Contents

1 Summary of Results

The fastest etch time is reached by a solution without any HYDROGEN PEROXIDE. In general, HYDROGEN PEROXIDE slows down the reactions. See: 5.5

2 Etchant Make-Up

The QuickEtch in theory and practice.

2.1 Physical Properties

Common compounds of Acid-Peroxide etchant.

Common Name	Compound	g/ml	g/mol	mol/ml
Hydrochloric Acid	HCl	1.2000	36.4600	0.0329
Hydrogen Peroxide	H_2O_2	1.4500	34.0147	0.0426
Acetic Acid	CH_3CO_2H	1.0500	60.0500	0.0175

Where:

g/ml	also: g/cm^3	Specific Gravity or Density
g/mol		Formula Weight
mol/ml	M/1000	Molarity Volume Fraction

2.2 Solution Properties

Common (retail) compound solution concentrations.

Common Name	Compound	Wt/Wt	g/ml	mol/ml	M
Hydrochloric Acid	HCl	31.45%	0.3774	0.0104	10.3511
Hydrogen Peroxide	H_2O_2	35.00%	0.5075	0.0149	14.9200
Acetic Acid	CH_3CO_2H	99.85%	1.0484	0.0175	17.4592

2.3 Reactant Balance

In general:

- All reactions are in solution with an excess of WATER.
- COPPER(I) compounds form before COPPER(II) compounds.
- COPPER(I) can be oxidized to COPPER(II), in a reversible manner.
- OXIDES form before CHLORIDES.

The three pathways, expressed as a ratio of moles, in the order: H_2O_2:HCl:CH_3CO_2H

- COPPER(II) ACETATE: 3:0:2
- COPPER(II) CHLORIDE: (un-buffered) 1:2:0; (buffered) 1:2:2

- COPPER(I) CHLORIDE: (un-buffered) 1:4:0; (buffered) 1:4:4

If all three pathways where independent: (un-buffered) 5:6:2; (buffered) 5:6:8

2.3.1 Copper(II) Acetate

In summary form:

H_2O_2	HCl	CH_3CO_2H	Cu	Equation	Product	Excess
2mol		2mol		7	$2\,CH_3CO_3H$	H_2O
1mol			1mol	9	$Cu(CH_3CO_2)_2$	$2\,H_2O$

The etchant for this path is expected to be a ratio of 3:0:2, H_2O_2:HCl:CH_3CO_2H

2.3.2 Copper(I) Chloride

In summary form:

H_2O_2	HCl	CH_3CO_2H	Cu	Equation	Product	Excess
2mol				2	O_2	$2\,H_2O$
			4mol	16	$2\,Cu_2O$	
	4mol			17	$4\,CuCl$	$2\,H_2O$
	4mol			18	$4\,CuCl_2^{1-}$	$4\,H_3O^{1+}$

The etchant for this path is expected to be a ratio of 1:4:0, H_2O_2:HCl:CH_3CO_2H

2.3.3 Copper(II) Chloride

In summary form:

H_2O_2	HCl	CH_3CO_2H	Cu	H_2O	Equation	Product	Excess
1mol			1mol		11	CuO	H_2O
	2mol				12	$CuCl_2$	H_2O
				6mol	14 or 15		

The etchant for this path is expected to be a ratio of 1:2:0, H_2O_2:HCl:CH_3CO_2H

2.3.4 Test Conditions

- All of the samples to be etched are approximately the same, Pyralux with a single sided, 2oz. (.007cm) copper plate.
  The sample squares are 2cm on a side, 4cm^2 in area, about 0.028cm^3 in volume, for approximately 0.0038 moles of copper.

- All tests are made with the etchant in excess, about 10 to 12 times that of the copper used.

- All solutions are at room temperature (82F, 28C) at the start of each test.
  These test conditions have a very low thermal mass and are exothermic reactions, so the temperature rises quickly.
  Such a temperature change increases the reaction rate, which is a positive feedback to the reaction rate.

