3.17 Peroxide-Forming Chemicals and Other Time-Sensitive Materials – Procedures for Safe Handling and Management

Some laboratory chemicals, known as time-sensitive chemicals, can become dangerous with age. This can be due to chemical reactions, over-pressurization of containers, toxicity, and other hazardous properties. For this reason, handling and management of time-sensitive chemicals are of particular importance. These chemicals include the following:

- Chemicals that form peroxides upon aging;
- Picric acid and other multi-nitro aromatics;
- Chloroform;
- Anhydrous hydrogen fluoride and hydrogen bromide;
- Liquid hydrogen cyanide;
- Formic acid; and
- Alkali metals (such as potassium, sodium and lithium).

Other relevant sections of this Plan include; SOP 3.2, Procedures for Proper Labeling, Storage, and Management of Chemicals; SOP 3.7, Reactive Chemicals; and the table of Peroxide-Forming Chemicals in Appendix B.

3.17.1 Peroxide-Forming Chemicals

The peroxide-forming chemicals include common organic solvents and can react with atmospheric oxygen to undergo autoxidation or peroxidation, producing unstable and dangerous organic peroxides and hydroperoxides.

Formation of peroxides is accelerated by light and heat. Substances which have undergone peroxidation are sensitive to thermal or mechanical shock and may explode violently. All laboratory workers must learn to recognize and safely handle peroxidizable compounds. Peroxide-forming substances include aldehydes, ethers (especially cyclic ether), compounds containing benzylic hydrogen atoms, compounds containing the allylic structure (including most alkenes), vinyl and vinylidine compounds. A list of these chemicals can be found in Appendix B.

3.17.1.1 Safe Handling and Usage

- The material must be less than 12 months old or less than the expiration date on the label. Labels on peroxide-forming substances must contain the date the container was received and the date it was first opened.
- Include a notice such as **Warning Peroxide-Former** on the container.
- If the material is greater than 12 months old or past the expiration date, it should be assessed for other factors such as; duration of exposure to sunlight, volume of container, security of the seal; and exposure to changes in temperature. If you do not know the answer to any of these questions, find someone who does. **Do not open the container to check for peroxide formation, as the material could be shock-sensitive.** Call IUEHS for your respective campus for technical assistance.
- If the container is more than 12 months old or past the expiration date, do not move the container. Post a sign reading "DANGER: possible shock-sensitive chemical" and contact IUEHS for your respective campus for technical assistance.
- Never use a metal spatula with peroxides. Contamination by metals or disturbance of the crystals can lead to explosive decompositions.
- Store peroxides and peroxide-forming compounds according to the manufacturer's recommendations, away from light and heat.

- If storing peroxide formers in a refrigerator, the refrigerators must be designed for the storage of flammable substances. Do not use domestic refrigerators to store flammable liquids.
- Distilled solvents stored for later use must be dated upon distillation. Distilled solvents placed in storage must be sealed and stored under nitrogen or argon.
- Do not open the container if 1) crystals are visibly present on or in the container or lid, 2) if a precipitate has formed or an oily viscous layer is present, or 3) if the container has been opened and is more than 12 months old or past the expiration date. Call University Environmental Health and Safety (IUEHS) at your respective campus for assistance.

3.17.1.2 Disposal

- Dispose of Class A (see table in Appendix B) peroxidizable solvents within 3 months of receipt (or synthesis). Date all containers upon synthesis of the material. See IU Waste Management Program for disposal.
- Dispose of Class B and C peroxide-formers within 12 months of reciept or on or before the If the container has a manufacturer's expiration date on the label.
- Distilled peroxide-forming solvents contain no stabilizer and must be disposed within 3 months of distillation.
- Turn all materials in to IUEHS for your respective campus.
- The lab or department is responsible for any extra charges (i.e. high hazard disposal) that may be incurred in the event that containers of peroxide forming solvents have not been managed properly including management or abandonment of solvents being distilled and stored for later use.
- Additional information can be found in the IU Waste Management Program.

3.17.2 Picric Acid and Other Multi-Nitro Aromatics

Picric acid ($C_6H_3N_3O_7$ and other multi-nitro aromatics) can be extremely dangerous if allowed to dry. Picric acid with a moisture content of greater than 30% is considered a flammable solid by the Department of Transportation (DOT). Picric acid with a moisture content of less than 30% is considered a Class 1.1D explosive by DOT and is very shock sensitive. DO NOT OPEN OR MOVE a container of dry picric acid.

3.17.3 Chloroform

Chloroform ($CHCl_3$) reacts with air to form phosgene gas (CCl_2O) which has a very low IDLH (Immediately Dangerous to Life or Health) value of 2 parts per million. Always open chloroform in a fume hood.

3.17.4 Formic acid

Formic acid (90-100% CH_2O_2) decomposes to form carbon monoxide and water (CO + H_2O). Pressure greater than 100 psi can develop with prolonged storage of 1 year or greater which is sufficient to break a sealed glass container. Vent containers frequently and read the product literature. Some have pressure relief caps and some Safety Data Sheets may recommend refrigeration.

3.17.5 Anhydrous Hydrogen Fluoride, Hydrogen Bromide, and Other Corrosive Gases

Anhydrous hydrogen fluoride and hydrogen bromide are in a liquid phase above 15 psi. Stored in carbon steel cylinders (lecture bottles) they can react with the steel to form iron fluoride and hydrogen gas. Lecture bottles have a typical working pressure of 1800 psi and these chemicals have a 2-year shelf life. Several anhydrous hydrogen fluoride cylinders have failed (at interior pressures greater than 2,400 psi) after 14-24 years of storage although there have been no reported problems with hydrogen bromide.

Other corrosive gases such as hydrogen chloride and hydrogen sulfide must be returned for disposal every two years.

3.17.6 Liquid Hydrogen Cyanide

Liquid hydrogen cyanide (CHN) is a liquid that boils at 26^{o} C and is stored in low pressure cylinders. With no stabilizer (e.g. 1% sulfuric acid) present polymerization can occur along with the production of ammonia which also helps catalyze the process. A crust can form on the liquid that, when jarred, can break off and fall into the liquid causing rapid exothermic polymerization and rupture of the cylinder causing fragmentation and release of this acutely toxic gas.

3.17.7 Alkali Metals

The alkali metals (such as potassium, sodium lithium and sodium-potassium alloys) can react with dissolved oxygen when stored under mineral oil to form oxides and superoxides that can catch fire upon cutting. The oxidation forms a yellow or orange crust or coating. Lithium stored under nitrogen can form nitrides and the formation of the nitride is autocatalytic and can eventually autoignite.