Peroxide-Forming Chemicals

1. Purpose / Background

Peroxide-forming chemicals include many common solvents and reagents that are known to form organic peroxides on exposure to air and light, e.g. tetrahydrofuran, ethers, isopropanol, dioxanes, styrene, 2-hexanol, etc). The relatively weak oxygen-oxygen bond is the characteristic structure of organic and inorganic peroxides molecules and is the basis for their reactivity and tendency for spontaneous decomposition. A combination of factors, including the rate of peroxidation, the maximum peroxide concentration, volatility of the parent compound, and reactivity of the peroxides formed, determines the actual risk. Peroxides are very sensitive to shock, sparks, elevated temperatures, light, strong oxidizing and reducing agents, and friction, such as a cap being twisted open.

Peroxide-forming chemicals are classified in groups depending on their ability to form peroxides (see Appendix B for more information).

Peroxidation Potentials

- **Chemical structures:**
  - Peroxide-forming chemicals invariably contain an auto oxidizable hydrogen atom that is activated by adjacent structural components
  - Appendix A shows peroxidization moieties in order of decreasing hazard.
  - The risk of hazardous peroxidation generally decreases as the molecular weight of the compound increases. Ten or more carbon atoms at a peroxidizable site are considered low risk.

- **Storage conditions:**
  - Peroxidation may be accelerated by exposure to heat, light, and oxygen or air. Storing chemicals in open, partially empty or transparent containers and at elevated temperature may promote peroxidation.
  - Exposure of susceptible compounds to oxygen always enhances peroxide formation, whereas the effects of heat, light and contaminants are variable and unpredictable.
  - Ultraviolet light, including sunlight, promotes both autooxidation and depletion of inhibitors.

- **Concentration by evaporation or distillation:**
  - Distillation, evaporation, or other concentration of some peroxide-forming chemicals can present a high risk of explosion.
    - Distillation of chemical removes stabilizers or inhibitors.

        - Peroxides are less volatile than the parent compound, and thus they concentrate as the parent compound evaporates.
    - Chemicals fall into Group B (see Appendix B) do not usually accumulate potentially explosives concentrations unless the volatile organic material is reduced in volume e.g. evaporation and distillation of diethyl ether, tetrahydrofuran, cyclohexane, glycol ethers and isopropanol.
    - Most of the solvents in Group B are also volatile so that repeated opening of a container may allow enough evaporation and exposure to atmospheric oxygen to concentrate peroxides to a dangerous level.

- **Inhibitors:**
    - Peroxide-forming chemicals may be inhibited or uninhibited (this will likely be indicated on the chemical container).
    - Inhibition slows but does not eliminate peroxide formation. Inhibitors are depleted as peroxides are formed and degraded. Eventually, the inhibitor is totally depleted, and the peroxide-forming chemical will act as an uninhibited chemical. This may result in the rapid accumulation of peroxides in a chemical that has been stable for a long time.
    - An inhibitor such as hydroquinone, 2,6-di-tert-butyl-p-methylphenol (BHT), diphenylamine, or a similar compound is added to the chemical in trace quantities.
    - Use and storage under an inert atmosphere greatly reduces peroxidation in most cases. Phenolic compounds are often added to commercial vinyl monomers, which are ineffective if some oxygen is not present; thus, these inhibited chemicals should not be stored under inert gas.
    - Diethyl ether should be stored in steel containers because the iron tends to reduce peroxides. However, iron and other metals are not known to be effective for other chemicals.

2. Scope

This Standard Operating Procedure (SOP) provides information and procedures to assure that peroxide-forming chemicals are used, stored, and disposed of safely. If the PI determines that a material-specific and experiment-specific SOP for their work with peroxide-formers is warranted, this SOP can be used as a guideline.

3. Prerequisites

Laboratories working with peroxide-forming chemicals must have a Chemical Hygiene Plan. Shops working with peroxide-forming chemicals must have a Hazard Communication Program.

4. Procedures

4.1 Before Purchase

- **Information**: Read this SOP and safety data sheet (SDS) for all peroxide-forming chemicals being used. Due to the severe potential hazards of peroxide-forming chemicals, carefully review the handling and storage procedures and become familiar with the chemical and physical properties of each chemical before beginning work. Always review the incompatibility with other substances and the conditions to which the chemicals are sensitive. Always read the manufacturers' recommendations contained in supplementary documents, such as technical bulletins. Contact the EHS Office to review new uses of peroxide-forming chemicals.

- **Identification of Peroxide Groups:** Appendix B lists some peroxide-forming chemicals in the following groups:
    - Group A chemicals can form explosive levels of peroxides without concentration. Some of these chemicals may form explosive concentrations even if never opened.
    - Group B chemicals do not usually accumulate potentially explosives concentrations unless the volatile organic material is reduced in volume e.g. evaporation and distillation.
    - Group C chemicals may autopolymerize as a result of peroxide formation.
    - Group D chemicals may form peroxides, but these chemicals are not well characterized.

  Depending on which group that peroxide-forming chemical falls in, it determines the safe storage periods (Appendix C) and testing frequency (Appendix D).

  (Source: Kelly, Richard J., Chemical Health & Safety, American Chemical Society, 1996, Sept, 28-36). These lists are illustrative, not exhaustive.

- **Engineering Controls:** Peroxide-forming chemicals should be used in a chemical fume hood with the sash as low as feasible.

- **Standard Operating Procedure (SOP)**: A laboratory-specific SOP may be warranted for some peroxide-forming chemicals. See the Chemical Hygiene Plan for a recommended SOP format.

