STANDARD OPERATING PROCEDURE FOR HANDLING STORAGE AND DISPOSAL FOR TIME SENSITIVE CHEMICALS

1. PURPOSE & SCOPE
   1.1. This procedure describes methods for safely using, storing, and disposing of time sensitive chemicals. This procedure applies to all University of Notre Dame personnel whose work involves time sensitive chemicals.

2. RESPONSIBILITIES
   2.1. Principal Investigators shall ensure this procedure is implemented in their work areas and labs.
   2.2. Once notified, RMS shall ensure proper disposal of time sensitive chemicals, which are expired or no longer needed are properly disposed. RMS or designee shall manage the stabilization of time sensitive chemicals that are suspect and could create an explosion or fire hazard.

3. SPECIAL PRECAUTIONS:
   3.1. Time-sensitive materials should be monitored in the laboratory and properly disposed at regular intervals. If these materials are left in storage long enough to form hazardous by-products, their management and disposal becomes increasingly hazardous and costly.
   3.2. If you discover time-sensitive materials that have expired or are undated:
      3.2.1. DO NOT TOUCH THE BOTTLE.
      3.2.1.1. Never, under any circumstances, touch or attempt to open a container of peroxide-forming liquid if there are whitish crystals around the cap and/or in the bottle. The friction of unscrewing the cap could detonate the bottle.
      3.2.2. Visually inspect the bottle for product identification and expiration date.
      3.2.3. Visually inspect for water content.
      3.2.4. If you determine that the container may have crystals - immediately secure the area and notify RMS (631-5037)

4. HAZARD DESCRIPTION:
   4.1. Time Sensitive Chemicals are any chemical or chemical product that develops additional hazards upon prolonged storage. Examples of these chemicals include peroxidizables, polynitrated aromatics, chloroform and anhydrous HF. (Appendix A presents additional examples of time sensitive chemicals.)
   4.2. Peroxidizables are oxygenated organic compounds that will react with atmospheric oxygen to form explosive peroxides.
   4.3. Polynitrated aromatics have reactive nitrate groups that can form explosive picrate salts when exposed to certain metals.
   4.4. Chloroform will react with air over time to form phosgene.
4.5. Anhydrous HF easily liquefies and can react with a carbon steel cylinder to create hydrogen and can cause an increase in pressure inside the cylinder.

5. CONTROLS:
5.1. Time sensitive chemicals should not be stored in ground glass stoppered bottles or in bottles with metal foil lined caps. Instead, they should be stored in dark colored glass to avoid reactions with light.
5.2. Purchase the smallest quantity that is practical for all time-sensitive materials. Substitution with less hazardous materials is preferable.

6. SPECIAL DETECTION METHODS:
6.1. With any time sensitive material, the date the material was purchased and the date it was opened or transferred to a secondary container shall be clearly marked on the container by the user/owner of the chemical.
6.2. The following methods may be used to identify hazardous conditions:
   6.2.1. Peroxidizables may be characterized by having a “mossy” look around the cap. There may be a white film or residue around the neck, threads or cap of container or there may be crystals in the liquid.
   6.2.2. Peroxide test strips, which turn to an indicative color in the presence of peroxides, are available commercially (VWR # EMD 10081-1). These strips must be air-dried until the solvent evaporates and then exposed to moisture for proper operation. To use most of these, simply dunk the strip in the suspect material and then compare the color on the strip to the calibration chart that comes with the test kit. This gives a quantitative peroxide concentration, usually in parts per million (ppm). Caution:
      6.2.2.1. These strips have finite ranges. You may need to buy several different test kits to cover all possible ranges - read the product information or call the manufacturer for more information.
   6.2.3. Polynitrated Aromatics (Picric Acid) which have dehydrated will be pale in color and there will be crystals formed.
   6.2.4. Chloroform will have a normal appearance. The only way to determine stability is by determining the age of the material by the lot number or date marked on the container.
   6.2.5. Anhydrous HF cylinders may show a build up of pressure in the regulator of the cylinder.

