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### EMERGENCY - MARTRON 704-289-1934 CHEMTREC 800-424-9300

# REF # - MFC-002003, 002021, 002022 and 002026

# MARTRON PPG-100S PROCESS

INDEX BASED DUAL ADDITIVE SYSTEM FOR BRIGHT NICKEL PLATING

Martron PPG-100S Process	Two additives provide control of brightener and carrier individually.
Martron PPG-100S Process	Excellent physical properties such as leveling, brightness, and ductility for automotive applications.
Martron PPG-100S Process	Superb coverage for plating complex geometries.
Martron PPG-100S Process	Can be used in duplex or multilayer nickel systems where extended corrosion resistance is required.
Martron PPG-100S Process	Can be used in air or mechanically agitated plating baths, as well as barrel plating.
Martron PPG-100S Process	Minimizes rejects from brittleness or cracking.

# **SECTION 1: OPERATING PARAMETERS**

OPTIMUM

RANGE

Temperature	57° - 65°C (135° - 150°F)	60°C (140°F)	
рН	3.5 - 4.4	4.2	
Nickel sulfate (NiSO <sub>4</sub> .6H <sub>2</sub> 0)	110 - 375 g/L (15 - 50 oz/gal)	180 g/L (35 oz/gal)	
Nickel chloride (NiCl <sub>2</sub> .6H <sub>2</sub> O)	38 - 150 g/L (5 - 20 oz/gal)	75 g/L (10 oz/gal)	
Boric acid (H <sub>3</sub> BO <sub>3</sub> )	38 - 50 g/L (5 - 6.5 oz/gal)	45 g/L (6 oz/gal)	
Martron Index Adjuster	5 - 18 mL/L (0.5 - 1.8%/vol)	12 mL/L (0.5 – 1.2%/vol)	
Martron M-1	15 - 50 mL/L (2.5 - 5.0%/vol)	32 mL/L (3.2%/vol)	
Martron M-2	· · · · · · · · · · · · · · · · · · ·		
w/air agitation	0.5 - 1.5 mL/L	0.75 mL/L	
w/mech. agitation	0.75 - 1.75 mL/L	1.0 mL/L	
Martron APA-2	0.5 – 1.0 mL/L		
Current Density	2.2 - 8.6 ASD (20 - 80 ASF)	4.3 ASD (40 ASF)	
Agitation	Air agitation from a low-pressure blower. Compressed air must not be		
	used. Mechanical agitation is also suitable.		
Anode Current density	3.2 ASD (30 ASF) for air agitated solutions.		
	1.8 ASD (17 ASF) for mechanica		
Anode to Cathode Ratio	1:1 to 2:1		
Current – DC	Less than 5% ripple		
Voltage	2 - 10 volts		
Deposition Rate	1.0 mil in 30 minutes at 40 Amps/ft2		
·	(25.4 microns in 30 minutes at 4.3 Amps/dm2)		
Cathode Efficiency	94 - 96%		
Filtration	Continuous, 1 - 2 turnovers per hour, through a five-micron		
	polypropylene cartridge or a horizontal plate filter packed with		
	diatomaceous earth.	· · ·	
Ventilation	Consult with an industrial enginee	r for recommendations.	
	0		

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### **SECTION 2: SOLUTION MAKE-UP**

### <u>Material</u>

Nickel sulfate (NiSO<sub>4</sub>.6H<sub>2</sub>O) Nickel chloride (NiCl<sub>2</sub>.6H<sub>2</sub>O) Boric acid (H<sub>3</sub>BO<sub>3</sub>) **Martron Index Adjuster Martron M-1 Martron M-2** w/air agitation w/mech. agitation **Martron APA-2**  100 Liters 18 kg 7.5 kg 4.5 kg As needed 3.2 liters 75 ml 100 ml As required

#### 100 Gallons

150 pounds (1 gal/5 lbs) 62.5 pounds (1 gal/6.31 lbs) 37.5 pounds As needed 3.2 gallons

0.075 gallons 0.10 gallons

# **SECTION 3: SOLUTION PREPARATION**

The plating solution should be made-up in a clean separate tank. Clean tank by filling with water then add 0.3%/vol sulfuric acid and 1 cc/Liter of the **Martron APA-2**. Let solution leach overnight, then empty tank and rinse.

