

PIRANHA SOLUTION SAFETY GUIDELINES

The Piranha solution is used in etching processes to remove organic residues from substrates. Two different solutions can be used. The most common is the acid Piranha which consists of a 3:1 mixture of concentrated sulfuric acid (H_2SO_4) with 30% hydrogen peroxide (H_2O_2). Also used is the base Piranha which is a 3:1 mixture of ammonium hydroxide (NH_4OH) with 30% hydrogen peroxide (H_2O_2). Both are equally dangerous when hot, although the reaction in the acid Piranha is self-starting, whereas the base piranha must be heated to $60^\circ C$ before the reaction takes off. Anyone who works in laboratories containing Piranha solution should familiarize themselves with its SDS and a clear Standard Operating Procedure (SOP) should be established. Therefore, careful precaution should always be taken when handling this solution. This document discusses the properties, health and safety hazards, how to properly handle and store a Piranha solution. Also included are emergency procedures for dealing with accidental Piranha solution contact, including first aid treatment information.

☠️*WARNING*☠️: 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 bin to an explosion with a huge shock wave with possible acid (or base)-gown shredding glass sharps. 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.

1. Properties

Names:

chemical name: *Piranha solution, Piranha etch*
solution: a) *Acid Piranha: usually mixture of 3:1 sulfuric acid and 30% hydrogen peroxide (but some protocols call for as much as 7:1 mixtures)*
b) *Base Piranha: usually mixture of 3:1 ammonium hydroxide and 30% hydrogen peroxide*

Chemical Formulas:

Sulfuric Acid: H_2SO_4
Ammonium Hydroxide: NH_4OH
Hydrogen Peroxide: H_2O_2

CAS #

Sulfuric Acid: 7664-93-9

Ammonium Hydroxide: 1336-21-6

Hydrogen Peroxide: 7722-84-1

2. Hazard Classification

Sulfuric Acid (concentrated)

WHMIS 1988



D1B: Material causing immediate and serious toxic effects (toxic)
E: Corrosive liquid

WHMIS 2015



Corrosive to metals (Category 1)
Skin Corrosion/irritation (Category 1)
Serious Eye Damage/Eye Irritation (Category 3)
Specific target organ toxicity (single exposure) Target Organs -
Respiratory system (Category 3)

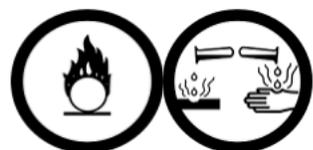
NFPA



Flammability: Non-flammable
Health hazard: Highly toxic; severe acute and chronic health effects.
Instability/Reactivity: Sulfuric acid mixtures with certain compounds can be unstable and lead to explosion.
Reacts violently with water.

Hydrogen Peroxide (20-40% w/w in water)

WHMIS 1988



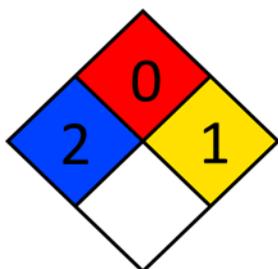
C: Oxidizing material
E: Corrosive liquid

WHMIS 2015



Oxidizing liquids (Category 2)
Corrosive to metals (Category 1)
Skin Corrosion/irritation (Category 1)
Serious Eye Damage/Eye Irritation (Category 1)
Specific target organ toxicity (single exposure): Target Organs -
Respiratory system. (Category 3)

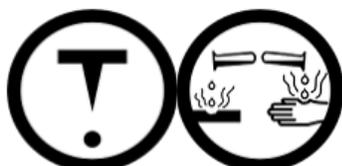
NFPA



Flammability: Non-flammable
Health hazard: Hazardous in case of skin and eye contact or ingestion.
Instability/Reactivity: Unstable at high temperatures. Slightly explosive in the presence of open sparks or flames, heat or organic materials, metals and acids.

Ammonium Hydroxide (25-30% w/w in water)

WHMIS 1988



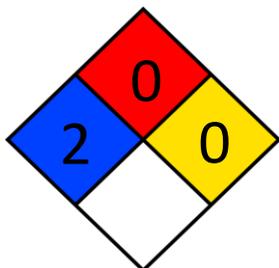
D2B: Material other toxic effects
E: Corrosive liquid

WHMIS 2015



Skin Corrosion/irritation (Category 1B)
Serious Eye Damage/Eye Irritation (Category 1)
Specific target organ toxicity (single exposure): Target Organs -
Respiratory system. (Category 3)

NFPA



Flammability: Non-flammable
Health hazard: Very hazardous in case of skin and eye contact or ingestion.
Instability/Reactivity: Stable however can form explosive compounds when mixed with heavy metals or halogens.

3. Reactivity, Fire and Explosion Hazards

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 H₂O₂ is added immediately before the process because it immediately produces an exothermic reaction with gas (pressure) release. If the H₂O₂ 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.

4. Health Hazards

Piranha solution is a strong oxidizer. Both liquid and vapour 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.

5. Safety Precautions for Piranha Solution Use

a) Training

Students and employees who handle Piranha solutions must have received training on the hazards of Piranha solutions from their respective department. They must know what to do in the event of a spill or an exposure incident. The SDS of the different components of the solution must always be kept within the immediate vicinity of the working area along with the Standard Operating Procedure (SOP) developed by the student / employee's department.

b) Ventilation / Fume Hood

Because highly corrosive vapors are generated when preparing Piranha solutions, all work should be conducted inside a certified chemical fume hood.

c) Eye Protection

Splash goggles and a face shield **MUST** be worn when handling Piranha solutions.

d) Gloves

Regular nitrile gloves do not provide sufficient protection. Heavy duty neoprene or rubber gloves must be worn.

e) Protective Clothing

The handling of Piranha solutions requires special protection equipment in addition to the standard laboratory clothing (lab coat). An acid-resistant Neoprene apron must be worn on top of the lab

coat. Legs should also be covered by wearing a full size chemically resistant suit. Close leather shoes must also be worn.

f) **Safe Work Practice**

1. Piranha solution should be contained in glass or Pyrex containers. Piranha will melt plastics.
2. Always add hydrogen peroxide to sulfuric acid slowly. Never vice versa.
3. The hydrogen peroxide component should typically be kept to below 30%, never to exceed 50%.
4. Prepare small amounts of solutions to be used up for each application. Do not store Piranha solution in stock.
5. Adding any acids or bases to piranha or spraying it with water will accelerate the reaction.
6. Do not mix Piranha solution with incompatible materials such as organic acids, bases and organic solvents.
7. Ensure containers and substrates are rinsed and dried before coming into contact with the Piranha solution.
8. Leave the hot Piranha solution in an open container until cool.
9. Do not seal containers containing Piranha solution. Avoid using airtight containers as pressure can build up inside of them.
10. Never use Piranha solution unless another, knowledgeable person is accompanying you, should an emergency situation occur.
11. Do not store wash bottles containing organic compounds on the Piranha deck.

6. **Storage, Spill and Waste Issues**

a) **Storage and Waste Handling**

Do not store Piranha solution. Mix fresh solution for each use. The primary hazard from storage of Piranha etch waste is the potential for gas generation and over pressurization of the container when the solution is still hot. If you store a hot solution in an air tight container, it will explode! Prior to discarding the Piranha solution, it must be left in an open container in order to cool down for several hours (overnight) in a fume hood. It is the researcher's responsibility to make sure that the open container is clearly labeled and left in a safe area for overnight cool down. Once cooled down, the waste solution has to be stored in waste container **with vented cap**. The container must be very clearly labeled with the solution name and composition and must include VERY VISIBLE warning signs not to add any other types of chemicals. Contact EHS (hazardouswaste@concordia.ca) for waste pick-up.

b) **Spills**

Only employees trained in the handling of Piranha solutions should clean up spills. In the event of a small spill:

1. Notify personnel from the immediate area to stay away from area.
2. Wear appropriate PPE to clean spill.

3. If spill kit is present, use acid or base neutralizing material to neutralize Piranha solution. Test with litmus paper or colour-indicating solution until the spilled material is within the neutral range of pH 6-8.
4. Clean the area with inert absorbent materials (vermiculite, dry sand, oil-sorb, or kitty litter). The area should be soaked with detergent, then rinsed with water. Discard contaminated materials in hazardous waste glass vented bottles and clearly label the bottles indicating they contain Piranha etch waste.
5. Advise your supervisor and complete an incident report.

In the event of a large spill located outside a chemical fume hood:

1. Advise and warn co-workers.
2. Evacuate the area immediately.
3. Restrict the access to the area.
4. Notify Security at **3717** or **514 848-3717**, providing them with the following information:
 - a. Location of the spill
 - b. Name of hazardous material
 - c. Quantity involved
 - d. Related health risks and precautions to be taken
5. Provide the Safety Data Sheets (SDS) or appropriate documentation.

7. Emergency Procedures

a) Skin Contact

1. Remove contaminated clothing and immediately wash the affected area with large amounts of water until all evidence of the chemical has been removed (approximately 15 minutes).
2. Call Security at **3717** for emergency medical assistance.

b) Eye Contact

1. Immediately wash the affected eye with large amounts of water until all evidence of the chemical has been removed (approximately 15 minutes).
2. Do not allow the victim to rub or keep eyes closed.
3. Call Security at **3717** for emergency medical assistance.

c) Inhalation

1. Immediately move the victim to fresh air.
2. Call Security at **3717** and ask for medical assistance; seek medical attention in the event of respiratory irritation, cough, or tightness in the chest. Symptoms may be delayed.

d) Ingestion

Not a likely route of exposure.

In all cases of exposures, a copy of the Safety Data Sheet (SDS) of the different components must be brought to the emergency room as the treating physician might be unaware of the treatment measures for Piranha solution. All Piranha solution incidents must be reported to your Supervisor and to Environmental Health & Safety. An [injury/near-miss report](#) must be filled for any incident involving a Piranha solution spill or exposure.

If you have any concerns about the use of Piranha solution at Concordia University, please contact EHS at ehs@concordia.ca.

Preparation date: November 2012

Revision date: November 2016

References:

- Fisher Scientific, Safety Data Sheet of Sulfuric Acid (concentrated), revision date: 21/04/2014
- Fisher Scientific, Safety Data Sheet of Hydrogen Peroxide (20-40%), revision date: 15/07/2015
- Fisher Scientific, Safety Data Sheet of Ammonium Hydroxide (25-30%), revision date: 21/07/2016
- Information on piranha solutions, Environmental Health & Safety Stanford University, OH&S Report 08-111, 08/01/08
- Piranha Solutions Laboratory Safety Guideline, Office of Environmental, Health, and Safety Management, Indiana University
- Handling Piranha Solutions, Environmental Health & Safety, Carnegie Mellon University