- **Training**: Anyone using peroxide-forming chemicals should have adequate training and knowledge of their hazards and of the practices and procedures for working with them safely. See Section 6 for detailed training requirements. Appendix D provides some of the main guidelines for safe handling and disposal of peroxide-forming chemicals.

- **Purchasing:**
    - Determine amount you need and check inventory before ordering. Minimize the amount purchased at one time and purchase just before

use. Purchase only an amount that will be used up within the safe storage time periods provided in Appendix C.
  - Always purchase with an inhibitor if available unless your specific experiment will not tolerate the inhibitor molecule.
  - Purchase peroxide test strips as well.

- **Personal Protective Equipment**: Wear gloves, lab coat, and eye protection when using peroxide-forming chemicals.

4.2 Upon Receiving Chemical

- **Labeling:** Check for manufacturer's expiration date & inhibitor info on the container. Label all containers with the date received, the date opened and assign an expiration date if one is not supplied by the manufacturer and update as necessary. Affixing a label stating "Peroxide-Forming Compound" with test dates and results to alert others is recommended. You may obtain peroxide-forming chemicals stickers from the EHS Office at https://ehs.mit.edu/campus-services-program/order-signs-stickers/.

- **Regular check-ins:**
  - Assign responsible person to periodically check the receipt, opened, and expiration dates.
  - If your lab has an up-to-date chemical inventory with CAS numbers in the EHS Office-supported inventory system (EHS Assistant), there is a filter you can run to extract peroxide forming chemicals inventory. You can also indicate expiration dates and the system can highlight expired chemicals.

- **Storage:**
  - Storing peroxide-forming chemicals should be part of a comprehensive chemical storage plan that is outlined in the Chemical Storage SOP. The SDS for each material should be read to determine specific storage recommendations or special storage conditions.
  - Although the autoxidation reaction is a relatively slow process (months to years), extended storage provides time for accumulation of unstable products. **Recommended safe storage periods** for peroxide forming chemicals are provided in Appendix C.
  - Storage of peroxide forming chemicals in open, partially empty or transparent containers greatly increases the risk of peroxide formation. Store away from light and heat**. Protect from light with amber bottles.**
  - Protect from heat, light, friction, static discharge, mechanical shock, contact with a catalyst, physical damage or other conditions listed in the SDS that the compound may be sensitive to.
  - Store peroxide-forming chemicals in a flammable cabinet and date the bottle upon receipt and when opened.

- Regularly inventory and monitor the container dates and avoid keeping peroxide-forming chemicals longer than the recommended safe storage periods listed in Appendix B.
- If these chemicals need to be stored at cool temperatures, the lab must use laboratory safe (flammable safe) refrigerators.
- Refrigeration of volatile peroxide is a double-edge sword. In some cases, it slows oxidation. However, peroxide accumulation may actually be enhanced by refrigeration, as the rate of peroxide degradation is slowed more than is the rate of peroxide formation. Excess cooling, approaching the freezing point of the chemical may case the precipitation of peroxides from solution, which makes the container very shock sensitive and dangerous.
- Do not return unused peroxide-forming chemicals to their original containers.

- **Usage:**
  - DO NOT OPEN containers of peroxide-forming chemicals that have obvious precipitation or crystals around the lid, visible discoloration, multiple layers, or stratification. If any of the above changes are noted, treat the chemical as explosive and call the EHS Office 617-452-3477 immediately.
  - Mixing with other chemicals in experiments should be carefully planned and the potential consequences should be evaluated. An SOP for the experiment may be necessary, as noted above. Safety precautions appropriate to what is expected should be taken.
  - Do not use metal spatulas to handle peroxides.
  - **Gases:** Peroxidizable pressured gases such as butadiene, tetrafluoroethylene, vinyl acetate and vinyl chloride should be relatively resistant to autoxidation in manufacturer's cylinders. When transferring to another container in labs, an inhibitor should be placed in receiving vessel. The hazard of peroxide may become much greater if these gases are condensed inside the cylinder or secondary vessel.

- **Distillation or Evaporation:**
  - The autoxidation products are less volatile than the parent compound, and therefore become extremely hazardous when evaporation concentrates the unstable autoxidation products to increasingly dangerous levels.
  - **Test for peroxides before distilling or evaporating peroxide-forming chemicals.** Do not distill without treating to remove peroxides. Any distillation operation using peroxide formers should leave at least 10% liquid at the bottom of the flask. During distillation, the solution must be stirred with a magnetic stirrer or an inert gas bleed.

- **Uninhibited Group A and B chemicals**: Can be extremely dangerous to distill or significantly concentrate unless known to be free of peroxidation products.
- **Uninhibited Group C chemicals**: Should not be distilled. It is important to add a suitable polymerization inhibitor prior to distilling or concentrating.

- **2-Propanol (Isopropanol / IPA):**
  - 2-Propanol is a common solvent in labs, yet awareness around its classification as a Group B peroxide-forming chemical is lacking. There have been several reports of explosions occurring during the distillation of 2-propanol that have resulted in injury to researchers in other institutions.
  - Peroxide formation in 2-propanol depends on storage conditions. Here are the summary findings on a study of peroxide formation in 2-propanol that stored in different types bottles in a hood with constant light for 6 months:
    - Colorless glass media bottle - generate peroxides after a few days and had the highest level of peroxides
    - Semi-opaque white plastic commercial bottle and squirt bottles – significant amounts of peroxides
    - Amber commercial bottle and media bottle – trace amounts of peroxide
  - Recommend to store 2-propanol in a flammable cabinet when not in use. Store in amber bottle if you need to keep 2-propanol on bench and in hood.
  - 2-Propanol is not readily available with inhibitors. Follow the storage and testing frequency for Uninhibited Group B in Appendix D.
    - After safe storage period, it requires more frequent testing (every 3 months and before each use).
    - When it is stored in dark and closed container, test every 12 months

  (Source: Cismesia, M.A, Reconsidering the Safety Hazards Associated with Peroxide Formation in 2-Propanol, Organic Process Research & Development, 2022, 1558-1561.)