Some to the reaction paths create reaction catylists, which are also a positive feedback to the reaction rate.

- All etchant solutions have water in excess.
- All etchant solutions are mixed immediately prior to use.
- All tests are made with a total of 20 ml. of etchant.

3 Component Paths

These are the assumed reaction pathways.

3.1 Decomposition of Hydrogen Peroxide

HYDROGEN PEROXIDE will, slowly, spontaneously, decompose:

$$2\,H_2O_2 \longrightarrow 2\,H_2O + O_2 \tag{1}$$

The decomposition of HYDROGEN PEROXIDE is catalyzed by the COPPER(II) ION:

$$2\,H_2O_2 \xrightarrow{Cu^{2+}} 2\,H_2O + O_2 \tag{2}$$

The catalyzed decomposition is presumed to proceed as two reactions:

$$Cu^{2+} + H_2O_2 \longrightarrow CuO_2 + 2\,H^{1+} \tag{3}$$

$$CuO_2 + 2\,H^{1+} + H_2O_2 \longrightarrow Cu^{2+} + 2\,H_2O + O_2 \tag{4}$$

The intermediary is COPPER(II) DIOXIDE.
In the presence of HCl there is a path to regenerate H_2O_2, see: (8)

3.2 Disassociation of Hydrochloric Acid

The disassociation of HYDROCHLORIC ACID, a strong acid, is nearly complete:

$$HCl + H_2O \longrightarrow H_3O^{1+} + Cl^{1-} \tag{5}$$

3.3 Acetic Acid

Acetic acid takes on two roles in this set of reactions.

3.3.1 Disassociation of Acetic Acid

The disassociation of ACETIC ACID, a weak acid, is slight:

$$CH_3CO_2H + H_2O \rightleftharpoons H_3O^{1+} + CH_3CO_2^{1-} \tag{6}$$

This weak acid serves to buffer any changes in the concentration of H_3O^{1+}.
The addition of H_3O^{1+} to the solution drives the reaction to the right.

3.3.2 Formation of Peracetic Acid

PERACETIC ACID is formed from ACETIC ACID and HYDROGEN PEROXIDE.

$$H_2O_2 + CH_3CO_2H \rightleftharpoons CH_3CO_3H + H_2O \tag{7}$$

PERACETIC ACID is a stronger oxidizer than HYDROGEN PEROXIDE.
The equilibrium constant is dependent on the concentrations and conditions of the reaction.

3.4 Regeneration of Hydrogen Peroxide

With the presence of COPPER(II) DIOXIDE (See: (3), (4)) in the solution of HYDROCHLORIC ACID and HYDROGEN PEROXIDE, there is a pathway to regenerate HYDROGEN PEROXIDE:

$$CuO_2 + 2\,HCl \longrightarrow CuCl_2 + H_2O_2 \tag{8}$$

4 Reaction Overview

There are at least three reaction pathways involving the solid COPPER.

4.1 Copper(II) Acetate

The anhydrous formation:

$$Cu + 2\,CH_3CO_2H + H_2O_2 \longleftrightarrow Cu(CH_3CO_2)_2 + 2\,H_2O \tag{9}$$

Is a low explosive when dry, sensitive to heat and shock.
The monohydrate formation:

$$Cu + 2\,CH_3CO_2H + H_2O_2 \longleftrightarrow |Cu(CH3CO2)2, H2O| + H_2O \tag{10}$$

Is non-explosive and commercially available.

4.2 Copper(II) Chloride

COPPER(II) CHLORIDE is produced in a solution of HYDROGEN PEROXIDE and HYDROCHLORIC ACID with COPPER(II) OXIDE as an intermediary:

$$Cu + H_2O_2 \longrightarrow CuO + H_2O \tag{11}$$

$$CuO + 2\,HCL \longrightarrow CuCl_2 + H_2O \tag{12}$$

The starting point may be either from COPPER (11) or from COPPER(II) OXIDE (12).

