UNIVERSITY OF VICTORIA Occupational Health, Safety and Environment

Chemical Safety - Special Hazards

Safe Work Procedure (SWP – 009) Piranha Solution

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REVISION HISTORY

Revision Date Author Position

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DOCUMENT APPROVAL

Approved by: Laboratory Safety Committee

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^{*}This revision replaces all previous versions of this document. If a copy is printed, it is the users' responsibility to verify the copy is the most current version of the document.

PURPOSE

To provide guidance and instruction of the safe preparation and use of Piranha solution in laboratories. In addition to this general Safe Work Procedure (SWP), each lab must develop a lab-specific work procedure unique to the experiments and activities being performed. The Lab SWP must be reviewed by OHSE (see Procedures, #7)

SCOPE

The SWP applies to preparation and use of Piranha solution, also referred to as Piranha etch, being both a strong acid and oxidizer. It is commonly used as an agent to remove organic residues from substrates (e.g. silicon wafers). Piranha solution is a mixture of concentrated sulfuric acid (H_2SO_4) with hydrogen peroxide (H_2O_2) typically in a 3:1 ratio but piranha solution also can be prepared as 4:1 or 7:1 mixture ratios. This SWP will not cover base Piranha solution which is a 3:1 ratio of ammonium hydroxide (NH_4OH) and hydrogen peroxide (NH_2O_2).

TRAINING

The following training is required to be completed prior to being permitted to prepare and work with Piranha solution:

- WHMIS
- Lab Safety for Lab Workers
- Lab SWP with documented signoff by the individual and their supervisor.

Refresher training in the General and Lab SWP must be provided when:

- there has been an extended timeframe of inactivity, or
- · there has been an incident or injury, or
- 2 years has elapsed since the original training

REGULATION AND POLICY

The University of Victoria will follow WorkSafeBC Occupational Health and Safety Regulation, specifically sections 30.20 (1-4) and the University of Victoria Occupational Health, Safety & Environment Department.

RESPONSIBILITY

It is the responsibility of personnel undertaking activities with special hazards to complete all required training and adhere to these safe work procedures, including any additional lab or job-specific procedures.

It is the PI's or supervisor's responsibility to ensure that individuals working with special hazards have been trained prior to commencing work and have demonstrated competency in safely performing all duties associated with the special hazard in accordance with these procedures.

DEFINITIONS

<u>Circumvent®</u> caps: A vented cap liner to relieve pressure in containers while maintaining integrity against liquid leaks/spills

MATERIALS

Acid waste container equipped with a venting cap (such as Circumvent® caps which are available at Science Stores) dedicated to Piranha solution to ensure no incompatible materials are mixed in by other lab users. Dedicated lab bench area clearly delineated and labelled for Piranha solution use only. Working containers must be in glass or Pyrex containers.

Spill X-A or sodium bicarbonate are commonly used acid neutralizers. When sodium bicarbonate is used to neutralize acids, carbon dioxide gas is released which is a non-toxic, non-flammable gas. Spill X-A is a proprietary product comprised of magnesium oxide (60-100%) blended with other chemical additives. Spill X-A has a reddish colour and minimal gas release is produced.

HAZARD

Piranha solution is a strong acid and oxidizer. Both liquid and vapour forms are corrosive to skin and respiratory tract. Piranha solution can become hot, more than 100 °C. Explosion can occur when gas generated from Piranha solution pressurizes closed containers or when Piranha solution is in contact with organic compounds. Before you work with Piranha, you should consider less hazardous alternatives to achieve the desired goal.

PROCEDURE

1. Handling

- a. Ensure the area where Piranha solution is handled an acid-neutralizing spill kit (Spill X-A, sodium bicarbonate or equivalent) is immediately accessible to neutralize accidental spills.
- b. In addition to wearing normal laboratory attire, one must wear neoprene, neoprene apron and face shield while working with Piranha solution.
- c. Piranha solution will self-heat to hot temperatures (up to 100 °C). Heat insulated gloves may be necessary.
- d. Conduct all work with Piranha solution inside a fume hood.
- e. Keep all organics away from the area when preparing and using Piranha solution as they will react violently.
- f. Use glass or Pyrex containers. Piranha solution is not compatible with plastic.
- g. Use a secondary container when preparing Piranha solution in case it over flows.
- h. Ensure containers and substrates are rinsed and dried before coming into contact with Piranha solution.
- i. Prepare small amounts of solutions to be used up for each application. Do not store Piranha solution
- j. Use 30% hydrogen peroxide; avoid concentrations of hydrogen peroxide greater than 50% to prevent explosions upon preparation
- k. Add hydrogen peroxide always to sulfuric acid slowly. Never vice versa.
- I. Do not mix Piranha solution with incompatible materials such as organic acids, bases and organic solvents.
- m. Do not seal containers containing Piranha solution because toxic gases will pressurize the container; use venting caps (such as <u>Circumvent</u>® caps)

2. Storage

- a. Do not store Piranha solution.
- b. Dispose excess Piranha solution as hazardous waste.

3. Spills

- a. Follow OHSE's general spill response instructions
- b. Specific steps for piranha solution spills:
 - i. Don personal protective equipment neoprene gloves, safety glasses, lab coat and closed toe shoes
 - ii. Slowly neutralize using an acid spill kit (Spill X-A, sodium bicarbonate, or equivalent) from outside of the spill inward.
 - iii. Wait for 15 minutes
 - iv. Test with pH paper until the spilled material is within the neutral range of pH 6-8.
 - v. Scoop the absorbed neutralized material into an appropriately sized plastic (polyethylene or polypropylene) container.
 - vi. Wipe up any residue with a moist paper towel or rag
 - vii. Soak the area with detergent, then rinse with water.
 - viii. Collect and label all materials used in the clean-up for disposal through the hazardous waste system indicating the material is "Neutralized Piranha solution spill absorbent and debris"
- c. Complete a <u>Department Incident & Investigation Report</u> to document and review the spill incident.

4. Decontamination

a. Ensure containers and substrates are rinsed with copious amounts of water in a sink after coming into contact with the Piranha solution.

5. First Aid and Emergencies

- a. Call 911 to summon an ambulance if there is a medical emergency.
- b. Call Campus Security at 250-721-7599 for first aid.
- c. If material has contacted the eyes, use emergency eyewash and flush for at least 15-20 minutes.
- d. For skin contact, flush affected area with running water for at least 15-20 minutes.
- e. For inhalation, move immediately to fresh air; seek medical attention in the event of respiratory irritation, cough or tightness in the chest. Symptoms may be delayed.

6. Waste Disposal

- a. Leave hot Piranha solution to cool to room temperature in either an open container or a container with a vented cap in a certified fume hood for several hours (overnight) before disposal as waste.
- b. Do not mix Piranha waste with other waste.
- c. Label container carefully indicating "Caution, Piranha solution (sulfuric acid & hydrogen peroxide). May explode in closed container" and the Piranha waste solution disposal date.
- d. Do not use an airtight container for Piranha waste. Store waste solutions in a glass bottle with a vented cap, such as the Circumvent caps which can be obtained from Science Stores.
- e. Affix a green hazardous waste sticker on the bottle.
- f. Submit online request for hazardous waste pick-up from OHSE.

7. Lab SWP

In additional to this general SWP, each lab that is using Piranha solution requires a Lab SWP that includes specific procedures for:

- a. Volume of Piranha solution to be prepared
- b. Secondary spill containment using trays of glass
- c. How to decontaminate any surfaces or reusable lab ware
- d. The clear delineation of fumehood work space with a sign stating "Piranha solution (sulfuric acid & hydrogen peroxide), No organic material"
- e. Spill containment and response

REFERENCES

- WorkSafeBC OHS Regulations Part 30.20 Explosive and highly reactive materials. Retrieved from https://www.worksafebc.com/en/law-policy/occupational-health-safety/searchable-ohs-regulation/ohs-regulation/part-30-laboratories
- 2. University of Toronto Procedure on handling and using Piranha solution. January 2017
- 3. Concordia University Piranha solution safety guidelines. n.d.
- 4. University of California, Los Angeles *Standard operating procedure: Piranha solution (Piranha etch)*. September 2012.