4.3 Testing

- **Before distilling or evaporating:** Test for peroxides before distilling or evaporating peroxide-forming chemicals.

- **Periodic testing:** Peroxide levels must **never be allowed to exceed 20 parts-per-million (ppm)**. To ensure that the 20-ppm peroxide level is not exceeded, testing for peroxides according to the frequency specified in Appendix D.

- **Testing procedures:** The easiest way to test for peroxides is to use peroxide test strips that are a semi-quantitative colorimetric method. Read and follow manufacturer's instructions to use peroxide test strips. Here are the generic steps:
  - Dip the test strips into the test solution.
  - Shake off excess liquid.
  - Wait for a while before comparing test field with the color scale.
  - Take the value which matches closest with the colored test field.
  - **To test for hydroperoxides in organic solvents, the test zone is wetted with one drop of water after evaporation of the solvent.**

- **Records:** Records of the testing date and results should be maintained and also recorded on the label. Write down the test date and results on the bottle. You may obtain peroxide-forming chemicals stickers from the EHS Office at https://ehs.mit.edu/campus-services-program/order-signs-stickers/.

- **Actions:**
  - Less than 20 ppm: You may keep the chemical until its safe storage period and continue testing periodically according to the frequency specified in Appendix D.
    - Uninhibited Group A, C and D chemicals: Must dispose by recommended safe storage periods.
    - Uninhibited Group B and D chemicals: If plan to store after safe storage period, test quarterly and before each use. Dispose immediately when approaching 20 ppm.
    - Inhibited Group B and D chemicals: If plan to store after safe storage period, test every 6 months and before each use. Dispose immediately when approaching 20 ppm.
  - Approaching 20 ppm: Dispose immediately. Place red tag on container, indicate peroxide levels, and request disposal.
  - More than 20 ppm: Contact EHS immediately.

- **For peroxide-forming chemicals with visible crystallization or solids formed inside or at the cap, do not test! Contact the EHS Office 617-452-3477 to evaluate the container.**
  - Any peroxidizable chemicals or containers with visible discoloration, crystallization, or liquid stratification should be treated as potentially explosive.
  - When chemicals are dispensed from screw cap bottles, some of the liquid may remain on the threads and cap. The liquid evaporates, leaving pure peroxides in the threads of the cap. Unscrewing the cap may initiate an explosion.

4.4 Disposal

- Avoid mixing peroxide-forming hazardous waste with other hazardous wastes.
- Immediately rinse empty containers of peroxide-forming chemicals. Do not let residues evaporate.
- Any chemical waste streams with concentrations of >25% peroxide-forming chemicals must be tested by the lab and levels indicated on the red hazardous waste label.
- Peroxide-forming chemical bottles without received, open or manufacturers expiration dates will need to be tested by the lab prior to disposal, again unless there is visible peroxide formation, at which point EHS should be contacted.
- Chemicals with organic peroxide levels higher than 20 ppm cannot be transported by our waste disposal vendor over public roadways. Therefore, material with greater than 20 ppm must undergo specialized treatment by professionals following strict safety procedures before it can be disposed. The DLC will bear this cost which can be up to $2000. If you have a chemical with peroxide levels above 20 ppm, then call the EHS to have the material removed and treated.

4.5 General Emergency Procedures

Plan ahead for possible emergencies involving peroxide-forming chemicals.

- All personnel who work in areas where there is the potential for an explosion should be trained in how to respond to an explosion emergency.
- Prior to using peroxide-forming chemicals, consult the SDS for the appropriate clean-up supplies and ensure that they are readily available. Spill control materials are designed to be inert and un-reactive with the reagent.
- Notify people in the area if a spill occurs. For a large spill, turn off sources of ignition and vacate the lab immediately. Dial 100 for emergency assistance. (Off campus, dial 617-253-1212).
- In case of fire or explosion, activate the fire alarm and dial 100 or 617-253-1212 from a safe location.

5. Roles & Responsibilities

5.1 The EHS Office is responsible for:

- Providing General Chemical Hygiene Training (web-based or classroom) and Hazard Communication Training that includes information on chemical hazards.
- Maintaining up-to-date guidance pertaining to peroxide-forming chemicals.
- Reviewing SOP's and new uses of peroxide-forming chemicals.
- Addressing questions or concerns pertaining to peroxide-forming chemicals.
- Assisting with inspections of use and storage areas for peroxide-forming chemicals.

5.2 PIs/Supervisors are responsible for:

- Evaluating the need for SOPs for peroxide-forming chemicals that are specific to the laboratory.
- Ensuring that those individuals that they supervise who work with peroxide-forming chemicals receive adequate training (see Section 6.0 for training requirements.)
- Ensuring that peroxide-forming chemicals are used and stored safely in the laboratory/work areas that they supervise.
- Ensuring peroxide-forming chemicals are used and stored in the smallest quantities necessary in the work areas that they supervise.
- Ensuring appropriate PPE is available for work with peroxide-forming chemicals.

5.3 The DLC EHS Coordinator or Chemical Hygiene Officer is responsible for:

- Addressing questions or concerns regarding the use or storage of peroxide-forming chemicals, and consulting with the EHS Office if necessary.
- Inspecting chemical storage areas, including the storage areas of peroxide-forming chemicals, twice a year during Level II inspections and notifying the laboratory personnel and the PI/Supervisor of problems found so that they can be corrected or prevented.

