Environmental Health & Safety
Peroxide-Forming Chemicals – Safety Guidelines

What is a Peroxide-Forming Chemical (PFC)?

Many organic solvents are peroxide formers, meaning they can slowly form unstable peroxides and hydroperoxides over time through auto-oxidation. While some of these solvents contain inhibitors to slow this process, peroxides can still accumulate under normal storage conditions. Peroxides are highly unstable and can cause serious injuries or fatalities due to their potential for violent explosions when exposed to light, heat, friction, or mechanical shock. In addition to the peroxide risk, peroxide-forming chemicals may present other hazards when initially supplied by manufacturers. Many common laboratory solvents are peroxide formers.

Common peroxide-forming compounds include: ethers (especially cyclic ethers and those with primary/secondary alkyl groups), acetals, ketals, aldehydes (such as acetaldehyde and benzaldehyde), and compounds with hydrogen atoms that can form stable radicals, such as benzylic and allylic hydrogens. Ethers, in particular, are the most notorious peroxide formers, commonly used in research and teaching. Other potential peroxide formers include alkylarenes with tertiary α-hydrogens, alkenes, vinyl compounds, dienes, ketones, amides, lactams, ureas, and secondary alcohols. The absence of inhibitors or stabilizers (e.g., BHT) can accelerate peroxide formation.

PLEASE NOTE: 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.

Classes of Peroxide-Forming Chemicals

Peroxide-forming chemicals (PFCs) are divided into four classes (A-D) which all have different testing and disposal requirements. A list of peroxide formers can be found in Appendix A.

Class A: Severe Peroxide Hazard

Spontaneously decompose and become explosive with exposure to air without concentration. These are the most hazardous and can form explosive peroxide levels even if not opened.

Test for peroxide formation before all procedures and discard within 3 months of receipt, even if unopened.

Class B: Concentration Hazard

Chemicals that form explosive levels of peroxides after concentration. Require external energy for spontaneous decomposition. Form explosive peroxides when distilled, evaporated or otherwise concentrated.

Test for peroxide formation before high-hazard procedures and at least every 6 months after opening. Dispose of by the expiration date or after 12 months unless testing indicates no peroxides present.

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. These materials are typically stored with polymerization inhibitors to prevent the polymerization reactions.

Test for peroxide formation before high-hazard procedures and at least every 6 months after opening. Dispose of by the expiration date or after 12 months unless testing indicates no peroxides present.

Class D: Miscellaneous Peroxide Hazard

Chemicals that may form peroxides but cannot clearly be placed in Classes A through C.

Test for peroxide formation before high-hazard procedures and at least every 12 months after opening.

Handling and Storage Guidelines

Proper storage and handling of PFCs will significantly reduce associated risks. Consider any container as open if you are uncertain. In all cases, EHS requires prompt disposal of any peroxide forming chemical that is past the manufacturer's expiration date.

- **Labeling and Storage**: Always label PFCs with dates received, opened, and tested (if applicable). Store in air-tight, light-resistant containers (preferably amber), away from heat, sunlight, and sources of ignition. Do not store at or below the temperature at which the chemical freezes or precipitates. Minimize quantities to the amount needed for immediate use and avoid open or partially empty containers.
- **Inhibitors and Stabilizers**: Purchase PFCs with inhibitors or stabilizers added. Do not store redistilled or unstabilized chemicals, as they are more prone to peroxide formation. If possible, store under inert gas (e.g., nitrogen) to reduce and slow peroxide formation.
- **Handling and Distillation**: Never distill PFCs to dryness; leave at least 10-20% residual still bottoms. Always test for peroxides before distillation or evaporation, especially for unstabilized PFCs. Use polyethylene containers and non-metal spatulas to avoid contamination and impact that could trigger explosive reactions.
- **Disposal and Expiration**: Dispose of PFCs in the appropriate time frame and in accordance with TCU's disposal procedures: three months (Class A), one year (Classes B & C), or the manufacturer's expiration date. Dispose of PFCs with peroxide concentrations >100 ppm immediately as hazardous waste. Never pour peroxides down the drain.
- **Monitoring**: Regularly check for peroxide formation. Signs such as suspended whisp-like structures in clear liquid, appearance of cloudiness, visible discoloration, gross contamination, or precipitated crystal formation appearing as chips, ice-like structures, or solid mass (within the chemical or around rim of cap) indicate the presence of shock-sensitive peroxides. In such cases, do not move the container and contact EHS immediately at safety@tcu.edu.