7. PEROXIDIZABLES:
   7.1. Materials from Table 1, Appendix A should be dated, tested before use and disposed of within three months of opening or receipt.
   7.2. Materials from Table 2, Appendix A should be dated, tested before use and disposed of within twelve months of opening or receipt.
   7.3. Materials from Table 3, Appendix A should be dated, tested and disposed of within twelve months of opening or receipt.
7.4. Materials should be marked with the date they were tested for peroxides.
   Note: Based on the chemical manufacturer’s recommendations, these
   expiration and disposal dates may be modified, as appropriate.
   7.4.1. Appendix B contains an example of a label.
7.5. Make sure the purchase of materials that contains an appropriate peroxide
   inhibitor, such as butylated hydroxytoluene (BHT). If non-inhibited material
   must be stored, be sure to store the material under an inert atmosphere of
   nitrogen or argon and test it for peroxides at least once a month.
7.6. Do not distill, evaporate or concentrate the material until you have first
   tested the material for the presence of peroxides. Peroxides are usually less
   volatile than their parent material and tend to concentrate in the (hot)
   distillation pot.
7.7. NOTE: Never, under any circumstances, touch or attempt to open a
    container of peroxide-forming liquid if there are whitish crystals around the
    cap and/or in the bottle. The friction of unscrewing the cap could detonate
    the bottle with disastrous results.
8. POLYNITRATED AROMATICS (Picric Acid, 2,4-dinitrophenol):
   8.1. Picric acid and its derivatives should be stored in small quantities, within
         the original container and in a cool, dry, well-ventilated area that is away
         from sources of heat.
   8.2. Picric acid is considered a flammable solid and is incompatible with
         oxidizers, reducing agents, inorganic salts, metals, alkaloids and albumin.
   8.3. Improperly managed or stored picric acid may become sensitive to shock,
         friction, and heat.
   8.4. Picric acid allowed to dry out to less than 10% water by volume, becomes
         unstable and may pose an explosion hazard. If the material appears dry, do
         not open or handle the container – immediately contact the RMS Office: 631-
         5037.
   8.5. Picric Acid should be monitored for water content every three months and
        disposed of as hazardous waste within two years of receipt.
9. CHLOROFORM:
   9.1. Chloroform should be stored in a cool, dry, well-ventilated area [less than 30
         degrees C (86 degrees F)] and in tightly sealed containers.
   9.2. Chloroform decomposes at normal temperatures in sunlight in the absence
         of air, and in the dark in the presence of air.
   9.3. Phosgene is a decomposition product of chloroform. Phosgene exposure can
         cause damage to the central nervous system in concentrations at only a
         small fraction of the permissible exposure limit of chloroform.
   9.4. If possible, chloroform that is stabilized with alcohol should be purchased. If
         non-stabilized chloroform is necessary for the work, it needs to be treated
         like peroxide forming compounds and be used up in a short amount of time.
         Amylène is also used as a stabilizer, but there is evidence that it may not
         prevent phosgene generation.
9.5. If an unstabilized chloroform older than one year is discovered it should be disposed as hazardous waste.

9.6. Stabilized chloroform should be disposed of after it has been open for longer than one year.

10. ANHYDROUS HF (GAS):

10.1. Hydrogen Fluoride may react with the iron in carbon steel cylinders to form iron fluoride and hydrogen. The gaseous hydrogen collects in the vapor space and builds pressure over an extended period of time.

10.2. In order to minimize the possibility that the pressure would build to unsafe levels, cylinders should be pressure checked with a suitable pressure gauge during the recommended maximum two-year shelf life period. Cylinders should be returned to the supplier after two years, if they are not being used.

10.3. A First In First Out (FIFO) inventory rotation should be applied to any cylinders that you may be using in your laboratory. The potential exists for pressure excursions of several hundred pounds to occur during the recommended storage time frame of Anhydrous HF. Pressures may continue to rise over longer storage periods. If you discover any HF cylinders that have been in storage longer than two years, immediately contact RMS: 631-5037.

11. PERSONAL PROTECTIVE EQUIPMENT (PPE):

11.1. Review the Material Safety Data Sheet (MSDS) for the specific compound that is being used for the appropriate PPE requirements. At a minimum, wear goggles, lab coat or apron, and appropriate gloves.

12. WASTE DISPOSAL:

12.1. Request a Hazardous Waste Pickup two months before the expiration date.

12.2. If there are time-sensitive materials that are expired or compromised, please contact RMS Waste Personnel prior to pick-up. Contact information is available on the RMS web site at http://riskmanagement.nd.edu/laboratory-safety/hazardous-waste-pickup-schedule/

13. RECORD KEEPING:

13.1. All chemicals shall be listed on the lab’s chemical inventory. Time sensitive chemicals shall also be dated on the inventory.