- 1. Fill the cleaned tank ½ full with water and heat to 60°C (140°F).
- 2. While stirring, add and completely dissolve the required amount of nickel sulfate and nickel chloride.
- 3. Raise the pH to 5.2 by adding nickel carbonate with vigorous stirring. When checking the pH, obtain a 100 ml sample and filter or allow the sample to settle to get a true pH reading.
- 4. Add 3 ml/Liter of 30% hydrogen peroxide, well diluted with water.
- 5. Add 1 ml/Liter of Martron APA-2.
- 6. Add 2.5 grams per liter of plating grade pulverized activated carbon. Stir for 1 hour, then keep heated overnight at 65°C (150°F) and allow the solution to settle.
- 7. Filter the solution into a clean plating tank that has been cleaned and leached like the storage tank.
- 8. Pack the filter with filter aid and carbon so there is approximately 0.2 g/L of each material.
- 9. With agitation add the required amount of boric acid.
- 10. Adjust the pH to 4.0 with 50% sulfuric acid.
- 11. Electrolyze the solution at a low current density, 0.54 ASD (5 ASF) using corrugated dummy cathodes. Usually this will take 8 hours, check low current density areas of the cathode for darkness. If darkness exists then continue dummy plating.
- 12. Clean filter then re-pack with filter aid.
- 13. Add the required amounts of addition agents.

# **SECTION 4: RECOMMENDED EQUIPMENT**

Tank or Liner -	CPVC, PVC, Koroseal-lined steel, or polypropylene.
Pumps -	Conventional plastic suitable for acid applications or high temperature.
Racks -	Plastisol-coated copper. Stainless steel should be avoided.
Heaters -	Quartz, titanium, or PTFE. The titanium should be grounded or anodically connected.
Filters -	1 - 2 turnovers per hour through a 5-micron polypropylene cartridge or
	horizontal plate filter packed with diatomaceous earth filter aid.
Anode Bags -	Dynel or polypropylene, washed then leached in a 5% by vol. sulfuric acid solution then flushed with hot water before use. Thread count should be about 38 x 29 per inch.
Anodes -	Sulfur depolarized nickel such as INCO S-Rounds, electrolytic squares or R-rounds.
Anode Hooks -	Monel or titanium
Anode Baskets -	Titanium

### **SECTION 5: MARTRON INDEX ADJUSTER**

Martron Index Adjuster is used for make-up of new solutions. The Martron Index Adjuster is synergistic with the Martron M-1, and the Martron M-2; together they produce bright leveled deposits. The proper amount of Martron Index Adjuster is in the Martron M-2. Normally extra additions of the Martron Index Adjuster are not required, unless high drag-out or extended high current density plating has occurred. Martron Index Adjuster

is not removed by carbon treatment.

### **SECTION 6: MARTRON M-1**

**Martron M-1** is added at solution make-up. **Martron M-1** is synergistic with the **Martron M-2** to produce brightness, leveling, and good ductility. Low concentrations of **Martron M-1** will reduce the bright throw, decrease tolerance to impurities, lower the chromium acceptance, lower leveling, and decrease the ductility of the deposit. High concentration will not be harmful but may precipitate at concentration above 5.0%. Over the side additions may be necessary to maintain concentration from losses such as carbon treatment or drag out. Carbon treatments above 4 pounds/100gallons (480 grams/100 liters) may remove up to 50% of the **Martron M-1**. Solution can be analyzed using the procedure in this technical data sheet. **Martron M-1** is added at 6340 amp-hr/Liter (24,000amp-hr/gallon) of operation.

### SECTION 7: MARTRON M-2

**Martron M-2** contains the secondary brighteners, and the **Martron Index Adjuster** in the consumptive proportions needed. High concentrations of **Martron M-2** will reduce the ductility of the deposit. **Martron M-2** is added at 5280amp-hr/Liter (20,000 amp-hr/gallon) of operation.

# **SECTION 8: MARTRON APA-2**

Wetting agents are added at solution make-up and replenished by checking the surface tension. Wetting agents are readily removed with carbon. Concentration of wetting agents should be determined after any carbon is in contact with solution. As an approximate usage **Martron APA-2** agent should be replenished at 20,000 amp-hr/Liter (75,000 amp-hr/gallon). Carbon treatments such as 4 pounds/100gallons (480 grams/100 liters) will remove most of the wetting agents. Solution can be analyzed using the procedure in this technical data sheet.