5.4 The EHS Representatives are responsible for:

- Assisting the PI/Supervisors with the safe use and storage of peroxide-forming chemicals in the work area. Specific duties may include periodically inspecting use and storage areas and keeping an inventory of peroxide-forming chemicals.

5.5 Individuals Using Peroxide-forming chemicals are responsible for:

- Knowing and following the peroxide-forming chemicals SOPs established in their laboratory/work area.
- Assuring that they have adequate training.
- Using materials in accordance with training guidance provided, such as SOPs.
- Reporting any incidents, problems or concerns with handling materials to PI.
- Wearing the PPE that is specified.
- Test peroxide-forming chemicals as specified in Section 4.3.

6. Training

All laboratory personnel working with peroxide-forming chemicals must have completed General Chemical Hygiene Training (web-based or classroom) and Lab-Specific Chemical Hygiene Training.

The Lab-Specific Chemical Hygiene Training, performed by a laboratory's PI or EHS Representative, should include the following information if peroxide-forming chemicals are used in the laboratory/work area:

- The hazards and safe use of peroxide-forming chemicals.
- The location and function of specialized equipment needed for the safe use and storage of peroxide-forming chemicals, including details about lab procedures for storage of the chemicals.
- Procedures to be used in case of an emergency with peroxide-forming chemicals.
- The location of SDSs and SOPs for peroxide-forming chemicals.

For non-laboratory personnel that use these chemicals in their work area, the required training is called "Hazard Communication," and it is offered through the EHS Office.

Awareness level training should be given to others who work in areas where peroxide-forming chemicals are present. Laboratories or DLCs desiring additional training for special or unusual applications of peroxide-forming chemicals may contact the EHS Office for help in developing and implementing training specific to their needs.

7. Monitoring Requirements

Work areas where peroxide-forming chemicals are used and stored should be inspected at least twice a year during the Level II Inspections to ensure that they are being used and stored safely and in accordance with the rules established for the area. Peroxide-forming chemicals that are no longer needed, past the safe storage period or contain peroxide more than 20 ppm should be identified and action taken to properly dispose of the chemicals. Contact the EHS Office for assistance as needed.

8. Record Management

The DLC EHS Coordinator and the EHS Office shall maintain records of Level II inspections of storage areas containing peroxide-forming chemicals. All records related to the use and storage of peroxide-forming chemicals should be maintained per the Records Retention SOP.

9. References

9.1. Standards

- OSHA 1910.1450 Occupational Exposure to Hazardous Chemicals in Laboratories
- OSHA 1910.106 Flammable and Combustible Liquids

9.2. Other SOPs

To view the SOPs/SOGs go to https://ehs.mit.edu/sops/ and search for the SOP/SOG listed. MIT Certificates are required to view SOPs/SOGs.

- EHS-0023: Chemical Storage SOP
- EHS-0020: Flammable and Combustible Liquids SOP
- EHS-04-0044: Records Retention SOP

9.3. Supplementary Documents

- MIT Environment, Health and Safety Policy
- MIT Chemical Hygiene Plan Template
- MIT Hazard Communication (HAZCOM) Program

9.4. Helpful Websites

- OSHA Regulations and Technical Manuals: http://www.osha.gov
- Kelly, Richard J., Chemical Health & Safety, American Chemical Society, 1996, Sept, 28-36. https://doi.org/10.1021/acs.chas.8b03515
- Cismesia, M.A, Reconsidering the Safety Hazards Associated with Peroxide Formation in 2-Propanol, Organic Process Research & Development, 2022, 1558-1561. https://doi.org/10.1021/acs.oprd.2c00112

10. Definitions

10.1. **Safety Data Sheet (SDS)** is a written document that outlines health and safety information for a hazardous chemical. An SDS is prepared in accordance with requirements of OSHA 29 CFR 1910.1200 Hazard Communication.

10.2. **Mixture** refers to any combination of two or more chemicals provided that the combination is not, in whole, or part, the result of a chemical reaction.

10.3. **Organic peroxide** is an organic compound that contains the bivalent -O-O- structure and which may be considered to be a structural derivative of hydrogen peroxide where one or both of the hydrogen atoms has been replaced with an organic radical.

10.4. **Unstable (reactive)** refers to a chemical which in the pure state, or as produced or transported will vigorously polymerize, decompose, condense, or will become self-reactive under conditions of shock, pressure, or temperature.

10.5. **Use** refers to packaging, handling, reacting, emitting, generating as a byproduct, or transferring.

