Peroxide-forming Chemicals

1. Purpose / Background
The purpose of this document is to provide information and procedures to assure that peroxide-forming chemicals are used safely per the MIT Environmental, Health and Safety (EHS) Policy and in accordance with the Guiding Principles in Support of the EHS Policy. To view the EHS Policy and Guiding Principles, go to http://ehs.mit.edu/site/content/ehs-policy.

Peroxide-forming chemicals include many common solvents and reagents that are known to form organic peroxides on exposure to air. Organic peroxides are highly flammable, low-power explosives that are very sensitive to shock, sparks, elevated temperatures, light, strong oxidizing and reducing agents, and friction, such as a cap being twisted open. Distillation, evaporation, or other concentration of some peroxide-forming chemicals, e.g. diethyl ether, tetrahydrofuran, acetaldehyde, or isopropyl ether, can present a high risk of explosion.

2. Scope
This SOP is a generic guideline that can be used to aid MIT laboratories and shops to use and store peroxide-forming chemicals 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 General Use Procedures
- **Information:** Acquire a material safety data sheet (MSDS) 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.

Appendix A lists some peroxide-forming chemicals in the following groups: Group A chemicals can form explosive levels of peroxides without concentration; Group B chemicals can form explosive levels of peroxides on concentration; Group C chemicals may autopolymerize as a result of peroxide formation; and Group D chemicals may form peroxides, but these chemicals are not well characterized (Source: Kelly, Richard J., Chemical Health & Safety, American Chemical Society, 1996, Sept, 28-36). These lists are illustrative not exhaustive.
• **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.

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

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

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

• **Work Practice Controls**
  - 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 B.
  - 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. Recommended safe storage time-periods for peroxide forming chemicals are provided in Appendix B. Affixing a label stating “Warning Peroxide Former” to alert others is recommended. Assign a responsible person to keep an inventory of peroxide-forming chemicals and periodically check the receipt, opened and expiration dates.
  - Organic peroxide levels above 20 ppm are not acceptable at any disposal facility in Massachusetts. Material with greater than 20ppm requires stabilization for disposal by the chemical waste vendor. 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 Office 2-3477 to have the material removed and treated. In Massachusetts, containers with peroxide levels above 20 ppm must be taken to a “remote opening” site that requires a permit from the Massachusetts Department of Environmental Protection and a Fire Department Detail.
  - To ensure that the 20-ppm peroxide level is not exceeded, monthly testing of peroxides after opening is recommended. Exception is isopropanol (2-propanol) which does not require testing until approaching its expiration date (refer to appendix B) and annually thereafter. Records of the testing date and results should be maintained and also recorded on the label. The easiest way to test for peroxides is to use peroxide test strips that are a semi-quantitative colorimetric method. **For peroxide-formers with visible crystallization or solids formed inside or at the cap, do not test!** Contact the EHS Office 2-3477 to evaluate the container.
  - 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 immediately. If peroxide testing results indicate no peroxides to be present in the chemical, a new date of testing with peroxide levels of 0 ppm should be indicated on the bottle. This bottle should be tested monthly until peroxides levels are present or the chemical is used to completion.
  - Any chemical waste streams with >25% peroxide forming chemicals by volume must be tested by the lab and peroxide levels indicated on the red hazardous waste label. The
exception would be if isopropanol is the only peroxide former >25% then the waste does not need to be tested.

- Test for peroxides before distilling or evaporating peroxide-forming chemicals. Do not distill without treating to remove peroxides.
- **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 2-3477 immediately.
- Protect from heat, light, friction, static discharge, mechanical shock, contact with a catalyst, physical damage or other conditions listed in the MSDS that the compound may be sensitive to.
- Do not return unused peroxide-forming chemicals to their original containers.
- Do not mix peroxide-forming hazardous waste with other hazardous wastes.
- Immediately rinse empty containers of peroxide forming chemicals. Do not let residues evaporate.
- 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.

### 4.2 General Storage Procedures

Storing peroxide-forming chemicals should be part of a comprehensive chemical storage plan that is outlined in the Chemical Storage SOP. The MSDS for each material should be read to determine specific storage recommendations or special storage conditions.
- 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 time-periods listed in Appendix B.
- Store away from light and heat. Protect from light with brown bottles or opaque containers.

### 4.3 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 MSDS 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 that a spill has occurred. 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 Individuals Using Peroxide-forming chemicals are responsible for:

An official hardcopy of this document exists in the EHS Office or on the EHS website.

See Legal Disclaimer at: [http://ehs.mit.edu/site/content/legal-disclaimer](http://ehs.mit.edu/site/content/legal-disclaimer)
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.

5.2 The EHS Office is responsible for:

- Providing General Chemical Hygiene Training (web-based or classroom) and MIT Overview HAZCOM 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.

5.3 PI’s/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.

5.4 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.

5.5 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.