4.2.1 Disassociation of Copper(II) Chloride

COPPER(II) CHLORIDE is a salt soluble in WATER and disassociates:

$$CuCl_2 \longrightarrow Cu^{2+} + 2\,Cl^{1-} \tag{13}$$

Note here the production of the COPPER(II) ION catalyst at work in (2).

4.2.2 Production of Copper(II) Indicator

COPPER(II) ION in WATER forms a coordinated complex with six WATER molecules:

$$Cu^{2+} + 6\,H_2O \longrightarrow |Cu(H2O)6|^{2+} \tag{14}$$

The distinctive blue color of the HEXAAQUACOPPER(II) complex is a specific indicator of the COPPER(II) ION.

When there are not enough water molecules, as in the case of a concentrated $CuCl_2$ solution, TETRACHLOROCUPRATE(II) is formed giving the solution a distinctive green color:

$$|CuCl4|^{2-} + 6\,H_2O \rightleftharpoons |Cu(H2O)6|^{2+} + 4\,Cl^{1-} \tag{15}$$

The color shift Green $\rightleftharpoons$ Blue and the exact complex formula depends on the relative concentration of the COPPER(II) CHLORIDE ions and the WATER molecules.

4.3 Copper(I) Chloride

The straightforward production of COPPER(I) OXIDE from COPPER:

$$4\,Cu + O_2 \longrightarrow 2\,Cu_2O \tag{16}$$

The presence of water and acids increase the rate of this process.

COPPER(I) OXIDE is soluble in HYDROCHLORIC ACID and reacts to produce COPPER(I) CHLORIDE:

$$2\,(\,Cu_2O + 2\,HCl) \longrightarrow 2\,(2\,CuCl + H_2O) \tag{17}$$

COPPER(I) CHLORIDE is insoluble in water and highly soluble in concentrated HYDROCHLORIDE ACID.

COPPER(I) CHLORIDE, a LEWIS ACID, disassociates in HYDROCHLORIC ACID:

$$4\,(\,CuCl + HCl) \longrightarrow 4\,(\,H_3O^{1+} + CuCl_2^{1-}) \tag{18}$$

The H_3O^{1+} produced here is subject to action of the ACETIC ACID buffer.

5 Test Runs

All ratios are MOLES shown in the order: H_2O_2:HCl:CH_3CO_2H

Test runs are calculated in terms of MOLES for the partially buffered condition.
Where "partially" means that only the H_3O^+ from HCl was considered.

WATER is substituted for the ACETIC ACID in the unbuffered condition.
This was done to maintain the same ratio and overall concentrations between the copper and the other etchant components.

5.1 H_2O_2 in excess

Seconds	Ratio	H_2O_2	HCl	CH_3CO_2H	Reference
98	4:1:0	4	1		5.1.1
25	4:1:1	4	1	1	5.1.2
15	2:1:0	2	1		5.1.3
09	2:1:1	2	1	1	5.1.4

Notes:

- The balance for the 9 second result can be read as: 1 mole PERACETIC ACID + 1 mole HYDROCHLORIC ACID with 1 mole of HYDROGEN PEROXIDE in excess.
- The balance for the 25 second result can be read as: 1 mole PERACETIC ACID + 1 mole HYDROCHLORIC ACID with 3 moles of HYDROGEN PEROXIDE in excess.
- It appears that the reaction(s) slow down with an increasing excess of HYDROGEN PEROXIDE.

5.1.1 4:1:0 (Not Buffered)

	Mole	ml/mol	ml	Rel. Vol.	ml/20ml
H_2O_2	4	67.02	268.1	0.64	12.7
HCl	1	96.61	96.6	0.23	4.6
H_2O					2.7
Total:					20

A two phase reaction to an inactive solution.

Time to dissolve Copper: 98 seconds.

Afterwards, reaction reached violent rate.

5.1.2 4:1:1 (Partially Buffered)

	Mole	ml/mol	ml	Rel. Vol.	ml/20ml
H_2O_2	4	67.02	268.1	0.64	12.7
HCl	1	96.61	96.6	0.23	4.6
CH_3CO_2H	1	57.28	57.3	0.14	2.7
Total:					20

A two phase reaction to an inactive solution.