11. Appendices

11.1. Appendix A: Peroxidizable Organic Moieties

11.2. Appendix B: Peroxide-Forming Chemicals

11.3. Appendix C: Safe Storage Periods for Peroxide-Forming Chemicals

11.4. Appendix D: Quick Guide for Peroxide-Forming Chemicals

11.5. Appendix E: Example of Peroxide-Forming Chemicals Label

Appendix A: Peroxidizable Organic Moieties

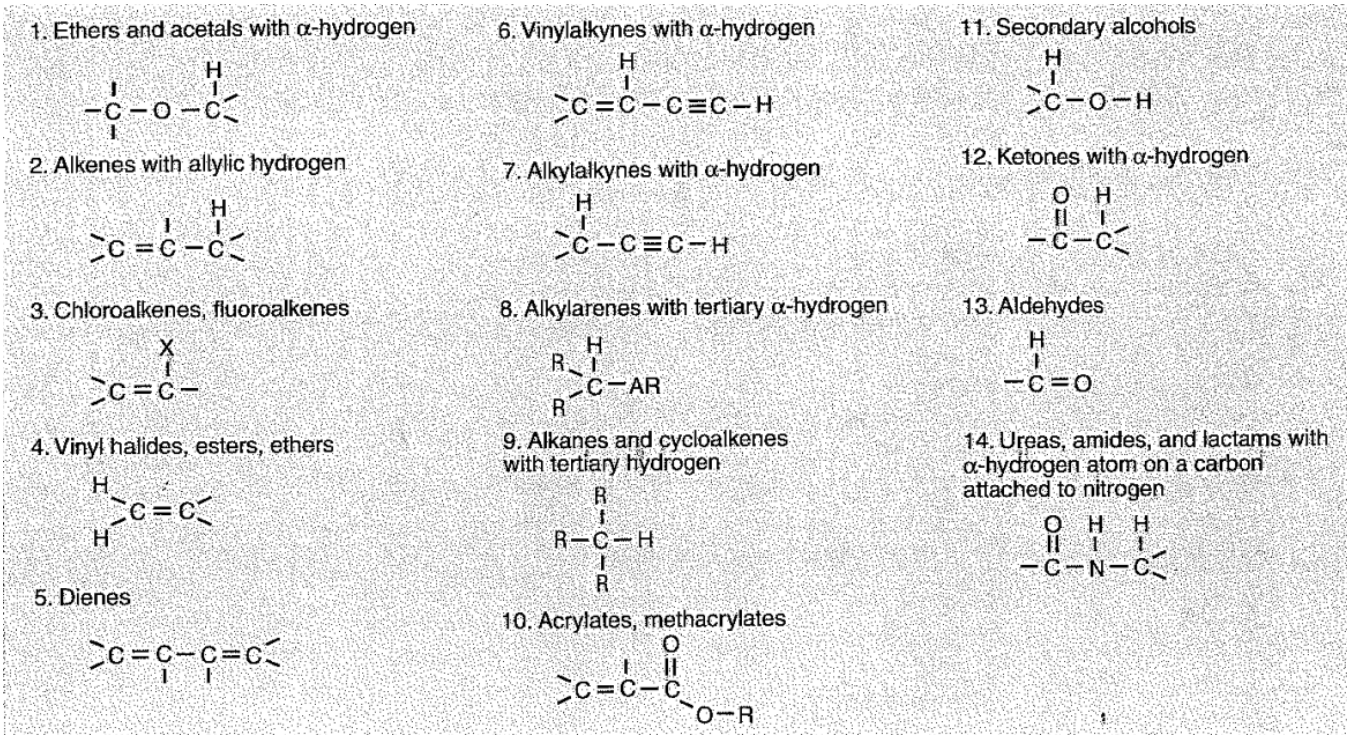


Figure 1: Peroxidizable organic moieties, numbered from most (1) to least (14) likely to form dangerous peroxides.

Peroxide-forming chemicals invariably contain an auto oxidizable hydrogen atom that is activated by adjacent structural components. Activated hydrogen atoms are often on a:

- Methylene group adjacent to an ethereal oxygen atom (-O-CH_2-, e.g. diethyl ether, THF, dioxane, diglyme)
- Methylene group adjacent to a vinyl group or benzene ring (C=C-CH_2- or Ph-CH_2-, e.g. allyl or benzyl compounds)
- CH group adjacent to two ethereal oxygen groups (-O-CH-O-, e.g. acetals or methylenedioxy compounds)
- CH group adjacent to two methylene groups (-CH_2-CH-CH_2-, e.g. isopropyl compounds and decahydronaphthalenes)
- CH group between a benzene ring a methylene group (-CH_2-CH-Ph-, e.g. cumene and tetrahydronaphthalenes)
- A vinyl group (-C=CH_2-, e.g. vinyl compounds, dienes, styrenes or other monomers)

Not all compounds containing these groups form peroxides, However, the presence of any of these groups in a compound (especially those with low molecular weight) provide a warning that hazardous concentrations of unstable peroxides might be present. Chemical structures that include more than one of these groups are at particular risk of peroxidation.

For example, isopropyl ether (Group A) is particularly dangerous: the presence of two tertiary carbon atoms in the molecule enhance the tendency to oxidize to corresponding hydroperoxide. The hydroperoxide then polymerizes to form a product that precipitates from the ether solution as an explosive crystalline solid.

Appendix B: Peroxide-Forming Chemicals

The following lists (pages 14-17) of chemicals **are not exhaustive**. Researchers must consult the SDS and other information sources for the chemicals used in their work areas to determine the potential for peroxide-formation.

Group A: Chemicals that form explosive levels of peroxides without concentration

Chemical Name	CAS	Synonyms	State
Butadiene [1]	106-99-0	1,3-Butadiene	l
Chloroprene [1]	126-99-8	2-Chloro-1,3- butadiene	l
Divinyl acetylene	821-08-9	1,5-Hexadien- 3-yne	l
Isopropyl ether	108-20-3		l
Tetrafluoroethylene [1]	116-14-3		l
Vinylidene chloride	75-35-4	1,1- Dichloroethylene	l

