| Standard Operating Procedure (SOP) | | | |
|---|---|---|---|
| *Title:* **Reactive Chemicals** | | | |
| *Approved by:* | | *Effective Date:* | April 25, 2007 |
| David A. Brown, |  | *Revised Date:* | |
| Director, EH&S | | *Section:* | **CHEM** |

## PURPOSE

To protect not only the persons using the listed materials from any untoward physical or health hazards associated with the materials but also all faculty and staff. This policy requires that a competent person review the written procedures and facilities associated with the use of these chemicals. The competent person will make recommendations to the Chemical Safety Committee that the work procedure is approved or that it is being modified before going forward.

## SCOPE

This policy applies to all faculty, staff and students located in facilities owned or leased by Wake Forest University Health Sciences.

## RESPONSIBILITIES

Environmental Health and Safety

- Review procedures and make recommendations.
- Develop Standard Operating Procedures for common water reactive and air reactive chemicals.

Competent Persons

- Review procedures involving listed chemicals and assess the probability that the proposed procedures can be done safely.
- Recommend changes to procedures under review.
- Recommend acceptance to the Chemical Safety Committee.

Principal Investigators

- Submit Chemical Safety Application for procedures involving reactive chemicals along with detailed procedure for use of chemical.

## PERSONAL PROTECTIVE EQUIPMENT

- Wear appropriate personal protective clothing while working with highly reactive materials. This might include: impact resistant safety glasses or goggles, a face shield, gloves, a lab coat (to minimize injuries from flying glass or an explosive flash), and a shield.
- Conduct work within a chemical fume hood as much as possible and pull down the sash as far, as is practical. While the experiment does not require you to reach into the fume hood, keep the sash closed.
- Barriers can offer protection of personnel against explosions and should be used. Many safety catalogs offer commercial shields that are commonly polycarbonate and are weighted at the bottom for stability. It may be necessary to secure the shields firmly to the work surface.

### Water Reactive Chemicals

- Store water reactive chemicals to ensure there is no way that they can come into contact with water.
- When water reactive materials come in contact with water, one or more of the following can occur:
    - Liberation of heat which may cause ignition of the chemical itself if it is flammable, or ignition of flammables that are stored nearby
    - Release of a flammable, toxic, or strong oxidizing gas
    - Release of metal oxide fumes
    - Formation of corrosive acids
- Water reactive chemicals can be particularly hazardous to firefighting personnel responding to a fire in a lab, because water is the most commonly used fire-extinguishing medium. Examples of water reactive materials:
    - alkali metals: silanes
    - lithium, sodium, potassium alkylaluminums
    - magnesium zinc
    - aluminum

**TABLE 1** lists some water reactive chemicals that react violently with water. These chemicals shall be handled and stored away from both water and water vapor.

| **TABLE 1 - WATER REACTIVE CHEMICALS** |
|---|
| Alkali metals, such as Sodium (Na), Potassium (K), Lithium (Li) |
| Alkali metal hydrides and alkali metal amides, like Lithium aluminum hydride ($LiAlh_4$) or sodium amide ($NaNH_3$) |
| Anhydrous metal halides of Aluminum (Al), Antimony (Sb), Arsenic (As), Iron (Fe), Phosphorous (P), Sulfur (S), Silicon (Si), Tin (Sn), Titanium (Ti), Zirconium (Zr) such as Aluminum chloride ($AlCl_3$), Titanium trichloride ($TiCl_4$) (very reactive), Titanium dichloride ($TiCl_2$), Zirconium tetrachloride ($ZrCl_4$), and Stannic chloride ($SnCl_4$) |
| Calcium carbide ($CaC_2$) |
| Halides of nonmetals, such as Boron Trichloride ($BCl_3$), Boron Fluoride ($BF_3$), Phosphorous trichloride ($PCl_3$), Phosphorus Pentachloride ($PCl_5$), Sulfur Chloride ($S_2Cl_2$), Silicon Tetrachloride ($SiCl_4$) |
| Inorganic acid halides, such as Phosphorus oxychloride ($P0Cl_3$), Thionyl chloride ($SOCl_3$), Sulfuryl Chloride , or Sulfur Oxychloride ($S0_2Cl_2$), and Phosphorus oxychloride and phosphorus pentoxide ($P_2O_5$) |
| Metal alkyls, such as lithium alkyls , aluminum and magnesium alkyls (Grignard reagents) |
| Metal hydrides of Aluminum (Al), Boron (B), Calcium (Ca), Potassium (K), Lithium (Li), Sodium (Na), like Aluminum hydride ($AlH_3$), Lithium hydride (LiH), Sodium hydride (NaH) |
| Organic acid halides and anhydrides of low molecular weight, like acetyl chloride and acetic anhydride |

