

# Reactives

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## General Characteristics

- 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 that can undergo a polymerization reaction is styrene.
- Water Reactive Materials
  - When water reactive materials encounter water, one or more of the following can occur: liberation of heat which may cause ignition of the chemical itself (if flammable) or nearby flammables; release of a flammable, toxic, or strong oxidizing gas; release of metal oxide fumes; and/or formation of corrosive acids.
  - Water reactive chemicals can be particularly hazardous to firefighting personnel responding to a laboratory fire because water is the most commonly used fire-extinguishing medium.
  - Examples of water reactive materials are listed below.

Alkali Metals (Lithium, Sodium, Potassium)	Aluminum
Silanes	Magnesium
Alkylaluminums	Zinc
- Pyrophorics
  - Pyrophoric materials can ignite spontaneously in the presence of air.
  - Examples of pyrophoric materials are listed below.

Tert-butyllithium	Triethylaluminum
Phosphorus	Several organometallic compounds
- Peroxide-Forming Materials
  - Peroxides are very unstable, and peroxide forming chemicals are commonly used in laboratories. This makes peroxide-forming materials some of the most hazardous substances found in a laboratory. 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 a bottle cap can provide enough energy to cause a severe explosion.
  - Examples of peroxide-forming materials are listed below.

Diisopropyl Ether	Divinylacetylene
Sodium Amide	Potassium Amide
Dioxane	Diethyl Ether
Tetrahydrofuran	Vinyl Ethers

Butadiene  
Acrylonitrile

Vinylpyridine  
Styrene

- Peroxide Testing

For certain classes of compounds (such as ethers), the date the container was opened should be written on the label. Peroxide formers should have the test history and date of discard written on the label as well.

  - The following tests can detect most (but not all) peroxy compounds, including all hydroperoxides:
    - Add 1 to 3 milliliters (mL) of the test liquid to an equal volume of acetic acid, add a few drops of 5% aqueous potassium iodide solution, and shake. The appearance of a yellow-to-brown color indicates the presence of peroxides. Alternatively, addition of 1 mL of a freshly prepared 10% solution of potassium iodide to 10 mL of an organic liquid in a 25-mL glass cylinder should produce a yellow color if peroxides are present.
    - Add 0.5 mL of the test liquid to 1 mL of 10% aqueous potassium iodide solution and 0.5 mL of dilute hydrochloric acid to which has been added a few drops of starch solution just prior to the test. The appearance of a blue or blue-black color within a minute indicates the presence of peroxides.
    - Peroxide test strips, which turn to an indicative color in the presence of peroxides, are available commercially.
  - None of these tests should be applied to materials (such as metallic potassium) that may be contaminated with inorganic peroxides.
- Other Shock-Sensitive Materials

These materials are also explosive and sensitive to heat and shock:

  - Chemicals containing nitro-functional groups fulminates
  - Hydrogen Peroxide with concentration greater than 30%
  - Ammonium Perchlorate and Benzoyl Peroxide (when dry)
  - Compounds containing the functional groups: acetylide, azide, diazo, halamine, nitroso, and ozonide

### Use and Storage of Reactives

Potential risks are best minimized by reducing the amount of material used in the project. 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
  - Water-reactive chemicals must be stored in an isolated part of the laboratory. An appropriate cabinet location is removed from water sources such as sinks, emergency showers, and chillers. Clearly label the cabinet "Water-Reactive Chemicals – No Water".
- Pyrophorics Material

- Pyrophorics materials must be stored in an isolated part of the laboratory in a clearly marked cabinet. Be sure to routinely check the integrity of the container and have the material disposed of through EHS if the container is corroded or otherwise damaged.
- Peroxide-Forming Materials
  - Do not open the chemical container if peroxide formation is suspected. The act of opening the container can be sufficient to cause a severe explosion. Visually inspect liquid peroxide-forming materials for crystals or unusual viscosity before opening. Pay special attention to the area around the cap. Peroxides usually form upon evaporation, so they will most likely form on the threads under the cap.
  - Date all peroxide forming materials with the date received. Chemicals such as diisopropyl ether, divinyl acetylene, sodium amide, and vinylidene chloride should be discarded after three months. Chemicals such as dioxane, diethyl ether, and tetrahydrofuran should be submitted to EHS for disposal after one year if opened or expired.
  - Store all peroxide-forming materials away from heat, light, and sources of ignition. Light accelerates the formation of peroxides.
  - Secure the lids and caps on these containers to discourage the evaporation and concentration of these chemicals.
  - Never store peroxide-forming materials in glass containers with screw cap lids or glass stoppers. Friction and grinding must be avoided.
  - If you suspect that peroxides may be present, contact EHS. If you notice crystal formation in the container or around the cap, do not attempt to open or move the container. Call EHS for proper disposal.
  - Never distill ether unless it is known to be free of peroxides.
  - Do not use metal spatulas.
  - Do not use glass containers with glass stoppers.
- Other 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 moist environment.

### **Health Hazards Associated with Reactives**

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 SDS, manufacturer, or EHS. However, there are some hazards common to the use of reactive materials. Injuries can occur due to heat, flames, inhalation of fumes, vapors, reaction products, and flying debris.

## **First Aid**

General first aid principles may be applied when treating injuries caused by reactives. For specific first aid instructions, please consult the specific SDS.

- If someone is seriously injured, the most important step is to contact emergency responders as quickly as possible. Explain the situation and describe the location clearly and accurately.
- If someone is severely bleeding, put on protective gloves and then apply a sterile dressing, clean cloth, or handkerchief to the wound. Next, place the palm of your hand directly over the wound and apply pressure. Keep the person calm, and 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 can also be used to douse flames.
- If a person goes into shock, have the individual lie on his or her back (if safe to do so) and raise the feet about one foot above the floor.

## **Personal Protective Equipment**

Wear appropriate personal protective clothing while working with highly reactive materials. This might include impact resistant safety glasses or goggles, face shield, gloves, flame-resistant lab coat, and a blast shield. Conduct work within a chemical fume hood as much as possible, and pull down the sash as far as is practical. When the project does not require you to reach into the fume hood, keep the sash closed.

Barriers protect employees against explosions and should be used. Many safety catalogs offer commercial shields, which are commonly polycarbonate and weighted at the bottom for stability. It may be necessary to secure the shields firmly to the work surface.