



PRODUCT INFORMATION

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MARTRON 4040 PROCESS

Bright Acid Copper Process

Section 1: PRODUCT DESCRIPTION AND FEATURES

Martron 4040 Process is an ultra-high-performance *dye-free* addition agent system for bright acid copper plating on metal or plastic substrates. The **Martron 4040 Process** offers unparalleled leveling, yet deposits are ductile, low stressed and readily accept subsequent coatings.

- Brightness and leveling are excellent across all normal current density ranges
- Provides excellent throwing power
- One component normally needed to maintain bath performance
- Brightener components fully consumed by electrolysis
- Free of tricyclic derivatives or dyes
- Ideal for automatic control by amp-hour feeder
- Less sensitive to higher temperatures
- Requires less frequent carbon treatment

This process consists of the following products:

Martron 4040C
Martron 4040B
Martron 4040 LCD KD
Martron 4040 Wetter

Section 2: SAFETY PRECAUTIONS

Always read and understand the Safety Data Sheet (SDS) for any chemical product prior to using the product to ensure familiarity with the methods of safe handling and health hazards associated with the **Martron 4040 Process**.

Section 3: MAKE UP and MAINTENANCE OF MARTRON 4040 PROCESS

Equipment

Tanks and any ancillary equipment should be constructed of Koroseal lined or PVC line steel, polyethylene or polypropylene. Rinse tanks after plating should also be lined. Fiberglass is not recommended because of the possible solubility of their bonding resins.

Air or mechanical agitation is required for optimum results. Air agitation supplied by a low-pressure blower is recommended. Compressed air should never be used. PVC pipe is suggested, directly beneath the parts being plated. The volume of air should provide uniform movement of solution throughout the tank including the anode area.

The anodes are made of phosphorized copper. Do not use copper anodes use high purity OFHC, forged balls or rolled electrolytic cast.

Anode hooks and anode bars should be cleaned periodically and checked for good contact. Burning and/or miss-plates can result from excessive scaling of anodes.

Anode bags must be acid resistant; such as polypropylene.

Ensure adequate ventilation is provided to remove the acid copper mist that may be generated during plating.

Rectification should be maintained with a ripple below 5% for optimum plating results.

Solution Make Up

	Optimum	Range
Copper Sulfate	25 oz/gal.	24 – 26 oz/gal.
Sulfuric Acid	4.5% (vol)	4.1 – 4.9% (vol)
Hydrochloric Acid (Reagent Grade)	0.7 ml/gal.	0.4 – 1.3 ml/gal.
Martron 4040C	0.6% (vol)	0.4 – 0.8% (vol)
Martron 4040B	0.3% (vol)	0.2 – 0.4% (vol)

Make Up Procedures

- Fill a makeup tank (not plating tank) to 75% of the final working volume with water.
- Agitate the water mechanically or with air while **SLOWLY** adding the required amount of sulfuric acid 66° Be'.
- While mixing, slowly add the required amount of copper sulfate pentahydrate.
- Once the copper sulfate is dissolved, the solution is treated with carbon at a rate of 0.03 pounds of activated carbon per gallon of solution.
- The solution is mixed by air agitation for 1 to 2 hours.
- Then allow to settle and cool before it is pumped through a filter into the plating tank.
- Add water to final working volume and mix well with air agitation.
- Analyze the solution for copper sulfate, sulfuric acid, and chloride ion, and make additions if required.
- Purify the solution by using pro-plated dummy cathodes at 10 – 30 ASF for 1 – 2 hours followed by 5 – 10 ASF for 2 hours.
- Add the required amounts of **Martron 4040C** and **Martron 4040B**.

Operating Conditions

	Optimum	Range
Copper Sulfate	25 oz/gal.	24 – 26 oz/gal.
Sulfuric Acid	11 oz/gal.	10 – 12 oz/gal.
Chloride Ion	80 ppm	50 – 150 ppm
Temperature	78 - 80°F	68 - 100°F
Current Density		20 – 100 ASF
Anode/Cathode Ration	2:1	1.5 – 2.5:1

Conversion of an Existing Acid Copper Solution

Most acid copper conversions are a slide-in process. A sample should first be sent **Martron Inc.** for analysis and conversion.

Function of Solution Components

Copper Sulfate

Copper Sulfate is normally added only during make-up because the copper ions required for plating thereafter will be maintained by electrolytic and chemical dissolution of the copper anodes. The concentration of copper sulfate is not particularly critical. However, the resistivity of the copper solution will increase as the copper sulfate concentration increases.