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 MSDSs and SOPs for peroxide-forming chemicals.

For non-laboratory personnel that use these chemicals in their work area, the required training is called “General HAZCOM Training”, 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 assure 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 or past the safe storage period listed in Appendix B 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
The following references are available through the EHS Office:

9.1. Standards
OSHA 1910.1450 Occupational Exposure to Hazardous Chemicals in Laboratories
OSHA 1910.106 Flammable and Combustible Liquids

9.2. Other SOPs
Chemical Storage SOP
Flammable and Combustible Liquids SOP
Records Retention SOP

9.3. Supplementary Documents
9.4. **Helpful Websites**

10. **Definitions**
10.1. Material Safety Data Sheet (MSDS) is a written document that outlines health and safety information for a hazardous chemical. An MSDS 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.
Appendix A

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

A. Chemicals that form explosive levels of peroxides without concentration

<table>
<thead>
<tr>
<th>Butadiene</th>
<th>Divinylacetylene</th>
<th>Tetrafluoroethylene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloroprene</td>
<td>Isopropyl ether</td>
<td>Vinyldiene chloride</td>
</tr>
</tbody>
</table>

B. Chemicals that form explosive levels of peroxides on concentration

<table>
<thead>
<tr>
<th>Acetal</th>
<th>Diacetylene</th>
<th>2-Hexanol</th>
<th>2-Phenylethanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetaldehyde</td>
<td>Dicyclopentadiene</td>
<td>Methylacetylene</td>
<td>2-Propanol</td>
</tr>
<tr>
<td>Benzyl alcohol</td>
<td>Diethyl ether</td>
<td>3-Methyl-1-butanol</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>2-Butan</td>
<td>Diethylene glycol</td>
<td>Methylcyclopentane</td>
<td>Tetrahydrophthaledehyde</td>
</tr>
<tr>
<td>Cumene</td>
<td>dimethyl ether</td>
<td>Methyl isobutyl ketone</td>
<td>Vinyl ethers</td>
</tr>
<tr>
<td>Cyclohexanol</td>
<td>Dioxanes</td>
<td>4-Methyl-2-pentanol</td>
<td>Other secondary alcohols</td>
</tr>
<tr>
<td>2-Cyclohexen-1-ol</td>
<td>Ethylene glycol</td>
<td>2-Pentanol</td>
<td></td>
</tr>
<tr>
<td>Cyclohexene</td>
<td>dimethyl ether</td>
<td>4-Penten-1-ol</td>
<td></td>
</tr>
<tr>
<td>Decahydronaphthalene</td>
<td>4-Heptanol</td>
<td>1-Phenylethanol</td>
<td></td>
</tr>
</tbody>
</table>