Group B: Chemicals that form explosive levels of peroxides on concentration

Chemical Name	CAS	Synonyms	State
Acetal	105-57-7		l
Acetaldehyde	75-07-0		l
Benzyl alcohol	100-51-6		l
2-Butanol**	78-92-2		l
Cyclohexanol	108-93-0		l
Cyclohexene	110-83-8		l
2-Cyclohexen-1-ol	822-67-3		l
Cyclopentene	142-29-0		l
Decahydronaphthalene	91-17-8	Decalin	l
Diacetylene	460-12-8		g
Dicyclopentadiene	77-73-6		l
Diethylene glycol dimethyl ether	111-96-6	Diglyme	l
Dioxane	123-91-1	1,4-Dioxane	l
Ethylene glycol dimethyl ether	110-71-4	1,2-Dimethoxyethane; Glyme	l
Ethyl ether	60-29-7	Diethyl ether	l
4-Heptanol	589-55-9		l
2-Hexanol**	626-93-7		l
Isopropyl benzene	98-82-8	Cumene	l
Methyl acetylene	74-99-7	Propyne	g
3-Methyl-1-butanol	123-51-3	Isoamyl alcohol	l
Methyl cyclopentane	96-37-7		l
Methyl isobutyl ketone	108-10-1	Methyl-i-butyl ketone; MIBK; Isobutyl methyl ketone; Isopropylacetone; 4-Methyl-2-pentanone	l
4-Methyl-2-pentanol	108-11-2	Isobutyl methyl carbinol; 3-MIC; MAOH; MIBC	l
2-Pentanol**	6032-29-7		l
4-Penten-1-ol	821-09-0		l
1-Phenylethanol	98-85-1	alpha-Methyl-benzyl alcohol	l
2-Phenylethanol	60-12-8	Phenethyl alcohol	l

Chemical Name	CAS	Synonyms	State
2- Propanol**	67-63-0	Isopropanol; Isopropyl alcohol; IPA; sec-Propyl alcohol	
Tetrahydrofuran	109-99-9		l
Tetrahydronaphthalene	119-64-2	1,2,3,4-Tetrahydronaphthalene; Tetralin solvent	l
Vinyl Ethers			
Other secondary alcohols			

Group C: Chemicals that may auto-polymerize as a result of peroxide accumulation

Chemical Name	CAS	Synonyms	State
Acrylic acid [2]	79-10-7		l
Acrylonitrile [2]	107-13-1		l
Butadiene [3]	106-99-0		g
Chloroprene [3]	126-99-8	2-Chloro-1,3-butadiene	g
Chlorotrifluoroethylene [3]	79-38-9		g
Methyl methacrylate [2]	80-62-6		l
Styrene	100-42-5		l
Tetrafluoroethylene [3]	116-14-3		g
Vinyl acetate	108-05-4		l
Vinylacetylene	689-97-4	Buten-3-yne; Butenyne; 1-Buten-3-yne	g
Vinyl chloride [3]	75-01-4	Mono-chloroethylene	g
Vinylidene chloride	75-35-4	1,1-Dichloroethylene	l
2-Vinyl pyridine	100-69-6		l
4-Vinyl pyridine	100-43-6		l

Note: **Secondary alcohols can be peroxide-forming chemical hazards, particularly anhydrous form of the alcohols, and are used in chemical processes (e.g., heating, distilling, performing chemical reactions, performing bulk evaporations). If these chemicals are used only for wipe cleaning or solvent extractions, risk is lower, nonetheless, peroxide may form when exposed to lights and air.

Group D: Chemicals that may form peroxides but cannot be clearly placed in Groups A-C.

Chemical Name	CAS	Chemical Name	CAS
Acrolein	107-02-8	1,3-Dioxepane	505-65-7
Allyl ether[4]	557-40-4	Di(1-propynl) ether[6]	111-43-4
Allyl ethyl ether	557-31-3	Di(2-propynl) ether	
Allyl phenyl ether	1746-13-0	Di-n-propoxymethane[4]	505-84-0
p-(n-Amyloxy)benzoyl chloride	36823-84-4	1,2-Epoxy-3-isopropoxypropane[4]	4016-14-2
n-Amyl ether	693-65-2	1,2-Epoxy-3-phenoxypropane	122-60-1
Benzyl n-butyl ether[4]	588-67-0	p-Ethoxyacetophenone	1676-63-7
Benzyl ether[4]	103-50-4	1-(2-Ethoxyethoxy)ethyl acetate	
Benzyl ethyl ether[4]	539-30-0	2-Ethoxyethyl acetate	111-15-9
Benzyl methyl ether	538-86-3	(2-Ethoxyethyl)-o-benzoyl benzoate	604-63-7
Benzyl-1-napthyl ether[4]	613-62-7	1-Ethoxynaphthalene	5328-01-8
1,2-Bis(2-chloroethoxy)ethane	112-26-5	o,p-Ethoxyphenyl isocyanate	
Bis(2-ethoxyethyl)ether	112-36-7	1-Ethoxy-2-propyne	
Bis(2-(methoxyethoxy)ethyl) ether	143-24-8	3-Ethoxypropionitrile	2141-62-0

Chemical Name	CAS	Chemical Name	CAS
Bis(2-chloroethyl) ether	111-44-4	2-Ethylacrylaldehyde oxime	99705-27-8
Bis(2-ethoxyethyl) adipate	109-44-4	2-Ethylbutanol	97-95-0
Bis(2-ethoxyethyl) phthalate	605-54-9	Ethyl-b-ethoxypropionate	763-69-9
Bis(2-methoxyethyl) carbonate	626-84-6	2-Ethylhexanal	123-05-7
Bis(2-methoxyethyl) ether	119-96-6	Ethyl vinyl ether	109-92-2
Bis(2-methoxyethyl) phthalate	117-82-8	Furan	110-00-9
Bis(2-methoxymethyl) adipate		2,5-Hexadiyn-1-ol	28255-99-4
Bis(2-n-butoxyethyl) phthalate	117-83-9	4,5-Hexadien-2-yn-1-ol	2749-79-3
Bis(2-phenoxyethyl) ether	622-87-7	n-Hexyl ether	112-58-3
Bis(4-chlorobutyl) ether	6334-96-9	o,p-Iodophenetole	
Bis(chloromethyl) ether	542-88-1	Isoamyl benzyl ether[4]	122-73-6
2-Bromomethyl ethyl ether	13057-17-5	Isoamyl ether[4]	544-01-4
β-Bromophenetole	589-10-6	Isobutyl vinyl ether	109-53-5
o-Bromophenetole	583-19-7	Isophorone	78-59-1
p-Bromophenetole	588-96-5	β-Isopropoxypropionitrile[4]	110-47-4
3-Bromopropyl phenyl ether	588-63-6	Isopropyl-2,4,5-trichlorophenoxy acetate	93-78-7
1,3-Butadiyne	460-12-8	Limonene	138-86-3
Buten-3-yne	689-97-4	1,5-p-Methadiene	
Tert-Butyl ethyl ether	637-92-3	Methyl p-(n-amyloxy)benzoate	
Tert-Butyl methyl ether	1634-04-4	4-Methyl-2-pentanone	108-10-1
n-Butyl phenyl ether	1126-79-0	n-Methylphenetole	
n-Butyl vinyl ether	111-34-2	2-Methyltetrahydrofuran	96-47-9
Chloroacetaldehyde diethylacetal[4]	621-62-5	3-Methoxy-1-butyl acetate	4435-53-4
2-Chlorobutadiene	126-99-8	2-Methoxyethanol	109-86-4
1-(2-Chloroethoxy)-2-phenoxyethane	2243-44-9	3-Methoxyethyl acetate	
Chloroethylene	75-01-4	2-Methoxyethyl vinyl ether	1663-35-0
Chloromethyl methyl ether[5]	107-30-2	Methoxy-1,3,5,7-cyclooctatetraene	
β-Chlorophenetole	622-86-6	β-Methoxypropionitrile	110-67-8
o-Chlorophenetole	614-72-2	m-Nitrophenetole	621-52-3
p-Chlorophenetole	622-61-7	1-Octene	111-66-0
Cyclooctene[4]	931-88-4	Oxybis(2-ethyl acetate)	628-68-2
Cyclopropyl methyl ether	540-47-6	Oxybis(2-ethyl benzoate)	
Diallyl ether[4]	557-40-4	β,β-Oxydipropionitrile	1656-48-0
p-Di-n-butoxybenzene		1-Pentene	109-67-1
1,2-Dibenzyloxyethane[4]	622-22-0	Phenoxyacetyl chloride	701-99-5
p-Dibenzyloxyethane[4]		α-Phenoxypropionyl chloride	122-35-0
1,2-Dichloroethyl ethyl ether	623-46-1	Phenyl-o-propyl ether	
2,4-Dichlorophenetole	5392-86-9	p-Phenylphenetone	
Diethoxymethane[4]	462-95-3	n-Propyl ether	111-43-3
2,2-Diethoxypropane	126-84-1	n-Propyl isopropyl ether	627-08-7
Diethyl ethoxymethylenemalonate	87-13-8	Sodium 8,11,14-eicosatetraenoate	
Diethyl fumarate[4]	623-91-6	Sodium ethoxyacetylide[6]	
Diethyl acetate[4]	105-57-7	Tetrahydropyran	142-68-7
Diethylketene[6]	24264-08-2	Triethylene glycol diacetate	111-21-7
m,o,p-Diethoxybenzene		Triethylene glycol dipropionate	141-34-4
1,2-Diethoxyethane	629-14-1	1,3,3-Trimethoxypropane[4]	
Dimethoxymethane[4]	109-87-5	1,1,2,3-Tetrachloro-1,3-butadiene	921-09-5
1,1-Dimethoxyethane[4]	534-15-6	4-Vinyl cyclohexene	100-40-3
Dimethylketene[6]		Vinylene carbonate	872-36-6
3,3-Dimethoxypropene	6044-68-4	Vinylidiene chloride[4]	75-35-4
2,4-Dinitrophenetole	610-54-8		

1. When stored as a liquid monomer.
2. Although these form peroxides, no explosions involving these monomers have been reported.
3. When stored in liquid form, these chemicals form explosive levels of peroxides without concentration. They may also be stored as a gas in gas cylinders. When stored as a gas, these

chemicals may auto-polymerize as a result of peroxide accumulation.

4. These chemicals easily form peroxides and should probably be considered under part B.
5. OSHA-regulated carcinogen
6. Extremely reactive and unstable compound.

(Source: Kelly, R.J., Review of Safety Guidelines for Peroxidizable Organic Chemicals, Chemical Health and Safety, American Chemical Society, 1996, Sept, 28-36.)

Appendix C: Safe Storage Periods for Peroxide Forming Chemicals

Peroxide forming chemical	Safe storage period
Unopened chemicals from manufacturer	Up to 12 months or manufacturer's expiration date whichever comes first
Opened containers: Chemicals in Group A	3 months or manufacturer's expiration date whichever comes first
Opened containers: Chemicals in Group B and D	12 months or manufacturer's expiration date whichever comes first
Opened uninhibited chemicals in Group C	24 hours
Opened inhibited chemicals in Group C	12 months* or manufacturer's expiration date whichever comes first

*Do not store under inert atmosphere, oxygen required for inhibitor to function.