# SECTION 9: NICKEL SULFATE

Complex shapes and/or the use of high current densities should have the higher nickel sulfate concentration. The nickel sulfate concentration contributes the nickel metal necessary to provide the latitude for the operating current density range. Lower nickel content can lead to high current density burning. Simple shapes and lower current densities may use concentrations of nickel sulfate as low as 15 oz/gal (112 g/L). Check nickel content to determine and maintain the correct nickel sulfate concentration.

# SECTION 10: NICKEL CHLORIDE

Nickel chloride provides approximately twice the conductivity of nickel sulfate. The nickel chloride concentration primarily contributes the chloride ion for proper anode corrosion and good bath conductivity. High concentrations can reduce ductility slightly.

# **SECTION 11: BORIC ACID**

The boric acid concentration contributes the cathode film buffering necessary for the bath to produce deposits with good ductility. High concentrations can cause sporadic pitting due to precipitation at lower temperatures. Air agitation pipes can also become clogged with high concentrations. Low concentrations can produce HCD burning, and reduced ductility.

# SECTION 12: pH

To lower the pH use, dilute or 50% Sulfuric acid. It is not common to need to raise the pH, however if this is

required add nickel carbonate to the slurry tank of the filter before exposing the nickel carbonate to the actual plating solution. Adding nickel carbonate directly to the solution can cause roughness.

### **SECTION 13: TEMPERATURE**

The temperature of the plating solution should be maintained between 135 - 150°F (57 - 65°C). Operating at higher temperatures will allow operation at higher current densities and improved solution conductivity and subsequent lower conductivity salts.

### **SECTION 14: CURRENT DENSITY**

The current density of the process should be maintained within the specified limits.

### SECTION 15: ANALYSIS OF MARTRON BRIGHT NICKEL INDEX BATHS

### Determination of Nickel Metal

### **Reagents**

Standard EDTA solution, 0.100 M

Ammonium Hydroxide, AR, concentrated

MUREXIDE INDICATOR - thoroughly grind about 0.25 grams of murexide powder with about five (5) grams of granulated table sugar. Transfer to a large wide mouth plastic capped jar and add about 95 grams sugar to the mixture. Shake vigorously to coat all sugar particles with the murexide mixture.

#### <u>Apparatus</u>

1 mL Pipette, volumetric. 10 mL Pipette, volumetric 10 mL Graduated cylinder. 250 mL Erlenmeyer flask.

### **Procedure**

- 1. Pipette 1.00 mL of plating solution into a 250 mL Erlenmeyer flask.
- 2. Add about 50 mL DI or distilled water, mix.
- 3. Add about 10 mL of concentrated Ammonium Hydroxide.
- 4. Add about 0.15 grams of the murexide indicator mixture prepared as above.
- 5. While swirling, titrate with 0.100 M EDTA solution until the yellowish color sharply changes to purple.
- 6. Calculate the nickel concentration as follows:
  - a.) Nickel (oz/gal) = (mL EDTA) x M EDTA x 7.83/mL sample
  - b.) Nickel (g/L) = Nickel (oz/gal) x 7.5

#### **Determination of Nickel Chloride**

### Reagents

Dichlorofluoresein indicator- (0.2% solution) 0.153N Silver Nitrate standardized solution

### <u>Apparatus</u>

2 ml Pipette, volumetric 250 ml Erlenmeyer flask 50 ml Burette

### Procedure

- 1. Pipette 2 ml of sample into a 250 ml Erlenmeyer flask.
- 2. Add 50 ml of DI water.
- 3. Add about 5 drops of Dichlorofluoresein indicator.
- 4. Titrate with the 0.153N Silver Nitrate solution to a definite light pink colored endpoint.
- 5. Calculate the total Nickel Chloride:
  - a.) NiCl<sub>2</sub>• 6 H<sub>2</sub>O (oz/gal) = (ml AgNO<sub>3</sub> used) x 1.23
  - b.) NiCl<sub>2</sub>• 6 H<sub>2</sub>O (g/L) = NiCl<sub>2</sub>• 6 H<sub>2</sub>O (oz/gal) x 7.5