## PYROPHORICS AIR REACTIVE CHEMICALS

- Pyrophoric materials can ignite spontaneously in the presence of air.
- Examples of pyrophoric materials:
    - Diethylzinc
    - Triethylaluminum
    - Many organometallic compounds

Air reactive chemicals are chemicals that oxidize readily and ignite spontaneously in air. These materials shall be stored in tightly closed containers under an inert atmosphere or liquid for example nitrogen or kerosene. Air Reactive Chemicals are listed in **TABLE 2**.

| **TABLE 2 – AIR REACTIVE CHEMICALS** |
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| Alkali metals, such as Lithium (Li), Potassium (K) and Sodium (Na) |
| Grignard reagents (RMgX), R= alkyl, X= Halides, like phenylmagnesium bromide |
| Metal alkyls and aryls, such as alkyl Lithium (RLi), alkyl Sodium (RNa), alkyl Aluminum ($R_3Al$), alkyl Zinc ($R_2Zn$), (i.e., tributylaluminum, butyllithium, etc.) |
| Metal carbonyls, such as Nickel Carbonyl ($Ni(C0)_4$), Iron Carbonyl ($Fe(C0)_5$), Cobalt Carbonyl ($Co_2(C0)_8$) |
| Metal powders, such as Aluminum (Al), Cobalt (Co), Iron (Fe), Magnesium (Mg), Manganese (Mn), Palladium (Pd), Platinum (Pt), Tin (Sn), Titanium (Ti), Zinc (Zn), Zirconium (Zr) |
| Metal hydrides, such as Sodium hydride (NaH), and Lithium Aluminum Hydride ($LiAlH_4$) |
| Non-metal hydrides, such Diborane ($B_2H_6$) and other boranes, Phosphene ($PH_3$), Arsine ($AsH_3$) |
| Non-metal alkyls, such as alkyl Boron ($R_3B$), alkyl Phosphorus ($R_3P$), Alkyl silver ($R_3Ag$) |
| Phosphorus (white) |

The class of reactive chemicals includes organic peroxides, peroxidable chemicals, air-reactive and water-reactive chemicals and some flammable solids.

Polymerization Reactions

- Polymerization is a chemical reaction in which two or more molecules of a substance combine to form repeating structural units of the original molecule.
- This can result in an extremely high or uncontrolled release of heat. An example of a chemical, which can undergo a polymerization reaction, is styrene.

Peroxide-Forming Materials

- Peroxides are very unstable and some chemicals that can form them are commonly used in laboratories. This makes peroxide-forming materials some of the most hazardous substances found in a lab.
- Peroxide-forming materials are chemicals that react with air, moisture, or impurities to form peroxides.
- The tendency to form peroxides by most of these materials is greatly increased by evaporation or distillation.
- Organic peroxides are extremely sensitive to shock, sparks, heat, friction, impact, and light. Many peroxides formed from materials used in laboratories are more shock sensitive than TNT. Just the friction from unscrewing the cap of a container of an ether that has peroxides in it can provide enough energy to cause a severe explosion.

Shock-Sensitive Materials

- These materials are explosive and sensitive to heat and shock.
- Examples of shock-sensitive materials:
  - Chemicals containing nitro groups
  - Fulminates

- Hydrogen peroxide (30% +)
- Ammonium perchlorate
- Benzoyl peroxide (when dry)
- Compounds containing the functional groups: acetylide, azide, diazo, halamine,
- Nitroso
- Ozonide.

Organic Peroxides

- Organic peroxide catalysts are classified as oxidizing or flammable materials. All peroxides tend to be unstable, and tend to become increasingly hazardous when allowed to come into contact with organic combustible materials. Protection against heat, shock, friction, contamination, electrical sparks and open flames shall be provided, and the manufacturer's recommended precautions shall be followed for each material.
- Organic peroxides shall be handled, stored, and used in areas remote from combustible materials, and then only by designated personnel who have been instructed in proper handling procedures.
- Deliveries of organic peroxides shall be delivered immediately to the designated storage place to prevent interim storage in general receiving areas.
- Inventory controls shall be established to guard against increased hazards resulting from materials deterioration in storage.
- Where storage of organic peroxides does not exceed 10 pounds, they may be stored in explosion-proof refrigerators. Quantities up to fifty pounds may be stored in explosion-vented room within the building. Quantities greater than fifty pounds shall be stored in a separate building located at least 100 feet from any other building. Storage facilities shall be well ventilated. If the peroxides being stored tend to be unstable at normal temperatures, they shall be refrigerated.