13.2. The chemical inventory shall be reviewed annually.

13.3. Remove time sensitive chemicals from the inventory when they have been disposed.

14. FREQUENCY OF REVIEW:

14.1. RMS will review SOP on an annual basis.

14.2. Review date will be added to SOP upon review.
APPENDIX A

List of Common Peroxide-Forming Chemicals

1. Chemicals that may auropolymerize as a result of peroxide accumulation. Uninhibited chemicals must be disposed of within 24 hours of being opened. RMS must be notified by the lab personnel before their purchase and use. Inhibited chemicals must be disposed of within 12 months of being opened:

<table>
<thead>
<tr>
<th>Acrylic acid $^b$</th>
<th>Tetrafluoroethylene $^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acrylonitrile $^b$</td>
<td>Vinyl acetate</td>
</tr>
<tr>
<td>Butadiene $^c$</td>
<td>Vinyl acetylene</td>
</tr>
<tr>
<td>Chloroprene $^c$</td>
<td>Vinyl chloride</td>
</tr>
<tr>
<td>Chlorotrifluoroethylene</td>
<td>Vinyl pyridine</td>
</tr>
<tr>
<td>Methyl Methacrylate $^b$</td>
<td>Vinyladiene chloride</td>
</tr>
<tr>
<td>Styrene</td>
<td></td>
</tr>
</tbody>
</table>

2. Chemicals that form explosive levels of peroxides without concentration by evaporation or distillation. Some of these may form explosive concentrations of peroxide even if never opened. These chemicals must be disposed of within 3 months of being opened:

<table>
<thead>
<tr>
<th>Butadiene $^a$</th>
<th>Isopropl ether $^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloroprene $^a$</td>
<td>Tetrafluoroethylene</td>
</tr>
<tr>
<td>Divinylacetylene</td>
<td>Vinylidene chloride</td>
</tr>
</tbody>
</table>

3. Chemicals that form explosive levels of peroxides on concentration by evaporation or distillation or otherwise treated to concentrate the peroxides. These peroxide formers that must be disposed of within 12 months of being opened:

<table>
<thead>
<tr>
<th>(2-Ethoxyethyl)-o-benzoyl benzoate</th>
<th>Buten-3-ylene</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt; 80% Hydrogen Peroxide</td>
<td>Chloroacetdehyde diethyl acetal</td>
</tr>
<tr>
<td>§ - Bromophenetole</td>
<td>Chloromethyl methyl ether $^e$</td>
</tr>
<tr>
<td>§ - Chlorophenetole</td>
<td>Chloromethylene</td>
</tr>
<tr>
<td>1 - Pentene</td>
<td>Cumene</td>
</tr>
<tr>
<td>1-(2-Chloroethoxy)-2-Phenoxyethane</td>
<td>Cyclohexanol</td>
</tr>
<tr>
<td>1-(2-Ethoxyethoxyethyl)ethyl acetate</td>
<td>Cyclohexene</td>
</tr>
<tr>
<td>1, 1-Dimethoxymethane</td>
<td>Cyclooctane</td>
</tr>
<tr>
<td>1, 2-Bis(2-chloroethoxy) ethane</td>
<td>Cyclopropyl methyl ether</td>
</tr>
<tr>
<td>1, 2-Dibenzyl oxyethane</td>
<td>Decahydronaphtalene</td>
</tr>
<tr>
<td>Chemical Name</td>
<td>Structural Formula</td>
</tr>
<tr>
<td>---------------</td>
<td>--------------------</td>
</tr>
<tr>
<td>1, 2-Dichloroethyl ethyl ether</td>
<td>Di(1-propynyl) ether</td>
</tr>
<tr>
<td>1, 2-Diethoxymethane</td>
<td>Di(2-propynyl) ether</td>
</tr>
<tr>
<td>1, 2-Epoxy-3-isopropoxypropane</td>
<td>Diacetylene</td>
</tr>
<tr>
<td>1, 2-Epoxy-3-phenoxyp propane</td>
<td>Diallyl ether</td>
</tr>
<tr>
<td>1, 3-Dioxapne</td>
<td>Dicyclopentadiene</td>
</tr>
<tr>
<td>1, 5-p-Methadiene</td>
<td>Diethoxymethane</td>
</tr>
<tr>
<td>1, 3 Butadiyne</td>
<td>Diethyl acetal isoamyl benzyl ether</td>
</tr>
<tr>
<td>1, 3, 3-Trimethoxy propene</td>
<td>Diethyl ether</td>
</tr>
<tr>
<td>1-Ethoxynaphthalene</td>
<td>Diethyl ethoxymethylene malonate</td>
</tr>
<tr>
<td>1-Ethyoxo-2-propyne</td>
<td>Diethyl fumarated</td>
</tr>
<tr>
<td>1-Phenylethanol</td>
<td>Diethylene glycol dimethyl ether</td>
</tr>
<tr>
<td>2, 2-Diethoxypropane</td>
<td>Diethylketene</td>
</tr>
<tr>
<td>2, 4-Dichlorophenetole</td>
<td>Dimethoxymethane</td>
</tr>
<tr>
<td>2, 4 Dinitrophenetole</td>
<td>Dimethyl ketene</td>
</tr>
<tr>
<td>2, 5 Hexadiyn-1-ol</td>
<td>Di-n-propoxymethane</td>
</tr>
<tr>
<td>2-Bromomethyl ethyl ether</td>
<td>Dioxanes</td>
</tr>
<tr>
<td>2-Butane</td>
<td>Ethoxyacetophenone</td>
</tr>
<tr>
<td>2-Chlorobutadiene</td>
<td>Ethyl §-ethoxypropionate</td>
</tr>
<tr>
<td>2-Cyclohexen-1-ol</td>
<td>Ethyl Vinyl Ether</td>
</tr>
<tr>
<td>2-Ethoxyethyl acetate</td>
<td>Ethylene glycol dimethyl ether (glyme)</td>
</tr>
<tr>
<td>2-Ethylacrylaldehyde oxime</td>
<td>Furan p-Phenylphenetone</td>
</tr>
<tr>
<td>2-Ethylbutanol</td>
<td>Isoamyl benzyl ether</td>
</tr>
<tr>
<td>2-Ethylhexanal</td>
<td>Isoamyl ether</td>
</tr>
<tr>
<td>2-Hexanol</td>
<td>Isobutyl vinyl ether</td>
</tr>
<tr>
<td>2-Methoxy ethanol</td>
<td>Isopropy 1, 2, 4, 5 trichlorophenoxyacetate</td>
</tr>
<tr>
<td>2-Methoxyethyl vinyl ether</td>
<td>1, 1, 2, 3 -Tetrachloro-1, 3-butadiene</td>
</tr>
<tr>
<td>2-Methyltetrahydrofuran</td>
<td>Limonene</td>
</tr>
<tr>
<td>2-Penten-1-ol</td>
<td>Isophorone</td>
</tr>
<tr>
<td>2-Phenylethanol</td>
<td>m, o, p-Diethoxybenzene</td>
</tr>
<tr>
<td>2-Propanol</td>
<td>Methox-y-1, 3, 5, 7-cyclooctetraene</td>
</tr>
<tr>
<td>3-Ethoxy-o-propionitrile</td>
<td>Methyl isobutyl ketone</td>
</tr>
<tr>
<td>3, 3-Dimethoxypropene</td>
<td>Methyl p-(n-amoxly) benzoate</td>
</tr>
<tr>
<td>3-Bromopropyl phenyl ether</td>
<td>Methyl-1-butanol</td>
</tr>
<tr>
<td>3-Isopropospropionitile d</td>
<td>Methylacetylene</td>
</tr>
<tr>
<td>3-Methoxy ethyl acetate</td>
<td>Methylcyclopentane</td>
</tr>
<tr>
<td>3-Methoxy-1-butyl acetate</td>
<td>m-Nitrophenetole 1-Octene</td>
</tr>
<tr>
