

Peroxide Formers and Other Potential Explosives SOP

SCOPE/PURPOSE

Scope: Any academic department that uses the types of chemicals defined herein.

Purpose: Certain solvents and other chemicals are known to form potentially explosive peroxides. Many of these are organic solvents; some are inorganic solids. An inhibitor is added to most peroxide-forming solvents by the manufacturer; this is usually effective until the container is first opened. After that, the inhibitor begins to be depleted. It can also become depleted during long storage without opening. High-purity solvents (e.g., HPLC grade) sometimes have no inhibitor added. The purpose of this plan is to define a peroxide former and set forth the guidelines that should be followed with regard to purchasing, storing, testing and using these chemicals. For more information, see section 4.D.3.2 and 6.G.3 in *Prudent Practices in the Laboratory*, The National Academies Press: 2011.

DEFINITION:

Peroxide structures present an explosive hazard. If they are present in a solvent, the hazard is compounded by the presence of a flammable liquid along with the explosive substance. Peroxides are also often shock sensitive compounds that can explode if subjected to mechanical shock, intense light, rapid changes in temperature, heat, friction, or in some cases, by spontaneous reaction. Chemicals that can potentially form peroxides (peroxidizables) are categorized into three classes (A-C) defined below. Included below are examples of chemicals in each class. Below are examples of chemicals in each class. These lists are not comprehensive.

Class A:

Class A peroxide formers are chemicals that form explosive levels of peroxides without concentration (in other words, without having been concentrated by evaporation or distillation).

Isopropyl ether	Sodium amide
Butadiene	Tetrafluoroethylene
Chlorobutadiene (chloroprene)	Divinyl acetylene
Potassium amide	Vinylidene chloride
Potassium metal	

Class B:

Class B peroxide formers are a peroxide hazard upon concentration (distillation/evaporation). A test for peroxide content should be performed if concentration is intended or suspected.

Acetal	Dioxane (p-dioxane)
Cumene	Ethylene glycol dimethyl ether
Cyclohexene	Furan
Cyclooctene	Methyl acetylene
Cyclopentene	Methyl cyclopentane
Diacetylene	Methyl-isobutyl ketone
Dicyclopentadiene	Tetrahydrofuran
Diethylene glycol dimethyl ether	Tetrahydronaphthalene
Diethyl ether	Vinyl ethers

Class C:

Unsaturated monomers that may autopolymerize as a result of peroxide accumulation if inhibitors have been removed or are depleted.

Acrylic acid	Styrene
Butadiene	Vinyl acetate
Chlorotrifluoroethylene	Vinyl chloride
Ethyl acrylate	Vinyl pyridine
Methyl methacrylate	

Types of compounds likely to autoxidize to form peroxides:

- Ethers containing primary and secondary alkyl groups (never distill an ether before it has been shown to be free of peroxide)
- Compounds containing benzylic hydrogens
- Compounds containing allylic hydrogens (C=C—CH)
- Compounds containing a tertiary C—H group (e.g., decalin and 2,5-dimethylhexane)
- Compounds containing conjugated, polyunsaturated alkenes and alkynes (e.g., 1,3-butadiene, vinyl acetylene)
- Compounds containing secondary or tertiary C—H groups adjacent to an amide (e.g., 1-methyl-2-pyrrolidinone)

STANDARD PROCEDURES:

Inventory

- Order the minimum amount necessary

- Date bottle: received, first opened, expiration, last tested
- Purchase with inhibitor whenever possible
- Purchase septum-capped bottles when possible and store under inert gas- especially those without inhibitor (except some class C chemicals that come with inhibitors that require oxygen).
- Use 'first in, first out' inventory
- Remove inventory to waste promptly when expired.

Storage

- Store separate from incompatible hazard classes, especially oxidizers. Oxidizers include 'organic peroxides' which might sound like they could go with 'peroxide formers', however that is not the case. Organic peroxides are organic compounds that already contain oxygen and are oxidizers because they easily donate oxygen to other compounds or reactions. Peroxide formers readily accept oxygen from any source, including ambient air, and create peroxide compounds that are extremely dangerous. Peroxide formers must be kept separate from any source of oxygen.
- Store away from heat, light, and ignition sources including static electricity
- Avoid storage in a refrigerator or freezer. Do not store at temperatures near the compounds melting/freezing point.

