3.7. **Reactive Chemicals** – Procedures for Safe Handling and Storage

Reactives are substances that have the potential to vigorously polymerize, decompose, condense, or become self-reactive due to shock, pressure, temperature, light, or contact with another material. All reactive hazards involve the release of energy in a quantity or at a rate too great to be dissipated by the immediate environment of the reaction system so that destructive effects occur. Reactive chemicals include: 1) **explosives**, 2) **organic peroxides**, 3) **water-reactives** and 4) **pyrophorics**. Effective control is essential to minimize the occurrence of reactive chemical hazards.

3.7.1. Explosives

A chemical that causes sudden, almost instantaneous release of pressure, gas, and heat when subjected to sudden adverse conditions. Heat, light, mechanical shock, detonation, and certain catalysts can initiate explosive reactions. Compounds containing the functional groups azide, acetylide, diazo, nitroso, haloamine, peroxide, or ozonide are sensitive to shock and heat and can explode violently.

- Appropriate personal protective equipment (e.g., face shield, safety goggles, leather outer gloves, chemical resistant gloves, fire-resistant or all cotton lab coat) must be worn when working with explosives.
- Before working with explosives, understand their chemical properties, know the products of side reactions, know the incompatibility of certain chemicals, and monitor environmental catalysts such as temperature changes.
- Containers should be dated upon receipt and when opened. Expired explosives should be disposed of through IUEHS for your respective campus promptly.
- Explosives should be kept to the minimum necessary for the procedure.
- If there is a chance of explosion, use protective barriers (e.g., fume hood sash and safety shield) or other methods for isolating the material or process.
- Explosives should be stored in a cool, dry, and protected area. Segregate from other material that could create a serious risk to life or property should an accident occur.

3.7.2. Organic Peroxides

These chemicals contain an -O-O- structure bonded to organic groups. These compounds can be considered as structural derivatives of hydrogen peroxide, H-O-O-H, in which one or both of the hydrogen atoms have been replaced by an organic group. Generally, organic peroxides are low-powered explosives that are sensitive to shock, sparks, and heat due to the weak -O-O- bond which can be cleaved easily. Some organic compounds such as ethers, tetrahydrofuran, and p-dioxane can react with oxygen from the air forming unstable peroxides. Peroxide formation can occur under normal storage conditions, when compounds become concentrated by evaporation, or when mixed with other compounds. These accumulated peroxides can violently explode when exposed to shock, friction, or heat.

- Appropriate personal protective equipment (e.g., safety goggles, gloves, fire-resistant or all cotton lab coat) must be worn when working with organic peroxides or peroxide-forming compounds.
- Containers must be labeled with the receiving and opening dates. Discard unopened material within the timeframes outlined in the IU Waste Management Guide for your respective campus.
- Containers should be airtight, and stored in a cool, dry place away from direct sunlight and segregated from incompatible chemicals.
- Do not refrigerate Peroxide-formers, liquid peroxides, or solutions below the temperature at which the peroxide freezes or precipitates. Peroxides in these forms are extra sensitive to shock (never store diethyl ether in a refrigerator or freezer).

- Unused peroxides should never be returned to the stock container.
- Do not use metal spatulas with peroxide-formers. Use only ceramic or plastic spatulas. Contamination by metal can cause explosive decomposition.
- Avoid friction, grinding, and all forms of impact, especially with solid organic peroxides. Never use glass containers with screw cap lids or glass stoppers. Instead, use plastic bottles and sealers.
- Containers with obvious crystal formation around the lid or viscous liquid at the bottom of the container must NOT be opened or moved. Call IUEHS for your respective campus (see Laboratory Safety Contacts) for guidance and disposal.
- Organic peroxides produce vapors during decomposition. This can result in pressure build-up. The rapid increase in pressure may cause explosive rupture of containers, vessels or other equipment.
- Ignition sources must be avoided.
- Organic Peroxides have a Self-Accelerating Decomposition Temperature (SADT). Never store organic peroxides where they may be exposed to temperatures above the SADT. At or above this temperature an irreversible runaway reaction will take place. The recommended storage temperature is printed on the product label and Safety Data Sheet.

For more information on organic peroxide-forming compounds please refer to SOP 3.17, Peroxide-Forming Chemicals and Other Time-Sensitive Materials, Procedures for Safe Handling and Management and Appendix B of this document, for a list of chemicals that can form peroxides upon aging.

3.7.3. Water-Reactives

A chemical that reacts with water or moisture in the air (humidity) releasing heat or flammable, toxic gas. Examples include alkali metals, alkaline earth metals, carbides, hydrides, inorganic chlorides, nitrides, peroxides, and phosphides.

- Appropriate personal protective equipment (e.g., safety goggles, gloves, fire-resistant or all cotton lab coat) must be worn when working with water-reactives.
- Water-reactives should be stored under mineral oil in a cool, dry place and isolated from other chemicals.
- Water-reactives must not be stored near water, alcohols, and other compounds containing acidic OH.

In case of fire, keep water away. Appropriate fire extinguishers should be available in areas where water-reactives are used (use a Type “D” fire extinguisher to extinguish active metal fires).

3.7.4. Pyrophorics

A chemical that ignites spontaneously in air below 130^{o} F (54^{o} C). Often the flame is invisible. Examples of pyrophoric materials include silane, silicon tetrachloride, white and yellow phosphorus, sodium, tetraethyl lead, potassium, nickel carbonyl, and cesium.

- Appropriate personal protective equipment (e.g., safety goggles, gloves, fire-resistant or all cotton lab coat) must be worn when working with pyrophorics.
- Pyrophorics must be used and stored in inert environments.
- Appropriate fire extinguishers must be available in areas where pyrophorics are used.

3.7.5. Synthesis

Synthesis of any reactive or energetic (explosive) compound is subject to the following requirements:

- The principal investigators written prior approval of the procedure is required. (use Chemical Reaction Hazard Assessment Form, Appendix A, Form LCS-7).
- The procedure must be documented in writing with specific step by step instructions.
- The principal investigator is required to provide documented procedure-specific training and documented daily supervision of the research.
- A written hazard analysis of the procedure is required prior to start up and whenever a change to the procedure is made. Worst case scenarios must be considered (Appendix A, Form LCS-7).
- Appropriate hazard controls, as determined by the hazard analysis, must be in place prior to the experiment.
- The synthesized quantity is limited to 100 milligrams. Synthesis of more than 100 mg of reactive or energetic compounds is prohibited.