

Standard Operating Procedure for Piranha Solution Usage

1- General notice

1. Piranha solutions are used to clean materials used in various fabrication processes. The most common is acid piranha: a 7:3 mixture of concentrated sulfuric acid (H_2SO_4) with 30% hydrogen peroxide (H_2O_2), which is used to remove organic residues from substrates. Also available is base piranha (also known as RCA-1): a 7:3 mixture of ammonium hydroxide (NH_4OH) with 30% hydrogen peroxide (H_2O_2), which leaves an oxide layer on silicon-based materials. Both are equally dangerous when hot. While the acid piranha reaction is self-starting, the base piranha must be heated to 60 °C before the reaction takes off.

Several conditions will cause the reaction to accelerate out of control. "Out of control" can mean anything from boiling over to an explosion. For instance, if the H_2O_2 concentration is $\geq 50\%$, an explosion could occur. Also, as acid piranha reacts violently with organic compounds, inadvertently adding an organic solvent (IPA, Acetone, etc.) could cause an explosion. Be conservative with the hotplate controls, as overheating the solution will cause it to boil over. Additionally, as both solutions will be fuming when heated, steps must be taken — keeping the fume hood sash down as much as possible; placing the hotplate(s) near the back of the fume hood — to prevent accidental inhalation.

2. If there is an accident while using Piranha solutions, call emergency personnel immediately (see Sec.5).

2 - Protection equipment

The handling of Piranha solutions requires special protective equipment in addition to the regular clean room protection outfit: a face shield, acid handling gloves (doubled over the nitrile gloves) and acid apron. Gloves, apron and mask are available next to the HF fume hood.

3 - Piranha solution handling

1. Piranha solutions, as well as any corrosive or hazardous substances, should only be used during operational hours (9 am to 5 pm, Monday through Friday). Please have a second person present if working with piranha after hours.
2. Whenever mixing Piranha, use only Pyrex (borosilicate) glass containers. Containers used during the experiment must be clearly labeled. Please include a date, time and user initials.
3. When preparing the Piranha solution, always add the peroxide to the acid or base.
4. Substrates should be cleaned, rinsed and dried before being placed in a piranha bath. Piranhas are used to remove photoresist (and other organic) **residues**, not the structures themselves.
5. Mixing hot Piranha with organic compounds may cause an explosion. This includes acetone, photoresist, isopropyl alcohol, and nylon.
6. Never store hot Piranha solutions. Piranha stored in a closed container will likely explode. When finished, remove the bowl of Piranha from the hotplate to a ceramic tile in the fume hood. Let the solution stand until cool. This usually takes ~20 minutes.

7. Never leave the cleanroom facility with Piranha solution left out. Always properly dispose of used Piranha before exiting the facility, even if for a short time.

4 - Piranha waste disposal

1. The primary hazard from storage of piranha waste is the potential for gas generation and over pressurization of the container when the solution is still hot. If you store a hot piranha solution in an airtight container, it will explode! Therefore, prior to storing piranha solution, it must be allowed to cool for at least 20 minutes in an open container. **It is your responsibility to make sure that the open container is clearly labeled while the solution is left to cool down. Please include a date, time and user initials.**
2. Once cooled down, transfer the solution to a labeled, closed glass container for waste storage. Do not tighten the cap, as the internal pressure can rise, causing the bottle to explode.
3. Do not attempt to neutralize the solution for sink disposal; in addition to being dangerous, it is a waste of time and materials. Acid Piranha solution is very reactive and corrosive.

5 - Emergency procedure

1. In case of large exposure, the victim should be removed from the contaminated area, and placed under a safety shower while emergency personal is contacted (call 911).
 - a. Additional contact information:
 - i. KU Public Safety Office: 4-5900
 - ii. KU EHS: 4-4089 (8 AM to 5 PM, Monday through Friday)
 - iii. KU EHS 24-Hour Emergency Pager: 838-7421
2. All contaminated clothing should be removed immediately with appropriate gloves and safely discarded.
3. In case of skin contact, the affected area must be immediately rinsed with large amounts of water for at least 15 min.
4. In case of eye contact, irrigate the eye for at least 30 minutes, keeping the eyelids apart and away from eyeballs during irrigation. Place ice packs on eyes until emergency personnel arrive. (From a chemistry discussion forum: "piranha bath spatter + eyeballs = Ray Charles")
5. In case of inhalation, conscious persons should be assisted to an area with fresh, uncontaminated air. Seek medical attention in the event of respiratory irritation, cough, or tightness in the chest. Symptoms may be delayed.

6 - Supply and storage

Do not store piranha. Mix fresh solution for each use. Excess solution should be properly disposed of (see Sec.4).