaminated. Yell for assistance and rinse for 15 minutes, removing all articles of clothing to ensure contaminate is completely removed. If skin contact requires medical attention or you are unsure if it does, call 911 or CPSO at 503-725-5911.

In case of eye contact

Go to the nearest emergency eyewash. Yell for assistance and rinse for 15 minutes, occasionally lifting the upper and lower eyelids. Remove contact lenses if possible. Call 911 or CPSO at 503-725-5911.

Spills

Small Spill

If a small spill occurs, lab personnel should be able to safely clean it up by following these spill clean-up procedures:

- Alert people in immediate area of spill

- Increase ventilation in area of spill (open fume hood sashes and press purge if you have the option)
- Wear personal protective equipment, including utility grade gloves
- Confine/adsorb spill of liquids with spill clean-up pads or absorbent
- Keep spills of solid peroxides wet with an appropriate inert solvent (e.g. water or aliphatic hydrocarbon). Cover the spill with a wet (water) mixture (1:1:1, by weight) of sodium carbonate, vermiculite, and sand.
- Collect residue, place in container, label container, and dispose of as hazardous waste
- Clean spill area with soap and water

<u>Larger Spill</u>

- Call 911 and EHS for emergency assistance (503-725-4312)
- Evacuate the spill area
- Post someone or mark-off the hazardous area with tape and warning signs to keep other people from entering
- Stay nearby until emergency personnel arrive and provide them with information on the chemicals involved

Please list the compounds used by this research group, which are covered by this procedure. The list should also include the building/room where they are used.

Lab Specific Protocol/Procedure: