GENERATION, USE AND DISPOSAL OF PIRANHA SOLUTIONS STANDARD OPERATING PROCEDURE

Type of SOP: ☑ Process ☐ Hazardous Chemical ☐ Hazard Class

1. HAZARD OVERVIEW

The Piranha solution is very energetic, exothermic and potentially explosive. It is very likely to become hot, more than 100°C. Handle with care! When preparing the Piranha solution, always add the peroxide to the acid. The H_2O_2 is added immediately before the process because it immediately produces an exothermic reaction with gas (pressure) release. If the H_2O_2 concentration is at 50% or greater, an explosion could occur. Piranha solution reacts violently with any organic materials. Avoid mixing with incompatible materials such as acids, bases, organic solvents (acetone, isopropyl alcohol) or nylon. Always ensure that all substrates are rinsed and dried before placing them in a Piranha solution. Only use clean glass or Pyrex containers; Piranha solutions are not compatible with plastic.

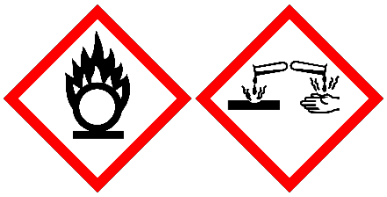
Piranha solutions are VERY DANGEROUS! In addition to being a corrosive liquid and strong oxidizer, there are many things which will cause the reaction to accelerate out of control ranging from foaming out of its vessel to an explosion. Piranhas burn (oxidize) organic compounds. If you provide sufficient fuel for them (i.e. photoresist, IPA), they will generate enormous quantities of heat and gas.

Piranha solution is a strong oxidizer. Both liquid and vapor forms are extremely corrosive to skin and respiratory tract. Direct contact will create skin burns and will be extremely destructive to mucous membranes, upper respiratory tract and eyes.

2. HAZARDOUS CHEMICAL(S) OR CLASS OF HAZARDOUS CHEMICAL(S)

Piranha solutions is a mixture of concentrated sulfuric acid (H_2SO_4) and 30% hydrogen peroxide (H_2O_2).

Sulfuric Acid
Signal word: Danger
Hazard statement(s):
H290 May be corrosive to metals.
H314 Causes severe skin burns and eye damage.



Hydrogen Peroxide
Signal word: Danger
Hazard statement(s):
H271 May cause fire or explosion; strong oxidizer.
H314 Causes severe skin burns and eye damage.
H318 Causes serious eye damage.

Most acids are liquids. Acids, especially when in concentrated form, are most likely to cause immediate pain when they come in contact with the body.

Concentrated aqueous solutions of inorganic acids are not in themselves flammable. Combustion can occur when an acid is mixed with other chemicals or with combustible materials. Acids also react with many metals, resulting in the liberation of hydrogen, a highly flammable gas. Some acids are strong oxidizing agents and can react destructively and violently when in contact with other materials. For this reason, it is essential to read warning labels indicating physical hazards.

3. PERSONAL PROTECTIVE EQUIPMENT (PPE)

a. Eye Protection

At a minimum, chemical splash goggles should be worn. A face shield should be worn when working with larger quantities.

b. Skin and Body Protection

Wear chemical resistant lab coat, long pants, and closed-toe shoes. These laboratory coats must be appropriately sized for the individual and be buttoned to their full length. Laboratory coat sleeves must be of a sufficient length to prevent skin exposure while wearing gloves.

A chemical resistant apron should be used when transferring or using large quantities and splashing is a possibility.

c. Hand Protection

At a minimum, wear a nitrile chemical-resistant glove. Consult with your preferred glove manufacturer to ensure that the gloves you plan on using are compatible with the chemical and usage.

http://www.ansellpro.com/download/Ansell_8thEditionChemicalResistanceGuide.pdf or http://www.showabestglove.com/site/default.aspx

4. ENGINEERING/VENTILATION CONTROLS

All chemicals should be transferred and used in an annually certified laboratory chemical fume hood with the sash at the certified position or lower. The hood flow alarm should be checked to be operating correctly prior to using the hood.

5. SPECIAL HANDLING PROCEDURES AND STORAGE REQUIREMENTS

Only use if the area is properly equipped with a certified eye wash/safety shower within ten seconds of travel. Inform colleagues that this material will be used and where. The fume hood should have signage posted on the sash stating the following, **"WARNING – Piranha Solution in Use"**.

It is essential that all strong corrosives be stored separately from all chemicals with which they may react. Ensure secondary containment and segregation of incompatible chemicals. Also, follow any substance-specific storage guidance provided in Safety Data Sheet (SDS) documentation.

The corrosive properties of these materials and their ability to produce fires or explosions by combination with combustible materials make the following considerations mandatory in the selection of a storage site:

- A relatively cool, dry environment free from extremes of temperature--humidity should be maintained.
- Acids and bases should be stored in a manner that separates them from other materials and from each other. Each acid or base should be stored in a manner consistent with its properties.
- Stored in material that is acid-resistant; this facilitates flushing and other cleanup procedures in the event of leaks or spills.
- Store on low shelves or in acid/base storage cabinets.
- Segregate oxidizing acids from organic acids, and flammable and combustible liquids.
- Segregate acids from active metals such as sodium, potassium, magnesium, etc.
- Use bottle carriers for transporting materials when possible.
- When mixing acids and water, always add acid to water. NEVER add water to acid!
- Store solutions of inorganic hydroxides in polyethylene containers.
- Store mineral acids together, separate from oxidizing agents and organic materials.
- Store acetic acid and other organic acids with the combustible organic liquids.

6. SPILL AND INCIDENT PROCEDURES

Chemical Spill - Dial 911 and EH&S 951-827-5528

Assess the extent of danger. Help contaminated or injured persons. Evacuate the spill area. Avoid breathing vapors. If possible, confine the spill to a small area using a spill kit or absorbent material. Keep others from entering contaminated area (e.g., use caution tape, barriers, etc.).

Small (<500 ml) – If you have training and do not perceive the risk to be greater than normal laboratory operations, use appropriate personal protective equipment and clean-up materials for chemical spilled. **In the event of a small piranha spill,** neutralize with sodium bicarbonate or other acid neutralizer and soak up with an inorganic-base absorbent. **Do not use paper towels, rags or sawdust because such materials may spontaneously ignite.** Place inside a piranha solution waste container, label, and arrange for chemical waste pick-up.

- *Large (>500 ml)* – Dial 911 and EH&S at 951-827-5528 for assistance. Notify others in area of spill. Turn off ignition sources in area. Evacuate area and post doors to spill area. Remain on the scene, but at a safe distance, to receive and direct safety personnel when they arrive.

Chemical Spill on Body or Clothes – Remove clothing and rinse body or affected skin with plenty of water or thoroughly in emergency shower for at least 15 minutes. Seek medical attention. Notify supervisor and EH&S at 951-827-5528 immediately.

Chemical Splash Into Eyes – Immediately rinse eyeball and inner surface of eyelid with water from the emergency eyewash station for 15 minutes by forcibly holding the eye open. Seek medical attention. Notify supervisor and EH&S at 951-827-5528 immediately.

Medical Emergency - Dial 911 and EH&S 951-827-5528

Refer to "Injuries and Medical Treatment" Flipchart posted in the laboratory.

7. DECONTAMINATION

Wear proper PPE, decontaminate equipment and bench tops using sodium bicarbonate and water. Dispose of all used contaminated disposables as hazardous waste following the Waste Disposal Section.

8. WASTE DISPOSAL

Piranha waste MUST be disposed through the EH&S Hazardous Waste Program. Staff dealing with hazardous waste disposal should have completed UCR Hazardous Waste Management training - http://ehs.ucr.edu/training/online/hwm/indexlms.html

Piranha solution disposal guideline:

- Affix an online hazardous waste tag using the Waste Accumulation Storage Tracking electronically (WASTe - https://ehs.ucop.edu/waste) on all waste containers as soon as the first drop of waste is added to the container.
- Affix the **"Piranha Waste – Add no other types of waste"** to the 2.5L coated bottle provided by EH&S.
- After the initial 24 hours has passed, the cooled piranha solution may be transferred to the piranha waste bottle. When performing the transfer, make sure no heat is produced or reactions are occurring.
- Piranha waste MUST be stored in a 2.5L coated glass bottle with a vented cap provided by EH&S.
- Do not over-fill piranha waste bottles. Leave at least 2" of head space in each bottle. *Over-filling prevents the vented caps from allowing gas to escape*. EH&S will not pick up bottles that are over-filled.

- Store piranha waste in closed containers, in secondary containment, and in a designated location. Do not let product enter drains. Discharge into the environment must be avoided.
- Waste must be under the control of the person generating and disposing of it.
- Dispose of routinely generated chemical waste within 90 days.
- Request a waste pick-up on-line: http://ehs.ucr.edu/services/waste.html

9. PRIOR APPROVAL/REVIEW REQUIRED

All work with Acid Solutions must be pre-approved by the Principal Investigator prior to use and all training must be well documented. In addition, the following shall be completed:

- Documented specific training and specific training on the techniques and processes to be used.
- Read and understand the relevant Safety Data Sheet.
- Demonstrate competence to perform work.

A review of this SOP and re-approval is required when there are any changes to procedures, personnel, equipment, or when an incident or near miss occurs.

10. DESIGNATED AREA

Work should be completed in a laboratory fume hood designated for Acid Solutions.

11. SAFETY DATA SHEETS

Online SDS can be found at http://www.ehs.ucr.edu/services/msds.html.

12. DETAILED PROTOCOL

Perform the following steps 4-6" inside a chemical fume hood:

Starting with 30% hydrogen peroxide and concentrated sulfuric acid, the mixing ratio should be in a range of 5:1, 4:1 or 3:1 (H_2SO_4:H_2O_2).

To make piranha solution:

1. Place a glass beaker of adequate size to accommodate the proposed volume onto a magnetic stir plate.
2. Secure the beaker using a 3-prong clamp attached to a ring stand.
3. Place a magnetic stir bar inside the beaker and power on the magnetic stir plate.
4. Add _____ mL of concentrated sulfuric acid to beaker.
5. Add _____ mL of hydrogen peroxide to the sulfuric acid **very slowly.** (The H_2O_2 is added immediately before the etching process because it immediately

produces an exothermic reaction with gas (pressure) release. If the H_2O_2 concentration at 50% or greater, and explosion will occur.

6. Use care when picking up the beaker as it is very likely to be hot, more than 100°C.
7. Rinse and dry substrate before placing into a piranha bath.
8. Use care when removing substrate for piranha bath.
9. Piranha solutions must be allowed to cool and off-gas in an open container left inside of the chemical fume hood for **at least 24 hours** after use.
10. After the initial 24 hours has passed, the cooled piranha solution may be transferred to a piranha waste container.

All lab workers who will be using Piranha Solution must review this SOP and sign the associated training/acknowledgment page. Lab workers must have specific training on the proper handling of Acid Solutions and understand the hazards.

When working in the lab, a laboratory worker must:

1) not work alone;
2) be cognizant of all of the SDS and safety information presented in this document;
3) follow all related SOPs in the laboratory SOP bank (PPE, syringe techniques, waste disposal, etc. as appropriately modified by any specific information in the SDS information presented in this document);
4) employ (< quantity) of this Piranha Solution in any given reaction (larger quantities REQUIRE the approval of PI or designee), and
5) Discuss ALL issues or concerns regarding this Acid Solutions with the PI prior to its use.

If there is an unusual or unexpected occurrence when using this material(s), the occurrence must be documented and discussed with the Principal Investigator or Lab Supervisor and others who might be using Acid Solutions. Unusual or unexpected occurrences might include a fire, explosion, sudden rise or drop in temperature, increased rate of gas evolution, color change, phase change, or separation into layers.

SOP Reviewed and Approved by:

Print name _____ Signature _____

Approval Date: _____

Facility/Lab Supervisor: _____

Acknowledgement

Standard Operating Procedure

Title: Generation, Use and Disposal of Piranha Solution

By my signature I acknowledge the contents, requirements, and responsibilities outlined in this Standard Operating Procedure (SOP):

Name	Identification*	Signature	Date
Supervisor / Principal Investigator:			

***Identification:** Enter your Student ID, Employee ID, UCR Net ID, UCR Email.*