Time to dissolve Copper: 25 seconds.
Afterwards, reaction reached an extremely violent rate.

5.1.3 2:1:0 (Not Buffered)

	Mole	ml/mol	ml	Rel. Vol.	ml/20ml
H_2O_2	2	67.02	134.0	0.47	9.3
HCl	1	96.61	96.6	0.34	6.7
H_2O					4.0
Total:					20

A two phase reaction to an inactive solution.
Time to dissolve Copper: 15 seconds.
Afterwards, reaction reached a sustained, moderate rate.

5.1.4 2:1:1 (Partial Buffered)

	Mole	ml/mol	ml	Rel. Vol.	ml/20ml
H_2O_2	2	67.02	134.0	0.47	9.3
HCl	1	96.61	96.6	0.34	6.7
CH_3CO_2H	1	57.28	57.3	0.20	4.0
Total:					20

A two phase reaction to an inactive solution.
Time to dissolve Copper: 9 seconds.
Afterwards, reaction reached a sustained, high rate.

5.2 H_2O_2:HCl equal

Seconds	Ratio	H_2O_2	HCl	CH_3CO_2H	Reference
26	1:1:0	1	1		5.2.1
13	1:1:1	1	1	1	5.2.2

Notes:

- The 13 second result can be read as 1 mole PERACETIC ACID + 1 mole HYDROCHLORIC ACID.
- The removal of the ACETIC ACID buffer clearly slows down the reaction(s).

5.2.1 1:1:0 (Un-Buffered)

	Mole	ml/mol	ml	Rel. Vol.	ml/20ml
H_2O_2	1	67.02	67.0	0.30	6.1
HCl	1	96.61	96.6	0.44	8.7
H_2O					5.2
Total:					20

Time to dissolve Copper: 26 seconds.

5.2.2 1:1:1 (Partial Buffered)

	Mole	ml/mol	ml	Rel. Vol.	ml/20ml
H_2O_2	1	67.02	67.02	0.30	6.1
HCl	1	96.61	96.6	0.44	8.7
CH_3CO_2H	1	57.28	57.3	0.26	5.2
Total:					20

Time to dissolve Copper: 13 seconds.

5.3 HCl in excess

Seconds	Ratio	H_2O_2	HCl	CH_3CO_2H	Reference
305	1:2:0	1	2		5.3.1
19	1:2:2	1	2	2	5.3.2
400	1:4:0	1	4		5.3.3
150	1:4:4	1	4	4	5.3.4

Notes:

The presence of the ACETIC ACID buffer increases the rate of the reaction(s).

The reaction(s) slow down with the increase in the amount of HYDROCHLORIC ACID in excess.

5.3.1 1:2:0 (Un-Buffered)

	Mole	ml/mol	ml	Rel. Vol.	ml/20ml
H_2O_2	1	67.02	67.0	0.18	3.6
HCl	2	96.61	193.2	0.52	10.3
H_2O					6.1
Total:					20

Time to dissolve Copper: 5 minutes, 5 seconds (305 seconds).

5.3.2 1:2:2 (Partial Buffered)

	Mole	ml/mol	ml	Rel. Vol.	ml/20ml
H_2O_2	1	67.02	67.0	0.18	3.6
HCl	2	96.61	193.2	0.52	10.3
CH_3CO_2H	2	57.28	114.6	0.31	6.1
Total:					20

Time to dissolve Copper: 19 seconds.

5.3.3 1:4:0 (Un-Buffered)

	Mole	ml/mol	ml	Rel. Vol.	ml/20ml
H_2O_2	1	67.02	67.0	0.10	2.0
HCl	4	96.61	386.4	0.57	11.3
H_2O					6.7
Total:					20

Time to dissolve Copper: 6 minutes, 40 seconds (400 seconds).