### Determination of Nickel Sulfate

### **Reagents**

None required

### **Apparatus**

None required

### Procedure

Calculate as follows: Nickel Sulfate (g/L) = [(g/L total Nickel) - (g/L Nickel chloride x .247)] x 4.47

### **Determination of Boric Acid**

### **Reagents**

Mixed indicator- Dissolve 0.1 grams of Bromocresol Purple and 0.02 grams of Bromothymol Blue in 100ml methanol. 0.1N Sodium Hydroxide standardized solution Mannitol

#### Apparatus

2 ml Pipette, volumetric 250 ml Erlenmeyer flask 50 ml Burette

#### **Procedure**

- 1. Pipette 2 ml of sample into a 250 ml Erlenmeyer flask.
- 2. Add 2 ml of DI water.
- 3. Add about 5 drops of Mixed indicator.
- 4. Add 5 grams of Mannitol.
- 5. Titrate with the 0.1N Sodium Hydroxide solution to a purple colored endpoint.
- 6. Calculate the Boric Acid concentration:
  - a.) Boric Acid (oz/gal) = (ml 0.1N NaOH used) x 0.414
  - b.) Boric Acid (g/L) = Boric Acid (oz/gal) x 7.5

### **Determination of Martron M-1**

### **Reagents**

Deionized or distilled water. Ethyl Acetate Methyl Alcohol Hydrochloric Acid

0.1N Standard Sodium Hydroxide solution 0.1% Bromocresol Purple indicator solution

### Apparatus

50 mL Pipette, volumetric. 300 mL Erlenmeyer flask 12 mL Separatory Funnel 50 mL Burette

### **Procedure**

- 1. Pipette a 50 mL sample of plating solution into the separatory funnel.
- 2. Add 1.0 mL of Hydrochloric acid.
- 3. Add 50 mL of Ethyl Acetate to the separatory funnel. Shake vigorously for 1-2 minutes. Allow to separate for 1-2 minutes.
- 4. After separation drain off the lower layer and discard solution.
- 5. Rinse side of separatory funnel with 25 mL D.I. water. Allow separation to form and drain off lower layer again.
- 6. Repeat step #4 three to four times.
- 7. Transfer remaining Ethyl Acetate layer to 300 mL Erlenmeyer flask.
- 8. Add 10 mL Methyl Alcohol.
- 9. Add 15 drops 0.1% Bromocresol Purple indicator solution.

Calculate the Martron M-1 as follows Martron M-1 (%/vol) = mL of 0.1N NaOH x 0.416%/vol x 10 = ml/L

### Determination of Martron Index Adjuster

### **Reagents**

0.100 N Standard Sodium Thiosulfate solution.
0.100 N Standard Potassium Bromate/Bromide solution.
1:1 Sulfuric acid solution
10 % w/v Potassium Iodide solution
1 % Starch Indicator solution

### Apparatus

10 mL Pipette, volumetric. 50 mL Graduated cylinder. 5 mL Graduated cylinder 250 mL lodine flask.

### Procedure

- 1. Pipet 10.00 mL of plating solution into a 250 mL lodine flask.
- 2. Add 50 mL DI or distilled water and stir to mix.
- 3. Pipet 10.00 mL of 0.100 N Potassium Bromate/Bromide solution into the flask and mix again.
- 4. Add 10 mL of 1:1 Sulfuric acid and immediately stopper and seal with water. Mix thoroughly.
- 5. Allow to stand for 10 minutes.
- 6. Add 5 mL 10 % Potassium lodide solution and immediately titrate with 0.100 N Sodium Thiosulfate solution.
- With mixing, begin titrating with the thiosulfate solution until the solution turns a light-yellow color. Add 1-2 mL of starch solution and continue the titration until the dark blue starch/iodine color disappears for at least 30 seconds. Record this titration as "B".
- 8. Run a blank using 10.00 mL DI water or distilled water in place of the plating solution. Record this titration as "A".
- 9. Calculate the Martron Index Adjuster as follows:

Martron Index Adjuster (%/vol) = (mL A - mL B) X 0.36%/vol X 10 = mL/L

### Determination of Surface Tension

### Apparatus

Stalagmometer

### **Procedure**

The **Martron APA-2** agent concentrations can be determined by checking the surface tension of the solution. The stalagmometer number of drops delivered for a certain volume is determined by the specific gravity, surface tension, and the specific gravity of the solution.

