Special Chemical Hazards

Fluorine Poisoning Compounds

Hydrofluoric acid in the SMFL represents a special danger in that it is a toxic. Death can and has occurred from exposure to hydrofluoric acid. The danger arises from the fluorine ion which reacts with the body's calcium to interfere with the transmission of nervous signals, proper functioning of muscles, and electrochemical imbalance. Concentrated hydrofluoric acid represents the greatest danger of fluorine poisoning, but there are other solutions in the SMFL that also represent a fluorine poisoning hazard.

- Hydrofluoric acid (HF) is a corrosive that is used extensively in semiconductor processing. Primarily for the etching of silicon dioxide.
- Ammonium Fluoride is also a corrosive that is used in the etching of silicon dioxide. Ammonium Fluoride is the main component of Pad Etch.
- BOE or Buffered Oxide Etch contains both Hydrofluoric Acid and Ammonium Fluoride.
- Pad Etch contains Ammonium Fluoride and is used for etching silicon dioxide deposited over aluminum.

- Special precautions are needed for the safe handling of HF, NH4F, BOE, and Pad Etch.
  They should all be considered as toxic and should never come in contact with the users skin.
  Immediate treatment is required should this occur.

References

- See the SMFL Users Manual for a full description of the dangers of HF and it's treatment.
  - Medical Information about Hydrofluoric Acid and Buffered Oxide Etch (HF & BOE)
  - Paper on HF Fatalities (American Journal of Industrial Medicine)
  - Hydrofluoric Acid SDS
  - Buffered Oxide Etch SDS
  - HF Medical Book by Honeywell
  - Centers for Disease and Control Information on HF
  - Image of severe HF burn and description of treatment - somewhat graphic - has a happy ending (New England Journal of Medicine)

Piranha

- A solution for removing photoresist / organic residues from surfaces. A mixture of sulfuric acid and hydrogen peroxide ranging from 1:1 to 4:1. At the SMFL, we only use solutions of 3:1 or 4:1.

- Piranha solutions are very exothermic when mixed, rapidly heating to over 100C in a short period.

- Safety Reminders For Use of Sulfuric Acid/Hydrogen Peroxide Mixtures
  - It is difficult to dispose of piranha because the waste continues to react and decompose for a long period of time. This builds up pressure in the waste bottles, causing them to burst.
  - Commercially stabilized versions of Piranha are available such as Nanostrip.
  - Personal protective equipment is always required when working with piranha solutions .
  - Whenever handling Piranha, only use glass containers, preferably Pyrex.
  - In preparing a Piranha solution, add hydrogen peroxide to the sulfuric acid - slowly!
    - Piranha solution is very energetic and potentially explosive. When being made it is very likely to become hot, more than 100 degrees C. Handle with care.
    - Substrates should be rinsed and dried before placing them in a piranha bath. Piranhas are used to remove residues of photoresist and acetone, not the compounds themselves.
    - Adding any acids or bases to piranha or spraying it with water will accelerate the reaction. This includes some photoresist developers , some of which are strong bases.
    - Leave the hot piranha solution in an open container until cool on one of the SMFL wetbenches.
    - Do not store piranha. Mix only enough fresh solution for each use. Excess solutions should be disposed via the drain (once cool), followed by flushing with copious amounts of water.
    - Mixing hot piranha with organic compounds may cause an a very violent reaction. This includes materials such as acetone, photoresist, isopropyl alcohol, and nylon.

Tetramethyl Ammonium Hydroxide (TMAH)

TMAH is used in two main areas of semiconductor processing. In higher concentrations (25%) it is used as a crystallographic etch of silicon – similar to KOH etching. In lower concentrations (2.4%), it is used as a positive photoresist developer.

All concentrations of TMAH solutions pose a toxic threat.

- TMAH acts to interfere with the nervous system, often shutting down breathing.

- There is no antidote at this time.
    - Death has occurred shortly (30 min) after exposure to quantities of 25% TMAH solutions (as little as 7% body surface area exposed).
    - Death occurred with 12% BSA of 8.75% TMAH
    - So far, there have been no reported deaths due to exposure of developer strengths (one case had the patient on a respirator in intensive care - 28% BSA of 2.38% TMAH).
- The key to TMAH poisoning appears to be strength of solutions and area exposed. Time to decontamination does not appear to be important – absorption through skin may be very rapid.
- Symptoms of TMAH poisoning
    - Muscle weakness
    - Salivation
    - 2nd or 3rd degree burns
    - Irregular breathing and heartbeat
    - Progressing to coma, shock and in most high concentration cases – death.

- The SMFL *does not* have high concentration TMAH solutions. We do have developers (CD-26) that are at the 2.4% strength.
    - A small amount of developer on your skin will most likely result in a chemical burn.
    - A large amount of developer splashed onto your body is a matter of serious concern that would require immediate hospitalization.

References

- Summary Paper on TMAH Exposures
- Paper on TMAH exposures with development of animal model
- IBM Study on TMAH Exposures

Peroxides

Peroxides are by their nature oxidizing materials. They are therefore stored separately from flammables and solvents. Hydrogen peroxide can form explosive mixtures with some organic substances.

Another hazard of peroxides is oxygen pressure buildup from decomposition. Once peroxide is taken from its original container, it should never be put back.

Used peroxide must be stored in vented cap containers or open containers until decomposition is complete.

The hydrogen peroxide that is found in the SMFL is a 30% solution. It should not be confused with the 3% hydrogen peroxide found in stores for treating skin abrasions/cuts/infections.

Nitric Acid

Nitric acid poses special hazards due to the fact that it is a strong oxidizer. As such, it should always be kept away from flammables, solvents and metals.

If nitric acid is being used at a manual processing bench, no solvents are allowed on the same bench.

The nitric acid at the SMFL is secured and must be requested by the lab users.