Standard Operating Procedure

ORGANIC PEROXIDES AND PEROXIDE FORMING COMPOUNDS*

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.

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. Stabilizers or inhibitors are sometimes added to the liquid to extend its storage life, but distillation will remove the inhibitor.

Examples of organic peroxides:

- Benzoyl peroxide
- Butyl Peroxydicarbonate
- Cyclohexanone Peroxide
- Methyl Ethyl Ketone Peroxide
- Methyl Isobutyl Ketone Peroxide

Common Peroxide Forming Chemicals & their Classification

See "Peroxide Forming Chemicals" safety guidelines for more specific storage and testing information.

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.

*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 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.

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 the Safety Data Sheet link on Yale's EHS webpage (ehs.yale.edu).

Personal Protective Equipment (PPE)

The University's Personal Protective Equipment Policy can be found on the EHS website (ehs.yale.edu)

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 4mil 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, refer to the chemical's SDS, use a glove manufacturer's 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, oversleeves) 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.
- 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).
- 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.

Waste Disposal

Organic peroxides or peroxide forming compounds must be collected as hazardous waste.

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

If inhaled
Remove to fresh air. Follow up with Acute Care or Employee Health as appropriate (203-432-0123).

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. Follow up at Acute Care/Employee Health as appropriate (203-432-0123).

In case of eye contact
Go to the nearest emergency eyewash. Yell for assistance and rinse for 15 minutes. Follow up at Acute Care/Employee Health (203-432-0123).

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)
- 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

Larger Spill
- Call EHS for emergency assistance (203-785-3555)
- 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