Hydrogen Peroxide H$_2$O$_2$ Pickle

by Bill Seeley

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Following is a paper on a special pickle I developed while attending graduate school at the University of Kansas. I had designed and constructed a rather complicated brass neck piece with many hard edges. After the construction was completed the piece was pickled by the ordinary means. This removed the black oxides from soldering, but there remained a though red oxide coating. Removal by abrasion would have destroyed the hard edged design. I had earlier come across a paper on a commercial pickling formulation using hydrogen peroxide. From this formula I sort of reverse engineered the following process. It is relatively safe, because it is based on drugstore variety hydrogen peroxide.

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Heat-treating and soldering of copper and copper based alloys can often coat the metals with a combination of black (cupric) and red (cuprous) oxide. The black oxide is easily removed in a standard warm sulfuric acid or Sparex bath. This will leave a red smut, which, with other undissolved oxides, forms a red oxide scale. This scale readily oxidizes further, leaving a dark, nonuniform patina. It can be imbedded in the metal during subsequent forging and drawing, so it should be removed. Abrasive removal of the oxides can result in loss of design details and crisp edges. This simple chemical treatment is offered as an alternate method for its removal.

Hydrogen peroxide (H$_2$O$_2$) pickle eliminates the need for abrasives, and has the added attraction of being relatively inoffensive. The following procedures and formulas provide for the removal of red scale from copper, brass, bronze, nickel silver, reticulation silver and some gold alloys. It will remove the copper coating from silver that has been accidentally pickled in an iron contaminated acid. Curiously, it will also remove the natural oxide layer found on aluminum. There is a great deal of latitude in the formulas and a variety of surface finishes and textures can be obtained.

It is suggested that you run some tests before applying these formulas to your work. Find the procedure that best fits your needs. When working with any acid the possibility of damaging your work always exists. These formulas can dissolve a brass piece and leave the silver solder seams standing.

Some points to remember when using hydrogen peroxide pickles:
1. Adding more acid to the solution will not improve its action. The acid is just a catalyst or starter.
2. Iron and silver will tend to shorten the life of the bath. This does not mean you cannot put these metals in the bath.
3. Use only sulfuric acid, Sparex or vinegar as the catalyst in these solutions.
4. Use 3% hydrogen peroxide available in drug stores, or mix a 2-3% solution from distilled water and concentrated \( \text{H}_2\text{O}_2 \) (usually 30%), available through a chemical supply house. More concentrated pickles (5%) can be mixed when deep, fast etching is desired.  
   (Warning! Concentrated acid is very dangerous. Do not attempt without proper training and equipment.)
   Always add acid to water!
5. Use these solutions warm(110°F), or about the temperature of a hot bath. The hotter the pickle; the faster and coarser the etch.

The following formulas can be made up as needed, or they can be premixed and kept for an extended time in the original brown bottle. It can be reused until saturated (blue) and it stops working. Hydrogen peroxide decomposes rapidly when exposed to light. The active life of these pickles is limited to about four exposed hours. Put your solution back in the brown bottle for storage.

The acid component of these solutions can be either measured or slowly added until bubbles begin to appear on a sample of the metal. This signals that the solution is active.

**SOLUTION #1(mild):**
2 parts Hydrogen Peroxide (3%).
1 part water.
2-4% fresh sulfuric acid (5-10%) or Sparex solution.

**SOLUTION #2(strong):**
1/2 cup Hydrogen Peroxide (3%).
1 Tablespoon fresh sulfuric acid (5-10%) or Sparex solution.

**PROCEDURE:**

1. Prepickle the piece in standard Sparex or sulfuric acid solution (5-10%) and rinse. All the black oxides should be removed.
2. Place the Hydrogen Peroxide pickle container in a second bowl of hot water to keep it warm. If possible suspend the piece in the warm pickle. After a moment bubbles should appear on the piece. Agitate or brush with a feather to clear the bubbles. Remove the piece from the bath every couple of minutes to check the progress. It may take 5-10 minutes. Rinse well.
3. Use a stiff tooth brush or brass brush to remove residue and rinse
4. Pickle again in standard Sparex or sulfuric acid solution (5-10%) to remove any remaining smut.
5. Repeat steps #2, #3 and #4 if necessary.
SOLUTION #3:
3 parts Hydrogen Peroxide (3%).
1 part white vinegar (5%).

PROCEDURE:

Follow the steps listed for solutions #1 and #2. When the metal emerges from the pickle, it will be coated with a thick brownish green smut. This will flash off when dipped in undiluted white vinegar.

Notes:
These solutions can also be applied to warm metal with a brush and worked into hard to get corners and intricate designs.

Long term exposure to these pickles can cause the copper to be dissolved out of an alloy's surface. Brass, for instance, can be pickled until it turns bright yellow. Even the mildest of the vinegar solutions can deeply etch if left unattended. A deep etch will often reveal the underlying crystal structure of the metal. Care should be taken and the process watched closely.

As is the case with all corrosive solutions, these formulas should be handled with care and in good ventilation.

Hydrogen Peroxide pickle does not remove firescale from sterling silver. Sorry!