General Services – Environmental Health and Safety

Peroxide Forming Chemical Management Plan

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1. Overview

Peroxide-forming chemicals are a class of compounds that have the ability to form shock-sensitive explosive peroxide crystals. Many of the organic solvents commonly used Pace University laboratories have the potential to form explosive peroxide crystals. Diethyl ether and tetrahydrofuran are two of the more common peroxide-forming chemicals used at Pace. Therefore, it is extremely important that this plan be followed regarding the identification, handling, storage, and disposal of peroxide-forming chemicals.

Under normal storage conditions, the materials listed in this document have the potential to generate and accumulate peroxide crystal formations, which may violently detonate when subjected to thermal or mechanical shock. Peroxide-forming chemicals react with oxygen—even at low concentrations to form peroxy compounds. The risk associated with peroxide formation increases if the peroxide crystallizes or becomes concentrated by evaporation or distillation. Factors that affect rate of peroxide formation include exposure to air, light and heat, moisture, and contamination from metals.

****Peroxide crystals may form on the container plug or the threads of the lid and detonate when the lid is twisted. Do not open a liquid organic peroxide or peroxide-forming chemical if crystals or a precipitate are present. ****

2. Applicability

This plan applies to all Pace University Faculty and Staff involved in the ordering, storage, or use of laboratory chemicals and reagents.

3. Definitions

A peroxide is a chemical that contains an oxygen-oxygen single bond or a peroxo (-O-O-) unit, one that has the chemical formula of O_2^{2-}.

4. Responsibilities

Environmental Health and Safety (EH&S) provides technical assistance to lab personnel about the safe handling, storage and disposal of peroxide-forming chemicals and training as needed.

Lab personnel ensure that peroxide-forming chemicals are properly managed and disposed in accordance with this Plan.

5. Procedures

1. Purchasing Considerations
    a. When possible, purchase only peroxide-forming chemicals that contain a peroxide inhibitor (i.e. tetrahydrofuran or diethyl ether inhibited with butylated hydrotoluene (BHT)).

b. Only purchase quantities of peroxide-forming chemicals that you expect to use within expiration and disposal timeframes.

2. Labeling Requirements
    a. All bottles of peroxide-forming chemicals must be marked with the date received.
    b. When the bottle is first opened, the container must be marked with the date opened.
    c. If a bottle is tested for peroxides, the container must be marked with the test date.
        i. A Sample label is found in Appendix A.
3. Storage and Use Requirements
    a. Do not store peroxide-forming chemicals in direct sunlight, as light can accelerate the chemical reactions that form peroxides.
    b. If the peroxide-forming chemical is flammable and requires refrigeration, an explosion-proof refrigerator must be used.
    c. Do not distill, evaporate or concentrate a peroxide-forming chemical until you have first tested it for the presence of peroxides (peroxides are usually less volatile than their parent material and will tend to concentrate in the hot distillation pot).
    d. NEVER, UNDER ANY CIRCUMSTANCES, touch or attempt to open a container of a peroxide-forming liquid if there are whitish crystals around the cap and/or in the bottle. The friction of screwing the cap may detonate the bottle. If you encounter such a bottle, contact EH&S (914-923-2818) immediately for removal. DO NOT TOUCH OR MOVE THE SUSPECT BOTTLE YOURSELF FOR ANY REASON.
4. Disposal Requirements
    a. There are four classes of peroxide-forming chemicals based upon the peroxide formation hazard:
        i. Class A – Severe Peroxide Hazard
        ii. Class B – Concentration Hazard
        iii. Class C – Shock and Heat Sensitive
        iv. Class D – Potential Peroxide-Forming Chemicals
    b. Peroxide-forming chemicals must be disposed within the timeframes specified in the table in Appendix B, regardless of whether or not the container has been opened. Disposal with a Hazardous Waste Vendor must occur within the timeframe allowed once the container is received or opened, whichever is earlier. NOTE: If the peroxide-forming chemical has a visible peroxide formation or is greater than a year old, contact EHS and your hazardous waste vendor immediately. Do not move or handle these containers.

Appendix A: Sample Sticker

Peroxide-Forming Material

This chemical to be either:

A. Disposed of or tested for peroxides with 6 months of opening, or-

B. If tested and deemed safe for continued use, dispose within 6 months of test date.

Note: Manufacturer Expiration dates must me observed.

Date Received: _____

Date Opened: _____

Date Tested: _____

Appendix B: Peroxide Forming Chemical Testing & Disposal Timelines

	Class A	Class B	Class C	Class D
Date Opened	3 Months	6 Months	6 Months	Only if peroxide crystals are present.
Date Received	1 Year	1 Year	1 Year	

Appendix C: Peroxide Forming Chemical List

The list below gives examples of peroxide-forming materials by Class. Materials listed are samples of Class A, B, C and D peroxide-forming materials, but are not all-inclusive.

Class A – Severe Peroxide Hazard
Spontaneously Decpmpose and become explosive with exposure to air without concentration.