C. Chemicals that may autopolymerize as a result of peroxide accumulation

<table>
<thead>
<tr>
<th>Acrylic acid</th>
<th>Chlorotrifluoroethylene</th>
<th>Vinyl acetate</th>
<th>Viniladiene chloride</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acrylonitrile</td>
<td>Methyl methacrylate</td>
<td>Vinylacetyle</td>
<td>Vinilpyrindine</td>
</tr>
<tr>
<td>Butadiene</td>
<td>Styrene</td>
<td>Vinyl chloride</td>
<td></td>
</tr>
<tr>
<td>Chloroprene</td>
<td>Tetrafluoroethylene</td>
<td>Vinylpyrindine</td>
<td></td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Acrolein</th>
<th>tert-Butyl methyl ether</th>
<th>Di(1-propynyl) ether</th>
<th>4-Methyl-2-pentanone</th>
</tr>
</thead>
<tbody>
<tr>
<td>Allyl ether</td>
<td>n-Butyl phenyl ether</td>
<td>Di(2-propynyl) ether</td>
<td>n-Methylphenetole</td>
</tr>
<tr>
<td>Allyl ethyl ether</td>
<td>n-Butyl vinyl ether</td>
<td>Di-n-propoxymethane</td>
<td>2-Methyltetrahydrofuran</td>
</tr>
<tr>
<td>Allyl phenyl ether</td>
<td>Chloroaetaldehydehydiethyal</td>
<td>1,2-Epoxy-3-isopropoxypropane</td>
<td>3-Methoxy-1-butyl acetate</td>
</tr>
<tr>
<td>p-(n-Amyloxy)benzoyl chloride</td>
<td>2-Chlorobutadiene</td>
<td>1,2-Epoxy-3-phenoxypropylene</td>
<td>2-Methoxyethanol</td>
</tr>
<tr>
<td>n-Amyl ether</td>
<td>1-(2-Chloroethoxy)-2-phen-</td>
<td>Ethoxyacetoephone</td>
<td>3-Methoxyethyl acetate</td>
</tr>
<tr>
<td>Benzyl n-butyl ether</td>
<td>oxyethane</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzyl ether</td>
<td>Chloroethylene</td>
<td>1-(2-Ethoxyethoxy)ethyl acetate</td>
<td>2-Methoxyethyl vinyl ether</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2-Ethoxyethyl acetate</td>
<td>Methoxy-1,3,5,7-cycloocta</td>
</tr>
</tbody>
</table>
Benzyl ethyl ether
Benzyl methyl ether
Benzyl 1-naphthyl ether
1,2-Bis(2-chloroethoxy)ethane
Bis(2-ethoxyethyl) ether
Bis(2-(methoxyethoxy)ethyl) ether
Bis(2-chloroethyl) ether
Bis(2-ethoxyethyl) adipate
Bis(2-methoxyethyl) carbonate
Bis(2-methoxyethyl) phthalate
Bis(2-n-butoxymethyl) phthalate
Bis(2-phenoxymethyl) ether
Bis(4-chlorobutyl) ether
Bis(chloromethyl) ether
2-Bromomethyl ethyl ether
β-Bromophenene
α-Bromophenene
p-Bromophenone
3-Bromopropyl phenyl ether
1,3-Butadiyne
Buten-3-yne
tert-Butyl ethyl ether
Benzyl ethyl ether
Chloromethyl methyl ether
β-Chlorophenetole
α-Chlorophenetole
p-Chlorophenetole
Cyclooctene
Cyclopropyl methyl ether
Diallyl ether
p-Di-n-butoxybenzene
1,2-Dibenzyloxethane
p-Dibenzyloxylene
1,2-Dichloroethyl ethyl ether
2,4-Dichloropropene
dethoxymethane
2,2-Diethoxypropane
Diethyl ethoxymethylenemalonate
Diethyl fumarate
Diethyl acetal
Diethylketene
m,o,p-Diethoxybenzene
1,2-Diethoxyethane
Dimethoxymethane
1,1-Dimethoxyethane
Dimethylketene
3,3-Dimethoxypropene
2,4-Dinitrophentole
1,3-Dioxepane
(2-Ethoxyethyl)-α-benzoyl benzoate
1-Ethoxynaphthalene
α, p-Ethoxyphenyl isocyanate
1-Ethoxy-2-propyne
3-Ethoxypropionitrile
2-Ethylacrylaldehyde oxime
2-Ethylbutanol
Ethyl β-ethoxypropionate
2-Ethylhexanal
Furan
2,3-Hexadiyn-1-ol
4,5-Hexadien-2-yn-1-ol
n-Hexyl ether
α-p-Iodophenetole
Isoamyl benzyl ether
Isoamyl ether
obutyl vinyl ether
Isophorone
β-Isooctoxypropionitrile
Isopropyl 2,4,5-trichlorophenoxyacetate
Limonene
Methyl p-(n-amylloxy)benzoate
tetraene
β-Methoxypropionitrile
1-Methyl-1-bromopropan-2-one
Oxybiphenyl chloride
Phenyl α-propyl chloride
Phenyl α-propynyl chloride
Phenyl α-propynyl chloride
Phenoxyacetyl chloride
Sodium 8,11,14-eicosatetraenoate
Sodium ethoxycacetyl
Tetrahydrofuran
Triethylene glycol diacetate
Triethylene glycol dipropionate
1,1,2,3,3-pentachloro-1-butyne
4-Vinyl cyclohexene
Vinylenecarbonate
Vinyllidene chloride

1 When stored as a liquid monomer
2 Although these chemicals form peroxides, no explosions involving these monomers
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 autopolymerize 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.
7 A slow peroxide former see Appendix B for storage period.
Appendix B
Safe Storage Period for Peroxide Forming Chemicals (Source: Kelly, Richard J., Chemical Health & Safety, American Chemical Society, 1996, Sept, 28-36)

<table>
<thead>
<tr>
<th>Peroxide forming chemical</th>
<th>Safe storage period</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unopened chemicals from manufacturer(^2)</td>
<td>Up to 12 months or manufacturer’s expiration date whichever comes first</td>
</tr>
<tr>
<td>Opened containers: Chemicals in Group A</td>
<td>3 months or manufacturer’s expiration date whichever comes first</td>
</tr>
<tr>
<td>Opened containers: Chemicals in Group B(^2) and D</td>
<td>12 months or manufacturer’s expiration date whichever comes first</td>
</tr>
<tr>
<td>Opened uninhibited chemicals in Part C</td>
<td>24 hours</td>
</tr>
<tr>
<td>Opened inhibited chemicals in Part C</td>
<td>12 months(^1) or manufacturer’s expiration date whichever comes first</td>
</tr>
</tbody>
</table>

\(^1\) Do not store under inert atmosphere, oxygen required for inhibitor to function.

\(^2\) Isopropanol, a slow peroxide former, is an exception; it can be stored for 60 months or manufacturer’s expiration date whichever comes first.