Copper sulfate has little effect on the grain size of the deposit. The refinement of the copper deposit is dependent more on the sulfuric acid concentration. If high cathode current densities are used, the copper sulfate concentration should be maintained at the upper limit of the recommended range. However, keep in mind that as the sulfuric acid concentration is increased, the solubility of the copper sulfate will decrease. A good rule to follow is that total oz/gal of copper sulfate plus the oz/gal sulfuric acid should equal 36 oz/gal. The electrolyte should be chemically adjusted as needed to maintain a total of 36 oz/gal.

Sulfuric Acid

Sulfuric Acid is used to provide conductivity to the copper plating solution and to dissolve the copper anodes. Changes in the sulfuric acid concentration have more effect on the anode and cathode polarization and solution conductivity than the copper sulfate concentration. Cathode polarization increases as the sulfuric acid concentration is increased.

Throwing power increases substantially in low copper sulfate and high sulfuric acid solutions. A high excess of sulfuric acid will increase the cathode over potential resulting in nodular precipitation. Therefore, for optimum copper deposits, the concentration of copper sulfate and sulfuric acid must be maintained in the established ranges for each component.

Chloride Ion

Chloride ion is used to reduce anode polarization and eliminate striated copper deposits in the high current areas. The chloride ion is effective over a wide operating range. Concentrations higher than 150 ppm can produce grainy deposits, reduced leveling, and can contribute to passivation of the anodes (white appearance.)

Concentrations lower than 50 ppm can produce rough or striated deposits, and cause step plating in the high current density area.

Function of Addition Agents

Martron 4040B

Martron 4040B is the primary maintenance component used at approximately 1 gallon per 6-8,000 ampere-hours. **Martron 4040B** is used to maintain brightness and leveling.

Martron 4040C

Martron 4040C is used for make-up of a new bath or conversion of an existing bath. High current density burning due to misuse of the **Martron 4040B** can be diminished by the addition of **Martron 4040C**. If **Martron 4040B** additions are properly maintained, **Martron 4040C** should not be needed.

Martron 4040 LCD KD

Martron 4040 LCD KD can be added only if the normal additions of **Martron 4040B** do not maintain the brightness of the low current density. To improve the low current density brightness without affecting the high current density brightness, add 0.1% by volume **Martron 4040 LCD KD**. Maintain the normal feed rate of the **Martron 4040B** and add **Martron 4040 LCD KD** only when necessary.

Martron 4040 Wetter

Martron 4040 Wetter is used in the event a wetting agent is necessary. The wetter is used within the concentration range of 0.1 to 0.5% by volume.

Process Control

Plating solution maintenance is a function of drag out, contamination, current density, and varies by application. Daily visual inspection of the plated work is required to help maintain the plating solution. Bath chemistry should be checked periodically by simple analytical methods to assure proper chemical balance. Contact **Martron Inc.** for recommended analytical methods. Also, Hull Cell testing can be useful and instructive in maintaining the plating solution additives.

Analytical Methods**Determination of Copper Sulfate in Acid Copper Plating Solution****Equipment Required**

- 2.0 ml pipet
- 250 ml Erlenmeyer flask
- 25 or 50 ml buret with stand

Reagents Required

- 10% Potassium Iodide Solution
- 10% Potassium Thiocyanate Solution
- Ammonium Bifluoride Purified Flake
- 0.1 N Sodium Thiosulfate Solution
- Starch Indicator Solution

Procedure

Method 1: To be used where the basis metal is non-ferrous and/or iron contamination is low (less than 0.4 oz/gal).

- Pipet a 2.0 ml sample of the plating solution into a 250 ml Erlenmeyer flask.
- Add approximately 75 mls of deionized water.
- Add 10 mls of 10% Potassium Iodide solution.
- Titrate with 0.1 N Sodium Thiosulfate solution to a pale-yellow color.
- Add 1 – 2 mls Starch Indicator solution and mix well.
- Continue titrating with 0.1 N Sodium Thiosulfate solution to the disappearance of the blue color.
- Calculation:

$$(\text{oz/gal}) \text{ Copper Sulfate} = \text{mls of } 0.1 \text{ N Na}_2\text{S}_2\text{O}_3 \times 16.7$$

Method 2: To be used where the basis metal is ferrous, or iron is suspected to be in high concentration (more than 0.4 oz/gal.).

- Pipet a 2.0 ml sample of the plating solution into a 250 ml Erlenmeyer flask.
- Add approximately 25 mls of deionized water.
- Add approximately ½ gram of Ammonium Bifluoride and swirl vigorously to dissolve.