5.3.4 1:4:4 (Partial Buffered)

	Mole	ml/mol	ml	Rel. Vol.	ml/20ml
H_2O_2	1	67.02	67.0	0.10	2.0
HCl	4	96.61	386.4	0.57	11.3
CH_3CO_2H	4	57.28	229.1	0.34	6.7
Total:					20

Time to dissolve Copper: 2 minutes, 30 seconds (150 seconds).

5.4 Reactants by formula

Seconds	Ratio	H_2O_2	HCl	CH_3CO_2H	Reference
2160	3:0:2	3	0	2	5.4.1
10	5:6:2	5	6	2	5.4.2
15	5:6:8	5	6	8	5.4.3

Note:

- The set of reactions are faster, the closer to having equal amounts HYDROCHLORIC ACID and ACETIC ACID.

5.4.1 3:0:2 End product, Copper(II) Acetate

	Mole	ml/mol	ml	Rel. Vol.	ml/20ml
H_2O_2	3	67.02	201.1	0.64	12.7
HCl	0	96.61	0.0	0.00	0.0
CH_3CO_2H	2	57.28	114.6	0.36	7.3
Total:					20

Time to dissolve Copper: 36 minutes (2160 seconds).

5.4.2 5:6:2 All Reactions (Un-Buffered)

	Mole	ml/mol	ml	Rel. Vol.	ml/20ml
H_2O_2	5	67.02	335.1	0.33	6.5
HCl	6	96.61	579.7	0.56	11.3
CH_3CO_2H	2	57.28	114.6	0.11	2.2
Total:					20

Time to dissolve Copper: 10 seconds.

5.4.3 5:6:8 All Reactions (Buffered)

	Mole	ml/mol	ml	Rel. Vol.	ml/20ml
H_2O_2	5	67.02	335.1	0.24	4.9
HCl	6	96.61	579.7	0.42	8.4
CH_3CO_2H	8	57.28	458.2	0.33	6.7
Total:					20

Time to dissolve Copper: 15 seconds.

5.5 Formula Acids

Seconds	Ratio	H_2O_2	HCl	CH_3CO_2H	Reference
6480	1:0:1	1	0	1	5.5.1
4	0:1:1	0	1	1	5.5.2
6	1:1:2	1	1	2	5.5.3
13	1:1:1	1	1	1	5.2.2

Notes:

- PERACETIC ACID (6480) is more corrosive to metals and a stronger oxidizer than HYDROGEN PEROXIDE.
  There is not a test here of the etching of HYDROGEN PEROXIDE by itself.
- The rate of the reaction(s) decreases with the addition of HYDROGEN PEROXIDE.
- The rate of the reaction(s) increases with the closer to equal amounts of HYDROCHLORIC ACID and ACETIC ACID.
  The overall winner is an equal amount of HYDROCHLORIC ACID and the ACETIC ACID buffer, without any HYDROGEN PEROXIDE.

5.5.1 1:0:1 Peracidic Acid

	Mole	ml/mol	ml	Rel. Vol.	ml/20ml
H_2O_2	1	67.02	67.0	0.54	10.8
HCl	0	96.61	0.0	0.00	0.0
CH_3CO_2H	1	57.28	57.3	0.46	9.2
Total:					20

Time to dissolve Copper: 1 hour, 48 minutes.

5.5.2 0:1:1 Buffered HCl

	Mole	ml/mol	ml	Rel. Vol.	ml/20ml
H_2O_2	0	67.02	0.0	0.00	0.0
HCl	1	96.61	96.6	0.63	12.6
CH_3CO_2H	1	57.28	57.3	0.37	7.4
Total:					20

Time to dissolve Copper: 4 seconds.

5.5.3 1:1:2 Both Acids

	Mole	ml/mol	ml	Rel. Vol.	ml/20ml
H_2O_2	1	67.02	67.0	0.24	4.8
HCl	1	96.61	96.6	0.35	6.9
CH_3CO_2H	2	57.28	114.6	0.41	8.2
Total:					20

Time to dissolve Copper: 6 seconds.