Peroxide Forming Compounds

- Peroxide forming compounds are a special group of chemicals unusually susceptible to oxidation. They require special storage and handling procedures to minimize the formation of unstable peroxides that may create an explosion hazard.
- Peroxides are formed by the action of atmospheric air on this group of compounds. This reaction can be avoided by maintaining an inert gas atmosphere in the vapor space during storage. Low temperature storage slows down the rate of oxidation, as does protection from light with brown bottles or opaque containers. Care must be taken to avoid concentrating peroxides during distillation or evaporation processes. Once formed, peroxides may be shock-sensitive and easily detonated.
- Types of compounds known to form organic peroxides include the following:
  - Aldehydes
  - Ethers - especially cyclic ethers and those derived from primary and secondary alcohol groups.
  - Compounds containing benzyllic hydrogen atoms.
  - Compounds containing allylic structure including most alkenes.
  - Vinyl and vinylidine compounds.
  - Minimizing inventory and retention time may reduce the risk of working with peroxidizable compounds.

## USE AND STORAGE OF REACTIVES

- A good way to reduce the potential risks is to minimize the amount of material used in the experiment. Use only the amount of material necessary to achieve the desired results.
- Always substitute a less hazardous chemical for a highly reactive chemical whenever possible.
- If it is necessary to use a highly reactive chemical, order only the amount that is necessary for the work.

Water Reactive Materials

- Store water-reactive chemicals in an isolated part of the lab. A cabinet far removed from any water sources, such as sinks, emergency showers, and chillers, is an appropriate location.
- Clearly label the cabinet "Water-Reactive Chemicals – No Water".
- Air reactive chemicals are chemicals that oxidize readily and ignite spontaneously in air.

Pyrophorics (Air Reactive)

- Store pyrophorics in an isolated part of the lab and in a clearly marked cabinet.
- Be sure to routinely check the integrity of the container and have the material disposed of through the EHS if the container is corroded or otherwise damaged.

Peroxidizable Compounds

All employees using peroxidizable compounds must follow these handling and storage practices.

- Limit quantity of the peroxidizable compounds to the minimum amount required. Peroxide-forming compounds used on an occasional basis are to be kept to an absolute minimum. Unused chemicals shall not be returned to the container.
- Date all containers of peroxidizable compound both with the date received and the date opened. See the next paragraph of this section for a listing of allowable storage times.
- Store peroxidizable substances at the lowest feasible temperature (e.g., in an explosion proof refrigerator or freezer). Keep containers blanketed with nitrogen or other inert gas.
- Other requirements applicable to peroxidizable compounds are found in Section 6 of the Chemical Hygiene Plan.

Shock Sensitive Materials

- Store these materials separately from other chemicals and in a clearly labeled cabinet.
- Never allow picric acid to dry out, as it is extremely explosive. Always store picric acid in a wetted state.
- Shock sensitive: Observe the following storage limits for these chemicals: 1 pound.

## HEALTH HAZARDS ASSOCIATED WITH REACTIVE CHEMICALS

Reactive chemicals are grouped as a category primarily because of the safety hazards associated with their use and storage and not because of similar acute or chronic health effects. For health hazard information on specific reactive materials consult the MSDS, the manufacturer, or EH&S. However, there are some hazards common to the use of reactive materials. Injuries can occur due to heat or flames, inhalation of fumes, vapors, and reaction products, and flying debris.

## FIRST AID

If someone is seriously injured the most important step to take is to contact emergency responders as quickly as possible. This is best accomplished by directly calling them at 716-9111. Explain the situation and describe the location clearly and accurately. If someone is severely bleeding, apply a sterile dressing, clean cloth, or handkerchief to the wound. Then put protective gloves on and place the palm of your hand directly over the wound and apply pressure and keep the person calm. Continue to apply pressure until help arrives. If a person's clothes are on fire, he or she should drop immediately to the floor and roll. If a fire blanket is available put it over the individual. An emergency shower, if one is immediately available, can also be used to douse flames. If a person goes into shock, have the individual lie down on their back if safe to do so and raise the feet about one foot above the floor.