Highly Reactive Chemicals-Generic Procedures for Safe Handling and Storage[1]

Highly reactive chemicals are those that have the potential to vigorously polymerize, condense, or become self-reactive due to shock, pressure, temperature, light, or contact with another material. Examples of highly reactive chemicals are explosives, peroxides, water-reactives, and pyrophorics. All work involving highly reactive chemicals must be approved by the PI before initiation of the work.

- Reactive chemicals must be handled with caution; this includes segregation in storage and prohibiting the mixing of even small quantities with other chemicals without consideration of appropriate procedures, and use of PPE.
- Chemical reactions conducted at temperatures or pressures above or below ambient conditions must be performed in a manner that minimizes hazards such as explosion or vigorous reaction. Provide a mechanism for adequate temperature control and heat dissipation.
- Minimize the quantity of reactive chemicals used or synthesized to the smallest amount needed.
- Utilize shields and barricades, and PPE (such as face shields with throat protectors and heavy gloves) whenever there is a possibility of explosion or vigorous chemical reaction.
- Glass equipment operated under vacuum or pressure must be shielded, wrapped with tape, or otherwise protected from shattering.

Shock/Heat Sensitive Materials are compounds containing the functional groups azide, acetylide, diazo, nitroso, haloamine, peroxide and ozonide are sensitive to shock and heat and can explode violently, causing 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. Appropriate personal protective (face shield, safety goggles, leather outer gloves, chemical resistant gloves, lab coat, etc.) must be worn when working with explosives.

- Before working with explosives, understand their chemical properties, know the products of side reactions, the incompatibility of certain chemicals, and monitor environmental catalysts such as temperature changes.
- Containers shall be dated upon receipt and when opened. Expired explosives should be discarded promptly.
- Explosives should be kept at 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.

Organic Peroxides are one of the most hazardous chemicals commonly used in laboratories. Most organic peroxides are sensitive to heat, impact, friction, light and readily react with oxidizing and reducing compounds, and are highly flammable. Since the sensitivity and instability of these compounds vary, always review the properties of specific compounds prior to their use. Common peroxidizable chemicals include; 2-

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butanol, benzyl alcohol, cyclohexane, 2-propanol, styrene, hydrogen peroxide, and other secondary alcohols. Appropriate personal protective equipment (safety goggles, gloves, lab coat, etc.) must be worn when working with organic peroxides or peroxide-forming compounds.

- Containers must be airtight and stored in a cool, dry place away from direct sunlight. Segregate from incompatible chemicals.
- Peroxide formers, liquid peroxides, or solutions must not be refrigerated 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 must never be returned to the stock container.
- Metal spatulas must not be used with peroxide formers. Only ceramic or plastic spatulas can be used. Contamination by metal can cause explosive decomposition.
- Friction, grinding, and all forms of impact, especially with solid organic peroxides should be avoided. Never use glass containers with screw cap lids or glass stoppers. Instead, use plastic bottles and sealers.
- Testing for the presence of peroxides shall be performed periodically as needed.
- Containers with obvious crystal formation around the lid or viscous liquid at the bottom of the container must not be opened or moved.
- Refer to Perxoide Forming Compounds for the DRI guidelines on peroxide formers and more information regarding safe handling and storage.

Water-reactives react with water or moisture in the air releasing heat or flammable, toxic gas. Examples include alkali metals, alkaline earth metals, carbides, hydrides, inorganic chlorides, nitrides, peroxides, and phosphides.

- Appropriate PPE should be worn when working with water-reactives.
- Water-reactives should be stored under mineral oil in a cool, dry place. Isolate 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 (Type “D” used for metal fires).

Pyrophorics ignite spontaneously in air below 130º F (54º 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 PPE must be worn when working with pyrophorics.
- Pyrophorics must be used and stored in inert environments.
- Appropriate fire extinguishers should be available in areas where pyrophorics are use.

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