Storage Time Limits

- Class A
 - 3 months from receipt
- Class B
 - With inhibitor: Manufacturer's expiration date
 - Without inhibitor: one year, or a tested peroxide level of >80ppm, whichever comes first.
- Class C
 - With inhibitor: manufacturer's expiration date
 - Without inhibitor: These are generally not sold without an inhibitor so if there is a compound without an inhibitor it was likely removed in a lab process. Once that process is complete an inhibitor should be added back to the compound immediately.
 - Gases: dispose after 1yr

Testing

- Class A

- Can be dangerous it is best to just dispose of within the designated time limit.
- Class B
 - With inhibitor: Testing not necessary unless an old bottle is found that is past its expiration date or it has been distilled or otherwise known to have lost its inhibitor.
 - Without inhibitor: Test every 3 months after having been opened until 80ppm peroxide level is detected, then dispose.
- Class C
 - Liquids: test every 6 months
 - Solids: Manufacturer's expiration date

Usage

- Inspect all bottles prior to use for peroxide crystal formation. If any crystal or solid is observed either within the bottle or on the cap threads DO NOT MOVE OR OPEN the bottle. Contact the CHO for assistance. An outside firm may need to be called to deal with the situation.
- Avoid contamination as it can promote peroxide formation.
 - Avoid metal sources such as metal spatulas and magnetic stir bars.
 - Use only original containers and do not reuse containers.
- Use extreme caution when distilling or evaporating.
 - Inspect bottle and test contents prior to distillation. Do not use if >80ppm peroxide content.
 - Consider adding non-volatile oil such as mineral oil and a polymer sleeve to ensure the distillation doesn't go to dryness and that friction is reduced.
 - Do not distill to dryness. Stop when 20% of starting volume remains.
 - Be cautious about agitation or shaking after distillation
 - Since distillation removes any inhibitor that may have been present it either needs to be replaced or store the solution under inert gas.

SHOCK SENSITIVE AND POTENTIALLY EXPLOSIVE CHEMICALS

The following are chemicals known to be shock sensitive or potentially explosive and need to be handled with care. The shock sensitivity and explosive potential is increased if they become dry, this is especially true for the solid chemicals. This list is not all inclusive.

<i>Chemical (CAS#)</i>	<i>Information</i>
Replacement stock of these may be purchased without special permission from the CHO.	
Benzoyl Peroxide (94-36-0)	White crystalline solid; requires 25-

	25%water
Dinitrophenyl hydrazine (119-26-6)	Red crystalline solid; requires >30%water
Nitromethane (75-52-5)	Colorless liquid; highly flammable, incompatible with amines, oxidizers, strong acids or bases
These may not be purchased without special permission from the CHO.	
Methyl ethyl ketone peroxide (1338-23-4)	Colorless liquid; strong oxidizer
Nitroglycerin (55-63-0)	Colorless liquid
Picramide (489-98-5)	Yellow crystalline solid; requires>30%water
Picric acid (88-89-1)	Yellow crystalline solid; requires >30%water. Incompatible with metals, oxidizers and reducers
Picryl chloride (88-88-0)	White crystalline solid; requires >30%water. Incompatible with oxidizers, inorganic nitrates
Picryl sulfonic acid (2508-19-2)	Flammable solid, corrosive; requires >30%water
Trinitroanisole (606-35-9)	
Trinitrobenzene (99-35-4)	Yellow crystalline solid; requires >30% water
Trinitrobenzoic acid (129-66-8)	
Trinitrotoluene (118-96-7)	
Urea Nitrate (124-47-0)	Colorless crystalline solid; requires > 10% water

CHECKING FOR PEROXIDE FORMATION

Visual Inspection

If the peroxide former is in a glass bottle, inspect the bottle visually before attempting to open it. Use a soft light source (flashlight) to light the interior of the bottle from the back or the side so you can get a good view of the liquid. Look at the entire inside of the container -- the bottom, the sidewalls, the portion above the contents, and the neck. Any hard crystal formations in the form of chips, ice-like structures, crystals, or solid masses; wisp-like structures floating in suspension or an obscure cloudiness are signs that peroxide crystals may have formed. If it appears that crystals have formed anywhere, **DO NOT** unscrew the cap! Likewise, if the container has not been opened for many months, **DO NOT** unscrew the cap! If crystals have formed in the threads (due to solvent evaporating under the cap), the friction of opening it could cause an explosion. Any container of a peroxidizable solvent which shows any signs of crystal formation should be isolated to prevent its being moved or disturbed, and a qualified firm should be called to come and stabilize it for disposal. With proper management and

routine testing of all peroxidizable solvents, this should rarely be necessary.

Solvents in metal cans cannot be visually inspected, and so it is very important to keep their lids sealed tightly and to check them for peroxide accumulation. Non-inhibited solvents should not be purchased in metal cans.

Test Strip Inspection

If no crystal formation is visible, place the container in a fume hood. Wearing goggles, a face shield, heavy oven gloves and a heavy rubber apron, lower the sash as far as possible and carefully unscrew the lid. Test the contents by using peroxide test strips with a range of 0-25 mg/L peroxide, following the package instructions. If the strip indicates near 25 mg/L, retest the solvent by using peroxide test strips with a range of 0-100 mg/L.

Fill the container headspace with nitrogen before re-closing it, to discourage peroxide formation. Mark the test results and the date on the peroxide test label affixed to the container (see example below). If no label is present, apply one. The result should also be posted into the department's chemical inventory.

Peroxide Conc.	Date
_____	_____
_____	_____

If peroxide was detected at less than 5 mg/L, the container can go back into storage but should be used up as soon as possible. If it is not likely to be used within the next 3 months, it should be disposed of.

If the result showed more than 5 mg/L of peroxide, the container should be stabilized, stored isolated and disposed of as soon as feasible. Consult with hazardous materials disposal reference books (available in the Chemical Hygiene Officer's office) for stabilization procedures. If the container results show more than 100 mg/L peroxide, one should consult with a firm that specializes in peroxide stabilization to determine if their expertise should be hired to safely handle and stabilize the container for disposal. Check with disposal firm to see if they will accept solvents whose testing results show peroxides are present.

Since testing peroxide forming solvents with test strips further exposes the chemical to oxygen and poses a certain risk to the tester it is best to control peroxide formers through rigid

inventory management. Only what is needed should be ordered and leftover should be promptly disposed of or used up.

SPECIFIC CHEMICALS

Potassium Metal

Potassium metal is stored under oil or kerosene to exclude water and air. Visually inspect the chunks, looking for any whitish or yellow coating of potassium superoxide on the surface. The darker yellow this layer is, the higher the peroxide concentration. Disturbing the peroxide layer by cutting through it or trying to scrape it off can result in violent explosion. Any potassium metal with a yellow coating should be handled as hazardous waste -- see discussion above. Oxide-coated potassium sticks may need to be stabilized by a qualified firm before disposal.

Sodium azide

Sodium azide, which presents an extremely high toxic risk, is not inherently unstable but may form highly explosive heavy metal azides if contaminated or used improperly. Disposal of sodium azide solutions to the sewer may cause the formation of lead or copper azide in plumbing pipes. Serious explosions can result. Care should also be taken that sodium azide is not heated rapidly or stored in containers with metal components (caps).

Perchlorates

Perchlorates should be avoided as much as possible. Perchlorate salts of organic, organometallic and inorganic cations are potentially explosive and can be set off by either heating or shock. Any metal perchlorate salts must be stored in containers that do not have metal components (caps). Contact of boiling undiluted perchloric acid or the hot vapor with organic matter or even easily oxidized inorganic matter will lead to serious explosions. This includes wood or other absorbent materials, which may become highly flammable after absorbing perchloric acid liquid or vapors. Perchloric acid evaporations must only be done in hoods connected to ductwork systems that have special wash-down provisions, and which are washed down after perchloric evaporations are done. (At present, Whitworth University does not have such a system.)

Current Perchlorate Inventory: (4/21/15)

Bar code	Name	CAS#	Location	Amount on hand	Last checked out
WHIT-01232	Sodium perchlorate	7791-07-3	129B 12/L	200g	Never

	monohydrate				
00745	Magnesium perchlorate anhydrous	10034-81-8	330 19/3/D	0.875lb	Never
00746	Potassium perchlorate	7778-74-7	330 19/4/A	0.8lb	1/15/15
05712	Potassium perchlorate	7778-74-7	330 19/4/A	23 vials	Never
05513	Silver perchlorate	7783-93-9	330 19/2/B	25grams	Never
00748	Sodium perchlorate	7601-89-0	330 19/4/I	0.86kg	2/17/08
05719	Sodium perchlorate	7601-89-0	330 19/4/I	1lb	Never

Halogenated compounds

Halogenated compounds such as chloroform, carbon tetrachloride, methylene chloride and other halogenated solvents should not be dried with sodium, potassium or other active metal; violent explosions usually result.

REFERENCES

Other reactive or explosive hazards are described on pages 96-104 of *Prudent Practices in the Laboratory*, The National Academies Press: 2011 and in L. Bretherick's *Handbook of Reactive Chemical Hazards*, Billing & Sons Ltd: Guildford and London, 1979. There is a copy of each of these available in the Chemical Hygiene Officer's office.

REVIEW

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