Acid Piranha Solution

Acid piranha solution (piranha etch) is generally a mixture of 3:1 sulfuric acid ($\text{H}_2\text{SO}_4$) and 30% hydrogen peroxide ($\text{H}_2\text{O}_2$) (but ratios may be as high as 7:1). This document does not address base piranha solutions (ammonium hydroxide ($\text{NH}_4\text{OH}$) with 30% hydrogen peroxide). Piranha solutions are commonly used to clean organic residue off substrates including glassware. Piranha solution hydroxylates most surfaces, making these surfaces more water soluble. Acid piranha solution is self-starting, meaning that the reaction takes off and will start generating heat without additional inputs.

HAZARD SIGNS

- Extremely corrosive.
- Causes destruction of living tissue at site of contact. Corrosive effects can occur not only on the skin and eyes, but also in respiratory tract, causing respiratory tract irritation. Toxic if inhaled, causes severe burns and eye damage.
- Very strong oxidizer. May ignite flammable/combustible materials. DO NOT mix with ORGANIC materials, especially solvents (e.g. ethanol). May result explosion.

Adapted from Harvard University’s Laboratory Safety Guideline
PRECAUTIONS

Before starting work:

- Before using piranha solution, more stable methods of removing stains, tars, or clogs should be attempted.
- Review manufacturer's Safety Data Sheets for sulfuric acid and hydrogen peroxide and additional chemical information.
- Ensure that a written experimental protocol including safety information is available.
- Be familiar with the Western Emergency Response Guide and the Exposure Response and Spill Response Posters.
- Identify the location of the nearest eyewash and shower and verify that they are accessible.
- Locate and verify that appropriate spill cleanup materials are available.
- Plan your experiments and processes using only the smallest amount of solution necessary.
- Do not perform hazardous work alone when at all possible. If you must work alone, notify your supervisor beforehand and ensure that you have a plan for handling an emergency.

During work:

- All handling of piranha solution MUST be done with glassware inside a fume hood. Never remove a container with piranha solution from the fume hood. Keep the sash as low as possible. Never raise it above the indicated position (18 inches).
- Always use glass (preferably Pyrex) containers as metals and plastics are incompatible. Piranha solution can become quite hot from oxidation reactions - more than 100°C, so be sure the glass used is heat resistant.
- ALWAYS add the hydrogen peroxide to the acid very slowly, never vice versa. Hydrogen peroxide concentrations should be kept below 30% and should never exceed 50% (or else explosion may occur).
- Perform all work in a secondary container that is clean and free of organic matter.
  - NEVER add more than trace organic materials to piranha solution; it could react violently. This includes any chemical containing a C-H bond, e.g., acetone, isopropanol, ethanol, photoresist, or detergents.
- Piranha solution should never be left unattended if hot.
- DO NOT STORE piranha solution. Apart from its hazardous byproducts and reactions, piranha solution quickly loses its effectiveness due to oxidation of its components. Mix fresh solutions for each use.
- Substrates should be cleaned, rinsed and dried before being placed in a piranha bath.

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PRECAUTIONS

• Wear appropriate PPE including:
  o Lab coat
  o Safety goggles
  o Appropriate gloves
    ▪ Recommended Glove Material: Rubber, Butyl, Neoprene, or Viton (regular Nitrile gloves will not provide appropriate protection).
    ▪ Recommended Gloves: Ansell Microflex 93-260 (Nitrile & Neoprene composite), Ansell AlphaTec® Solvex® 37-175 (Nitrile), Ansell AlphaTec® 38-514 (Butyl Polymer).
  o If handling volumes >500mL or if splashing is likely, wear an acid-resistant apron and face shield.
• Wash hands thoroughly each time gloves are removed.
• Use materials and containers appropriate for piranha solution use and remain aware of potential incompatibilities.
• Never put piranha solution in a closed vessel; evolved gases will cause pressure to build up. Allow the piranha solution cool completely before transferring to a container with a vented cap. In the absence of a vented cap, screw a regular cap on very lightly and be sure that labels clearly indicate that caps are not tightly sealed and should not be tightly sealed.

After completing the work:

• Dispose of piranha solution waste following Western’s Hazardous Waste Pickup Procedures:
  o Hazardous Waste Classification: Corrosive/Toxic/Oxidizer
  o Use a glass bottle with a vented cap. In the absence of a vented cap, screw a regular cap on very lightly and be sure that labels clearly indicate that caps are not tightly sealed and should not be tightly sealed.
  o Ensure that the waste container you are using is clean, dry, and does not have residual solvent or other organic materials in it. Piranha solution should be the sole waste constituent in the waste bottle. Piranha solution is a strong oxidizing agent and will react with organic chemicals.
  o Wash hands before leaving lab.

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EMERGENCY PROCEDURES

FIRST AID

SKIN CONTACT
- Flush skin with copious amounts of water for 15 minutes using the closest available sink, portable drench hose, or safety shower. Remove contaminated clothing.
- Call 360-650-3911 or 911 for emergency assistance.

EYE CONTACT
- Using eyewash, flush eyes while hold eyelid open and away from exposed eye.
- Call 360-650-3911 or 911 for emergency assistance.
- Continue flushing with water until emergency medical personnel arrive.

INHALATION
- If mist or vapors are inhaled, immediately move to fresh air.
- If someone else has been exposed and is unconscious, remove the individual only if safe for you to do so.
- Call 360-650-3911 or 911 for emergency assistance. Note that symptoms may be delayed. Symptoms may include respiratory irritation, coughing, and tightness in the chest.

INGESTION
- Do not induce vomiting. Never give anything by mouth to an unconscious person. If conscious, wash out mouth with water.
- Call 360-650-3911 or 911 for emergency assistance.

SPILL RESPONSE

OUTSIDE FUME HOOD or INSIDE FUME HOOD (>500mL)
- Alert others and evacuate to a safe distance and prevent entry.
- Contact EHS at 360-650-3064 during business hours or 360-650-3911 or 911 outside of business hours.
- Remain in a safe location until EH&S or other response personnel arrive.

INSIDE FUME HOOD (< 500 ml)
- Alert others of the spill.
- If you are working alone, are not trained in spill response, or not comfortable cleaning the spill, contact EHS at 360-650-3064 during business hours or 360-650-3911 or 911 outside of business hours.
- If trained and confident in spill response, don the appropriate PPE. Neutralize spill with soda ash or lime. Do not use absorbent until pH is between 6-8. Absorb neutralized spill with vermiculite or other inert absorbent material, then place in a suitable container for disposal. Clean surfaces thoroughly with water to remove residual contamination. Dispose of all waste and cleanup materials as hazardous waste.

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