<td>4-Heptanol</td>
<td>n-Amyl ether</td>
</tr>
<tr>
<td>4, 5-Hexadien-2-yn-1-ol</td>
<td>n-Butyl phenyl ether</td>
</tr>
<tr>
<td>Chemical Name</td>
<td>Molecular Formula</td>
</tr>
<tr>
<td>-------------------------------------</td>
<td>---------------------------------</td>
</tr>
<tr>
<td>4-Methyl-2-pentanol</td>
<td>n-Butyl vinyl ether</td>
</tr>
<tr>
<td>4-Methyl-2-pentanone</td>
<td>n-Hexyl ether</td>
</tr>
<tr>
<td>4-Penten-1-ol</td>
<td>n-Methylphenetole</td>
</tr>
<tr>
<td>4-Vinyl Cyclohexene</td>
<td>n-Propylisopropyl ether</td>
</tr>
<tr>
<td>Acetal</td>
<td>o, p-Ethoxyphenyl isocyanate</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>o,p-Iodophenetole</td>
</tr>
<tr>
<td>Acrolein</td>
<td>o-Bromophenetole</td>
</tr>
<tr>
<td>Allyl ether</td>
<td>o-Chlorophenetole</td>
</tr>
<tr>
<td>Allyl ethyl ether</td>
<td>Other Secondary Alcohols</td>
</tr>
<tr>
<td>Allyl phenyl ether</td>
<td>Oxy bis (2 ethyl acetate)</td>
</tr>
<tr>
<td>a-Phenoxypropionitrile chloride</td>
<td>Oxy bis (2-ethyl benzoate)</td>
</tr>
<tr>
<td>B,B Dioxidipropionitrile</td>
<td>p-(n-Amyloxy)benzoyl chloride</td>
</tr>
<tr>
<td>Benzyl 1-naphthyl ether</td>
<td>p-Bromophenetole</td>
</tr>
<tr>
<td>Benzyl alcohol</td>
<td>p-Chlorophenetole</td>
</tr>
<tr>
<td>Benzyl ether</td>
<td>p-Dibenzyloxybenzene</td>
</tr>
<tr>
<td>Benzyl ethyl ether</td>
<td>p-Di-n-butoxybenzene</td>
</tr>
<tr>
<td>Benzyl methyl ether</td>
<td>Perchloric Acid</td>
</tr>
<tr>
<td>Benzyl n-butyl ether</td>
<td>Phenoxy acetyl chloride</td>
</tr>
<tr>
<td>Bis(2-chloroethyl) ether</td>
<td>Phenyl o-propyl ether</td>
</tr>
<tr>
<td>Bis(2-ethoxyethyl) ether</td>
<td>p-Phenylphenetone</td>
</tr>
<tr>
<td>Bis(2-ethoxyethyl) phthalate</td>
<td>Sodium 8, 11, 14 elcosate traenoate</td>
</tr>
<tr>
<td>Bis(2-methoxyethyl) adipate</td>
<td>Sodium ethoxyacetylide</td>
</tr>
<tr>
<td>Bis(2-methoxyethyl) carbonate</td>
<td>Tert-Butyl ethyl ether</td>
</tr>
<tr>
<td>Bis(2-methoxyethyl) ether</td>
<td>Tert-Butyl methyl ether</td>
</tr>
<tr>
<td>Bis(2-methoxyethyl phthalate</td>
<td>Tetrahydrofuran (THF)</td>
</tr>
<tr>
<td>Bis(2-methoxymethyl) adipate</td>
<td>Tetrahydronaphthalene</td>
</tr>
<tr>
<td>Bis(2-n-butoxyethyl) phthalate</td>
<td>Tetrahydroxypropan</td>
</tr>
<tr>
<td>Bis(2-phenoxyethyl) ether</td>
<td>Triethylene glycol diacetate</td>
</tr>
<tr>
<td>Bis(4-chlorobutyl) ether</td>
<td>Trithylene glycol dipropionate</td>
</tr>
<tr>
<td>Bis(chloromethyl) ether</td>
<td>Vinyl ethers</td>
</tr>
<tr>
<td>Bis[2-(methoxyethoxy)ethyl] ether</td>
<td>Vinylene carbonate</td>
</tr>
<tr>
<td>B-methoxypropionitrile</td>
<td>Vinylidene carbonate</td>
</tr>
</tbody>
</table>

Key:

- When stored as a liquid monomer
- Although these chemicals form peroxides, no explosion involving these monomers have been reported.
- 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.
- OSHA regulated carcinogen.
- Extremely reactive and unstable compounds.
## APPENDIX B

### CAUTION

**PEROXIDE FORMING CHEMICAL**

<table>
<thead>
<tr>
<th>Date Received:</th>
<th>INHIBITOR ADDED</th>
</tr>
</thead>
<tbody>
<tr>
<td>Date Opened:</td>
<td>Y, N, or N/A</td>
</tr>
<tr>
<td>Date Expired:</td>
<td>Type</td>
</tr>
</tbody>
</table>

Limited shelf life. Store tightly closed away from light and heat.

<table>
<thead>
<tr>
<th>Test Date</th>
<th>Peroxide</th>
<th>Tester Initials</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Creation Date: 6/13

Developed by RMS

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Review Date: