Standard Operating Procedure for Piranha Solutions

(Reference: http://www.enma.umd.edu/LAMP/Sop/Piranha_SOP.htm)

1. General
When working with a chemical for the first time, please consult a safety data sheet (SDS) to identify the material hazards and proper handling and storage procedures. If you have additional questions, please contact the University of Chicago Environmental Health and Safety Office at 773-702-9999 or safety@uchicago.edu.

"Piranha" is used to remove organic residues from substrates. There are two different kinds of piranha solution used in the laboratory. The most common is the acid piranha: a 3:1 mixture of concentrated sulfuric acid (H\textsubscript{2}SO\textsubscript{4}) with hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}). Also used is the base piranha: a 3:1 mixture of ammonium hydroxide (NH\textsubscript{4}OH) with hydrogen peroxide (H\textsubscript{2}O\textsubscript{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°C before the reaction takes off.

There are many things that will cause the reaction to accelerate out of control. "Out of control" can mean anything from the piranha foaming and overflowing its container, to an explosion with a huge shock wave including glove and acid-gown shredding glass sharps. Piranhas burn organic compounds. If you provide sufficient fuel for them (i.e. photoresist, IPA), they will generate enormous quantities of heat and gas.

2. Personal Protective Equipment
The handling of Piranha solutions requires special protection equipment including: a full face shield, heavy duty rubber gloves (regular Nitrile gloves will not provide sufficient protection), as well as an acid apron to wear on top of the lab coat. Check for pinholes in gloves before putting them on.

3. Use, Procedures, and Storage
   - Whenever handling Piranha, only use glass containers (Pyrex). Piranha can melt and even attack plastic containers. Containers used during the experiment must be very clearly labeled and a warning sign, visible by any user working under the flow hood, must be posted at all time to indicate that the solutions contains Piranha mixture.
   - Mix the solution in the flow hood with the sash between you and the solution. Wear all protective equipment. When preparing the piranha solution, always add the peroxide to the acid very slowly. The H\textsubscript{2}O\textsubscript{2} is added immediately before the etching process because it immediately produces an exothermic reaction and releases both O\textsubscript{2} and CO\textsubscript{2}. Ignition sources and H\textsubscript{2}O\textsubscript{2} concentrations > 50% should be avoided. Typical H\textsubscript{2}O\textsubscript{2} concentration used is 25 ~ 30%.
   - Piranha solution is very energetic and potentially explosive. It is very likely to become hot, more than 100°C. Handle with care. Picking up a beaker that is this hot will be very painful, might melt your gloves, and may cause you to spill it!
   - Substrates should be rinsed and dried before placing them in a piranha bath. Piranhas are used to remove organic residue, not the compounds themselves
   - Leave the hot piranha solution in an open container until cool. (> 20 min)
   - Never store hot piranha solutions. Piranha stored in a closed container will likely explode.
   - Adding any acids or bases to piranha or spraying it with water will accelerate the reaction.
   - Mixing hot piranha with organic compounds may cause an explosion. This includes acetone, photoresist, isopropyl alcohol, and nylon.
   - Do not store wash bottles containing organic compounds on the piranha deck.
   - Do not transport chemicals around the room in beakers. Never pour chemicals back into the original container.
   - Do not store piranha. Mix fresh solution for each use. Excess solutions should be disposed properly.

University Police: 123 (on-campus phone); 773-702-8181 (off-campus phone)
City of Chicago Police/Fire/Emergency Medical Services: 911
University of Chicago Environmental Health and Safety Office: 773-702-9999, safety@uchicago.edu
4. Piranha Waste Disposal

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! Therefore the lid of designated container for piranha waste must be left open for several hours (overnight) until to be cooled down enough. 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.

Waste containers should be no more than 95% full, and should stay in the lab for no more than 6 months from the day the waste container is started. Waste containers must be marked to identify the contents, hazards, and accumulation start and end dates. To request waste pickup, log-on to the EH&S Assistant (http://ehs.uchicago.edu/ehsaweb/ehsawebisapi.dll/EXEC). Please contact the Safety Office at 2-9999 if you have questions about a specific type of waste.

5. Emergency Procedures

In case of large exposure, the victim should be removed from the contaminated area, placed under a safety shower while University Police are contacted at 123 or 773-702-8181

All contaminated clothing should be removed immediately with appropriate gloves and safely discarded.

In case of contact with the skin, may cause skin burns. The affected area must be immediately rinsed with large amounts of water for at least 15 min.

In case of contact with the eye, irrigate the eye for at least 15 minutes, keeping the eyelids apart and away from eyeballs during irrigation. Place ice pack on eyes until reaching emergency room.

In case of inhalation, it may irritate the respiratory tract. 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.