Management of High-Hazard Metallographic Etchants and Electropolishing Solutions

Introduction

Metallographic chemical etchants are reactive liquid or gas solutions used to dissolve, shape, or clean materials such as metals, semiconductors, and glass at a microscopic level for analysis. Electropolishing solutions are specialized electrolyte mixtures used in an electrochemical bath to smooth, deburr, and passivate metal surfaces. While many reagents pose only typical corrosive or flammable hazards, certain formulations contain combinations of strong oxidizers, organic solvents, hydrofluoric acid, cyanide-containing compounds, or energetic materials that substantially increase risk.

Several commonly used metallographic solutions may exhibit violent reactions, rapid decomposition, fire hazards, toxic gas generation, or explosive behavior if improperly prepared, stored, contaminated, or allowed to degrade over time. Due to the significant hazards associated with these materials, appropriate procedures, engineering controls, personal protective equipment (PPE), and training are required prior to use. Planning and hazard assessment are imperative to prevent serious injuries, fires, explosions, and property damage.

High-Hazard Etchants and Electropolishing Solutions

Certain metallographic reagents exhibit dangerous properties and require additional review and control measures to ensure the safety of lab personnel. The following solutions require the principal investigator or another qualified person in the lab to develop and maintain a Laboratory-Specific Operating Procedure (LSOP) for any etchant or electropolishing solution that meets any of the following criteria:

- Contains high concentrations of organic solvents (e.g., ethanol, methanol, isopropanol) combined with oxidizers or mineral acids.
- Contains chemicals that may decompose violently, detonate, or undergo uncontrolled exothermic reactions.
- Contains hydrofluoric acid, cyanide-containing compounds, perchloric acid, picric acid, or other particularly hazardous substances.
- Requires specialized engineering controls or emergency procedures.
- Presents hazards beyond those that can be addressed through routine laboratory procedures (e.g., solutions that cannot be stored, solutions requiring vented caps to prevent over pressurization, etc.).

Common High-Hazard Reagents Requiring LSOPs

The following table contains a number of commonly used etchants and electropolishing solutions that require principal investigators or other qualified person to develop LSOPs. The table is not exhaustive. Additional formulations may require LSOPs based on composition, concentration, scale, or operating conditions.

Common Chemical Etchants and Electropolishing Solutions			
Name	**Composition**	**Hazards**	**Description**
Perchloric Acid Alcohol	Perchloric acid + ethanol/methanol	High corrosivity, oxidizing, flammability, and explosion hazards.	Perchloric acid reactions with alcohols may form alkyl perchlorates, which are highly energetic and potentially explosive, particularly when stored for prolonged periods or exposed to elevated temperatures. Strict temperature control and prevention of contamination or solvent loss are required to prevent thermal runaway and violent decomposition.
Nital Etchant	Nitric acid + ethanol/methanol	High flammability, may detonate if improperly prepared or stored.	Nitric acid can react with alcohols to form unstable nitrate esters, including methyl nitrate and ethyl nitrate, which are highly flammable and potentially explosive, particularly under elevated temperatures or contaminated conditions.
Picral Etchant	Picric acid (2,4,6-trinitrophenol) + ethanol	High flammability and explosion hazards.	Picric acid is a high explosive that can form shock, friction, and heat sensitive residues. Prolonged

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			storage, solvent evaporation, or contamination may increase the risk of violent decomposition or detonation.
Vilella's Reagent	Picric acid (2,4,6-trinitrophenol) + hydrochloric acid + ethanol	High flammability and explosion hazards.	Picric acid is a high explosive that can form shock, friction, and heat sensitive residues. Prolonged storage, solvent evaporation, or contamination may increase the risk of violent decomposition or detonation.
Keller's Reagent	Hydrofluoric acid + hydrochloric acid + nitric acid + water	Highly corrosive and toxic acid mixture capable of causing severe chemical burns and systemic poisoning.	Strict prevention of skin contact and inhalation exposure is required, as hydrofluoric acid can cause delayed but potentially fatal fluoride toxicity while nitric acid contributes strong oxidizing properties and possible toxic nitrogen oxide gas generation.
Carpenter's Etchant	Ferric chloride + cupric chloride + hydrochloric acid + nitric acid + ethanol	Highly corrosive acidic etchant capable of causing severe chemical burns and generating toxic vapors.	The combination of nitric acid, hydrochloric acid, metal chlorides, and ethanol can present oxidizer-fuel incompatibility concerns, requiring strict control of contamination, temperature, and storage conditions to prevent hazardous decomposition reactions.

Common Chemical Etchants and Electropolishing Solutions			
Name	**Composition**	**Hazards**	**Description**
Murakami's Reagent	Potassium ferricyanide + potassium hydroxide + water	Highly toxic and corrosive alkaline solution capable of causing severe chemical burns.	Contact with acids can liberate highly toxic hydrogen cyanide gas from ferricyanide-containing solutions. Strict segregation from acids and prevention of contamination are required.

Note: The reagents listed in the table are examples of commonly encountered high-hazard metallographic etchants and electropolishing solutions. Novel formulations, modified recipes, concentrated mixtures, large-scale use, or unusual operating conditions may require additional review by UConn Environmental Health and Safety before use**.**

Standard Operating Procedure Requirements

Due to the inherent risks involved with high-hazard etchants and electropolishing solutions, laboratory personnel must identify hazards, assess risks, implement controls, and develop emergency procedures before use. The following elements must be included in all required LSOPs.

Documentation

All Laboratory-Specific Operating Procedures (LSOPs) must:

- Contain all the sections in the UConn Lab-Specific Standard Operating Procedures-Template or the Standard Operating Procedure Worksheet.
- Be reviewed, approved, and signed by the Principal Investigator (PI) or Laboratory Manager.
- Be reviewed and signed by all lab personnel involved with the procedure prior to conducting work.
- Be updated whenever procedures, materials, quantities, hazards, or any other information in the LSOP is changed and be resigned by all personnel involved, including the PI, to acknowledge the updates.
- Be readily accessible, in either hard-copy or electronic format, to laboratory personnel and EHS.

Administrative Controls

- Complete laboratory-specific training provided by the PI or other qualified staff prior to use.
- Review Safety Data Sheets (SDSs) for all chemicals prior to use.
- Develop and maintain a written LSOP addressing hazards and controls.
- Make the minimum quantity necessary to accomplish the intended task.
- Do not work alone. Conduct work under the supervision of trained personnel.
- Evaluate alternative, less hazardous reagents whenever possible.
- Ensure all personnel review and sign the LSOP prior to use.
- Contact EHS prior to generating any new high hazard etchant or electropolishing solution to ensure a licensed waste facility will accept the waste.

Engineering Controls

- Prepare and use etchants and electropolishing solutions in a properly functioning chemical fume hood.
- If perchloric acid is used, use a certified perchloric acid fume hood.
- Utilize splash shields or safety barriers when warranted by risk assessment.
- Ensure eyewash stations and safety showers are immediately available.
- Verify ventilation systems are appropriate for chemical hazards present.

Work Practice Controls

- Follow established preparation and mixing procedures.
- Label all reagent containers with the chemical names, hazards, preparation date, and expiration date.
- Prepare only the quantity needed for immediate use, unless an evaluation confirms that longer storage periods are allowed.
- Never mix incompatible materials without understanding the immediate and long-term reaction products.
- Inspect containers routinely for degradation, crystal formation, corrosion, leakage, or contamination. If present, contact EHS.
- Discontinue use if unexpected reactions, discoloration, gas generation, precipitation, or instability are observed. Contact the PI and EHS immediately.
- Ensure emergency procedures are established prior to beginning work.

Personal Protective Equipment

- Wear ANSI Z87.1 compliant chemical splash goggles or safety glasses, as indicated in the LSOP.
- Wear chemical-resistant gloves based on the requirements in the LSOP and SDSs for the specific chemicals in use. Check the breakthrough time, permeation rate, and performance levels from the glove manufacturer. Contact EHS with questions.
- Wear a properly sized and fastened laboratory coat.
- Wear long pants and footwear that covers the entire foot.
- Wear additional PPE such as face shields (in conjunction with safety eyewear), chemical aprons, or specialized gloves based on the hazards present, as indicated in the Workplace Hazard Assessment and LSOP.

Storage

- Determine the maximum storage time limit for unstable solutions to prevent degradation and hazardous decomposition and indicate in the LSOP. Contact EHS with questions.
- Store in compatible containers.
- Store away from incompatible chemicals.
- Keep containers tightly closed when not in use unless a vented cap provided by EHS is required to prevent over pressurization.
- If vented caps are required, store solutions in a properly functioning chemical fume hood or vented cabinet to minimize exposure.
- Ensure solutions that require low-temperature storage to maintain stability are stored in appropriate refrigerators. Flammable etchants and electropolishing solutions requiring low-temperature storage must be stored in an approved flammable-material refrigerator.
- Never store unlabeled solutions.
- Inspect picric acid-containing materials regularly to ensure they remain adequately wet.

Disposal

- Submit a chemical waste pick-up form to EHS to dispose of any high-hazard reagents prior to their expiration date.
- Ensure all wastes are labeled with “Hazardous Waste” stickers or tags provided by EHS, labelled with full chemical names and approximate percentages, stored in compatible waste containers, and are kept closed, unless vented caps are required.

- Notify EHS if wastes showed any signs of discoloration, gas generation, precipitation, or instability prior to being pick-up.

Emergency Procedures

Lab personnel must call 911 immediately if a spill, signs of over pressurization, a violent reaction, fire, explosion, or other emergency involving a high-hazard etchant or electropolishing solution occurs. Lab personnel must follow the emergency procedure below:

1. RELOCATE everyone in the immediate work area to a safe location.
2. ALERT- Dial 911. Follow the directions of the dispatcher. The person who dials 911 must meet UCFD upon arrival to provide further information about the emergency.
3. CONFINE- If it can be done safely, close doors to confine the area where the emergency occurred. Post an "Emergency Hangtag" on the door(s) to prevent reentry by other personnel.
4. EVACUATE the building through the nearest exit. Do not run. Do not use elevators.
5. REPORT to the lab's designated meeting site.
6. REENTER once emergency responders have cleared the lab.

Additional Resources

- OSHA Laboratory Standard (29 CFR 1910.1450)
- Prudent Practices in the Laboratory: Handling and Management of Chemical Hazards
- UConn Chemical Hygiene Plan
- UConn Laboratory-Specific Operating Procedure (LSOP) Template
- Applicable safety data sheets (SDSs) for all reagents and constituents