- Butadiene (liquid monomer)
- Isopropyl ether
- Sodium amide (sodamide)
- Chloroprene (liquid monomer)
- Potassium amide
- Tetrafluoroethylene (liquid monomer)
- Divinyl acetylene
- Potassium metal
- Vinylidene chloride

Class B – Concentration Hazard
Require external energy for spontaneous decomposition. Form explosive peroxides when distilled, evaporated or otherwise concentrated.

- Acetal
- Acetaldehyde
- Acrylonitrile
- Benzyl alcohol
- Cumene
- Cyclohexanol
- Chlorotrifluoroethylene
- Chloroprene
- Cyclohexene
- Decahydronaphthalene
- Diacetylene
- Dicyclopentadiene
- Diethyl ether
- Diethylene glycol dimethyl ether (diglyme)
- Dioxanes
- Ethylene glycol dimethyl ether (glyme)
- Furan
- Methyl isobutyl ketone
- Methylacetylene
- Methylcyclopentane
- Methyl methacrylate
- Other secondary alcohols
- Tetrahydrofuran
- Tetrahydronaphthalene
- Vinyl ethers
- 1-Phenylethanol
- 2-Butanol
- 2-Cyclohexen-1-ol
- 2-Hexanol
- 2-Pentanol
- 2-Phenylethanol
- 3-Methyl-1-butanol
- 4-Heptanol
- 4-Methyl-2-pentanol
- 4-Penten-1-ol

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.

- Acrylic acid
- Chlorotrifluoroethylene
- Vinyl acetate
- Acrylonitrile
- Methyl methacrylate
- Vinylacetylene (gas)

- Butadiene (gas)
- Styrene Vinylpyridine
- Vinyladiene chloride
- Chloroprene
- Tetrafluoroethylene (gas)
- Vinyl chloride (gas)

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-napthyl 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
- 3-Methoxyethyl acetate
- Bis(2-chloroethyl) ether
- Diethylketene
- 2-Methoxyethyl vinyl ether
- Bis(2-ethoxyethyl) adipate
- Diethoxybenzene (m-,o-,p-)
- Methoxy-1,3,5,7-cyclooctatetraene
- Bis(2-methoxyethyl) carbonate
- 1,2-Diethoxyethane
- b-Methoxypropionitrile
- Bis(2-methoxyethyl) ether
- Dimethoxymethane
- m-Nitrophenetole
- Bis(2-methoxyethyl) phthalate
- 1,1-Dimethoxyethane
- 1-Octene
- Bis(2-methoxymethyl) adipate
- Di(1-propynl) ether
- Oxybis(2-ethyl acetate)
- Bis(2-n-butoxyethyl) phthalate
- Di(2-propynl) ether
- Oxybis(2-ethyl benzoate)
- Bis(2-phenoxyethyl) ether
- Di-n-propoxymethane
- b,b-Oxydipropionitrile
- Bis(4-chlorobutyl) ether
- 1,2-Epoxy-3-isopropoxypropane
- 1-Pentene
- Bis(chloromethyl) ether
- 1,2-Epoxy-3-phenoxypropane
- Phenoxyacetyl chloride
- 2-Bromomethyl ethyl ether

- p-Ethoxyacetophenone
- a-Phenoxypropionyl chloride
- beta-Bromophenetole
- 1-(2-Ethoxyethoxy)ethyl acetate
- Phenyl-o-propyl ether
- o-Bromophenetole
- 2-Ethoxyethyl acetate
- p-Phenylphenetone
- p-Bromophenetole
- (2-Ethoxyethyl)-a-benzoyl benzoate
- n-Propyl ether
- 3-Bromopropyl phenyl ether
- 1-Ethoxynaphthalene
- n-Propyl isopropyl ether
- tert-Butyl methyl ether
- o,p-Ethoxyphenyl isocyanate
- Sodium 8-11-14-eicosatetraenoate
- n-Butyl phenyl ether
- 1-Ethoxy-2-propyne
- Sodium ethoxyacetylide
- n-Butyl vinyl ether
- 3-Ethoxypropionitrile
- Tetrahydropyran
- Chloroacetaldehyde diethylacetal
- 2-Ethylacrylaldehyde oxime
- Triethylene glycol diacetate
- 2-Chlorobutadiene
- 2-Ethylbutanol
- Triethylene glycol dipropionate
- 1-(2-Chloroethoxy)-2-phenoxyethane
- Ethyl-b-ethoxypropionate
- 1,3,3-Trimethoxypropene
- Chloroethylene
- Ethylene glycol monomethyl ether
- 1,1,2,3-Tetrachloro-1,3-butadiene
- Chloromethyl methyl ether
- 2-Ethylhexanal
- 4-Vinyl cyclohexene
- beta-Chlorophenetole
- Ethyl vinyl ether
- Vinylene carbonate
- o-Chorophenol
- 2,5-Hexadiyn-1-ol

Appendix D: References

National Safety Council: Data Sheet I-655 Rev. 87
NFPA: NFPA 432, Code for the Storage of Organic Peroxide Formulations
FDNY: New York City Fire Code