(Source: Kelly, Richard J., Chemical Health & Safety, American Chemical Society, 1996, Sept, 28-36)

Appendix D: Quick Guide for Peroxide-Forming Chemicals

Peroxide-forming chemicals include many common solvents and reagents that are known to form organic peroxides on exposure to air and light, e.g. tetrahydrofuran, ethers, isopropanol, dioxanes, styrene, 2-hexanol, etc). Peroxides are very sensitive to shock, sparks, elevated temperatures, light, strong oxidizing and reducing agents, and friction, such as a cap being twisted open.

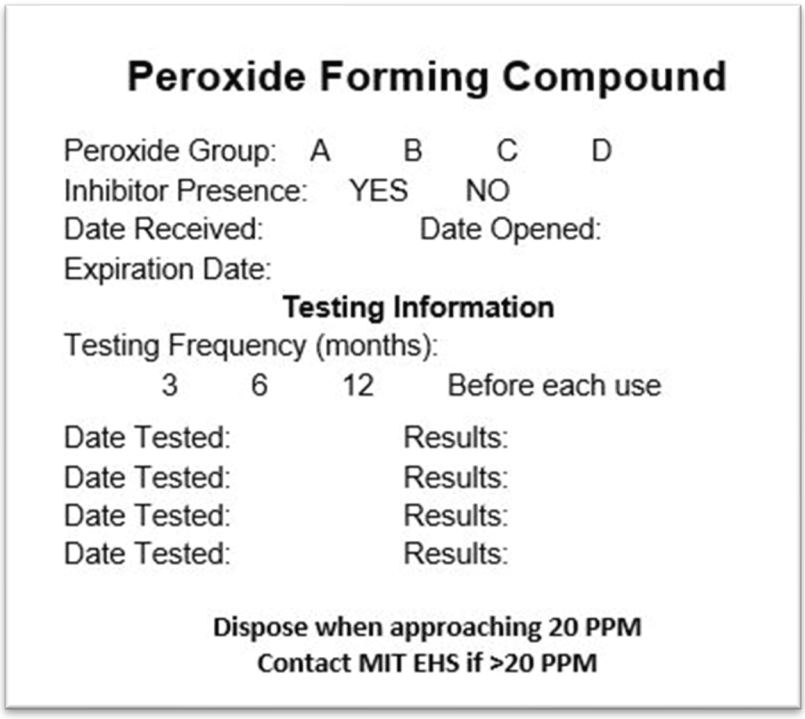
Please refer to the EHS Peroxide-Forming Chemicals SOP for more information.

This quick guide provides some of the main guidelines for safe handling and disposal of peroxide-forming chemicals:

1. Determine the Group of the chemical based on the potential of peroxide formation.
2. Purchase only what you need and always with an inhibitor if available (unless your specific experiment will not tolerate the inhibitor molecule).
3. Label with date received, date opened and assign an expiration date if one is not supplied by the manufacturer. Obtain peroxide-forming chemicals stickers from the EHS Office.
4. Use or dispose of chemical by expiration date.
5. Protect from light with amber bottles.
6. Test peroxide periodically as specified in table below. Test before each use for distillation or evaporation. Uninhibited Group C chemicals should not be distilled.
7. Write down the test date and results on the bottle.
8. **Do not attempt to test if there are possible crystals or particles in bottle or around the cap.**
9. **Dispose expired or chemical containing peroxides approaching 20 ppm immediately**.
   - Selected peroxide-forming chemicals may be allowed after safe storage period, subjected to more frequent testing and before each use.
10. Place red tag on container, indicate peroxide levels, and request disposal.
11. **If > 20 ppm or observed presence of crystals or particles, contact EHS.**

Group	**A**	**B**	**C**	**D**
Peroxide formation	Can form explosive levels of peroxides without concentration. Some of these chemicals may form explosive concentrations even if never opened.	Do not usually accumulate potentially explosives concentrations unless the volatile organic material is reduced in volume e.g. evaporation and distillation	May auto-polymerize as a result of peroxide formation	May form peroxides but cannot be clearly placed in Groups A-C
Examples	1,3-butadiene; Isopropyl ether; Vinylidene chloride	Tetrahydrofuran; Ethers; Isopropanol; Dioxanes; 2-Hexanol; Acetaldehyde	1,3-butadiene; Acrylonitrile; Acrylic acid; Vinyl pyridine; Methyl methacrylate; Styrene; Vinyl acetate	Acrolein; Ethers; Furan; 2-Methoxyethanol; 2-Methyltetrahydrofuran; 1-Octene
Safe Storage Period				
Open & Uninhibited	3 months	12 months	24 hours	12 months
Open & Inhibited	12 months	12 months	12 months	12 months
Unopen	12 months	12 months	12 months	12 months
Testing Frequency				
Within Safe Storage Period	3 months	6 months	6 months	6 months
After Safe Storage Period	Uninhibited – Must dispose by 3 months Inhibited – Must dispose by 12 months.	Uninhibited – Test every 3 months and before each use Inhibited – Test 6 months and before each use *For isopropanol that is stored in dark and closed container, test every 12 months.	Uninhibited – Must dispose by 24 hours Inhibited – Test every 6 months and before each use	Uninhibited – Test every 3 months and before each use Inhibited – Test every 6 months and before each use

Appendix E: Example of Peroxide-Forming Chemicals Label



Peroxide Forming Compound

Peroxide Group: A B C D
Inhibitor Presence: YES NO
Date Received: Date Opened:
Expiration Date:

Testing Information

Testing Frequency (months):
3 6 12 Before each use

Date Tested: Results:
Date Tested: Results:
Date Tested: Results:
Date Tested: Results:

Dispose when approaching 20 PPM
Contact MIT EHS if >20 PPM