Note: If appreciable tri-valent iron is present, the addition of this complexing agent will remove the green color of the solution and impart the characteristic blue of Acid Copper indicating all the iron is chemically tied up.

- Add 20 mls of 10% Potassium Iodide solution and mix thoroughly.
- Titrate with the 0.1 N Sodium Thiosulfate solution to a pale-yellow color.
- Add 10 mls of 10% Potassium Thiocyanate solution.
- Add 1 – 2 mls of Starch Indicator solution.
- Continue titrating with 0.1 N Sodium Thiosulfate solution to the disappearance of the blue color and development of a white or gray color.
- Wait one minute. If the blue color returns, complete the titration.
- Calculation:

$$(\text{oz/gal}) \text{ Copper Sulfate} = \text{ml of } 0.1 \text{ N Na}_2\text{S}_2\text{O}_3 \times 16.7$$

Determination of Sulfuric Acid in Acid Copper Plating Solution**Equipment Required**

- 2.0 ml pipet
- 250 ml Erlenmeyer flask
- 25 or 50 ml buret with stand

Reagents Required

- Bromophenol Blue Indicator Solution
- 0.1 N Sodium Hydroxide Solution

Procedure

- Pipet a 2.0 ml sample of the plating solution into a 250 ml Erlenmeyer flask.
- Add approximately 75 mls of deionized water.
- Add 4 – 6 drops of Bromophenol Blue Indicator solution.
- Titrate with 0.1 N Sodium Hydroxide solution to a deep blue endpoint.

Note: The presence of iron may interfere with the proper development of the blue color at the endpoint. If this occurs, record the volume of sodium hydroxide required to produce a slight turbidity indicating the appearance of iron hydroxide. This is the approximate endpoint of the titration.

- Calculation:

$$(\text{oz/gal}) \text{ Sulfuric Acid} = \text{mls of } 0.1 \text{ N NaOH} \times 3.28$$

Determination of Chloride Ion in Acid Copper Plating Solution**Equipment Required**

- 1.0 ml pipet
- 5.0 ml pipet
- 10 ml graduated cylinder
- 2 - 25 ml graduated mixing cylinders with glass stoppers
- 2 – Pyrex absorption cells
- Spectrophotometer capable of measuring 440 nm

Reagents Required

- Conc. Nitric Acid, reagent Grade
- Ethylene Glycol, Reagent Grade
- 0.1 N Silver Nitrate Solution

Procedure

- To each of two glass stoppered 25 ml graduated cylinders add 5 mls of Conc. Nitric Acid.
- Pipet a 5.0 ml sample of plating solution into each graduated cylinder.
- Stopper and mix well.
- To each graduated cylinder, add 10 mls of Ethylene Glycol.
- Dilute one cylinder to 25 mls with deionized water. Mark this cylinder Sample "A".
- Dilute the second cylinder to 24 mls with deionized water. Mark this cylinder Sample "B".
- Stopper and mix well.
- Pipet 1.0 ml of 0.1 N Silver Nitrate solution to Sample "B" and mix well.
- Allow these two samples to stand at room temperature in a dark plate for 30 minutes \pm 1.0 minutes.
- Transfer each sample to a Pyrex absorption cell and read the absorbance at 440 nm.
- Calculation:

$$(\text{ppm}) \text{ Chloride Ion} = \text{Absorbance "B"} - \text{Absorbance "A"} \times 152$$

Note: The factor may change due to individual instrument conditions. It is recommended that standards be checked on a regular basis to verify the analysis and the factor change accordingly.

Section 4: WASTE TREATMENT

Consult appropriate Federal, State, and local regulatory agencies to ascertain proper disposal procedures. Do not discharge into waterways or sewer systems. Disposal will depend on the nature of waste material.

Section 5: STORAGE

Avoid freezing of the **Martron 4040C** and **Martron 4040B** process components. Store the **Martron 4040C** and **Martron 4040B** components in an appropriate area with compatible materials. All chemicals should be stored in compliance with all applicable federal, state or local requirements.

Section 6: NON-WARRANTY and DISCLAIMER

The data contained in this bulletin is believed by **Martron Inc.** to be true, accurate and complete. Since the final methods of use of this product are in the hands of the customer, and beyond **Martron Inc.'s** control, **Martron Inc.** cannot guarantee that the customer will obtain any specific result. Accordingly, **Martron Inc.** does not assume any responsibility for the use of this product by the customer, the results obtained, nor the infringement of any patents of third parties.