Testing for Peroxides

Laboratories must test Class B and C peroxide-forming chemicals (PFCs) at least every six months after opening, and also before distillation or evaporation. If you cannot test for peroxides, the chemicals must be discarded according to TCU's disposal procedures. Any detectable level of peroxides is unsafe, and contaminated chemicals must be disposed of, regardless of peroxide concentration.

Peroxide testing strips provide the highest sensitivity and the most accurate quantification of peroxide concentration for routine testing. They are easier, faster, and safer to use than other methods and detect a wider range of peroxides. Peroxide testing strips must be stored in accordance with manufacturer recommendations, as they have a limited shelf life. For additional guidance regarding purchasing or testing procedures, please contact EHS at safety@tcu.edu.

Applicability

All researchers working with peroxide-forming chemicals must follow these general guidelines and are encouraged to reference chemical-specific guidelines, maintain a standard operating procedure (SOP), and consult EHS with any questions before starting work. This applies to all personnel involved in ordering, storing, or using chemicals with peroxide-forming hazards.

Precautions and Reminders

- Review this entire guidance document prior to starting work with any peroxide forming chemicals.
- Verify the chemical being ordered contains inhibitors and is shipped under inert gas. Unless absolutely necessary for the research, labs should never purchase uninhibited peroxide formers.
- Evaluate the potential hazards that could arise from use of peroxide formers, ensure that you and anyone else working on the procedure understand the safe processes to follow, is using the proper PPE, and is familiar with the emergency equipment in the area.
- Always read the Safety Data Sheet (SDS) for the specific chemical. Review Sections 2.3 (Hazards not otherwise classified), 7 (Handling & Storage), and 10 (Stability & Reactivity) of the SDS for incompatible chemicals.
- Never work alone while handling possible peroxide forming chemicals.
- Ensure that peroxide forming chemicals are stored and labeled properly, to track the date the material was received, opened, will expire, and prior peroxide testing.
- Inspect peroxide formers for visual signs of crystallization prior to handling, Test with an appropriate test strip prior to starting work.
- Notify EHS at safety@tcu.edu if material tests positive so that arrangements for safe collection and disposal of the chemical can be made.
- Never distill to dryness.
- Properly collect any chemical waste following chemical waste collection and labeling procedures.

APPENDIX A – Classification List of Peroxide-Forming Chemicals

Class A: Severe Peroxide Hazard

Spontaneously decompose and become explosive with exposure to air without concentration. These are the most hazardous and can form explosive peroxide levels even if not opened.

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

Class B: Concentration Hazard

Chemicals that form explosive levels of peroxides after concentration. Require external energy for spontaneous decomposition. Form explosive peroxides when distilled, evaporated or otherwise concentrated.

Acetal (1,1-diethoxyethane)	Diethylene glycol dimethyl ether (diglyme)	4-Mehtyl-2-pentanol
Acetaldehyde	Diethyl ether (ether)	2-Pentanol
Benzyl alcohol	Dioxanes	4-Penten-1-ol
2-Butanol	Ethylene glycol dimethyl ether (glyme)	1-Phenylethanol
Cumene	Furan	2-Phenylethanol
Cyclohexanol	4-Heptanol	2-Propanol
2-Cyclohexen-1-ol	2-Hexanol	Tetrahydrofuran (THF)
Cyclohexene	Methylacetylene (gas)	Tetrahydronaphthalene (tetralin)
Decahydronaphthalene (decalin)	3-Methyl-1-butanol	Vinyl ethers
Diacetylene (butadiene, gas)	Methyl cyclopentane	Other secondary alcohols
Dicyclopentadiene	Methyl isobutyl ketone	

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. These materials are typically stored with polymerization inhibitors to prevent the polymerization reactions.

Acrylic acid	Chlorotrifluoroethylene (gas)	Vinylacetylene (gas)
Acrylonitrile	Methyl methacrylate	Vinyladiene chloride
Butadiene (gas)	Styrene	Vinyl chloride (gas)
Chlorobutadiene	Tetrafluoroethylene (gas)	Vinyl pyridine
Chloroprene	Vinyl acetate	

Class D: Miscellaneous Peroxide Hazard

Chemicals that may form peroxides but cannot clearly be placed in Classes A through 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

References

Harvard – EHS –Peroxide Forming Chemicals
Millipore-Sigma – Peroxide Forming Solvents
Stanford – EHS - Peroxide Forming Compounds
University of Texas – EHS – Peroxide Forming Chemicals
UC Santa Cruz – EHS – List of Peroxide Forming Chemicals
UNT – Risk Management – Peroxide Forming Compounds
Weill Cornell Medicine – EHS – Peroxide-Forming Chemicals
Yale – EHS – Peroxide Forming Chemicals