The stalagmometer will supply directions with the instrument that should be followed.

Standards should be made with each stalagmometer using a plating solution that has no wetting agent. Standards should be made at 0.1, 2.0, 3.0, 4.0, and 5 ml/Liter to prepare a concentration versus surface tension graph. Take an average of three readings for each standard.

Calculate surface tension as:

SW x NW x D

Surface Tension (Dynes/cm) -

N x DW

D= Density of the Sample in grams/mI DW= Density of the water in grams/mI N= Counted number of drops of the sample NW= water number engraved on the stalagmometer. SW= Surface tension of the water (72.0 dynes/cm)

# **SECTION 16: TROUBLESHOOTING GUIDE**

<u>Problem</u>	Possible Cause	Corrective action
Dull deposits (LCD area)	<ol> <li>Excessive Martron M-2</li> <li>Metallic contamination (eg, Cu, Zn, Pb, Cd)</li> </ol>	1. "Dummy" solution at 4-5 ASF 2. "Dummy" solution at 4-5 ASF
	3. Low Martron M-1	3. Add Martron M-1
Cloudy deposits (MCD & HCD areas)	<ol> <li>Low Martron M-2</li> <li>pH to low</li> <li>Organic contamination</li> <li>Metallic contamination (eg, Fe, Si, Al. Cr<sup>+3</sup>)</li> </ol>	<ol> <li>Add Martron M-2</li> <li>Raise the pH</li> <li>Carbon treat.</li> <li>High pH treat solution.</li> </ol>
High consumption of: Carrier	<ol> <li>Drag-out is high</li> <li>High carbon usage</li> <li>Very high nickel concentration</li> </ol>	<ol> <li>Reduce drag-out</li> <li>Reduce amount of carbon used</li> <li>Reduce nickel concentration</li> </ol>
Poor ductility	<ol> <li>Excessive Martron M-2</li> <li>Low Martron M-1</li> <li>High pH</li> <li>Metallic contamination (eg, Zn, Cd)</li> <li>Organic contamination</li> </ol>	<ol> <li>"Dummy" solution at 4-5 ASF</li> <li>Add Martron M-1</li> <li>Adjust pH</li> <li>"Dummy" solution at 4-5 ASF</li> <li>Carbon treatment</li> </ol>
Poor leveling	<ol> <li>Low Martron M-2</li> <li>Low Martron M-1</li> <li>Low pH</li> <li>Low Martron Index Adjuster</li> </ol>	1. Add <b>Martron M-2</b> 2. Add <b>Martron M-1</b> 3. Adjust pH 4. Add <b>Martron Index Adjuster</b>

Burning	<ol> <li>Low nickel salts/boric acid</li> <li>High CD</li> <li>Low temperature</li> <li>Low agitation</li> <li>Chromate contamination</li> <li>Metallic contamination</li> </ol>	<ol> <li>Add nickel salts/boric acid</li> <li>Reduce CD</li> <li>Adjust temperature</li> <li>Increase agitation</li> <li>High CD "dummy" + high pH treatment</li> <li>High pH + carbon treatment</li> </ol>
Skip plating	1. High <b>Martron M-2</b> 2. Metallic contamination (eg, Pb, Zn, Cd)	1. "Dummy" solution at 4-5 ASF 2. "Dummy" solution at 4-5 ASF
Poor chromium	1. High <b>Martron M-2</b> 2. Low <b>Martron M-1</b>	<ol> <li>"Dummy" solution at 4-5 ASF acceptance.</li> <li>Add Martron M-1</li> </ol>

### **SECTION 17: HANDLING and STORAGE**

Wetter additives can produce temporary irritation when they come into contact with the skin. Therefore, care should be taken to prevent accidental eye and skin contact. Rubber gloves, a rubber apron, and protective goggles should be worn when handling Wetter additives. In case of contact, immediately flush with copious amounts of water and scrub well with soap and water. Wetter additives are stable on standing and have a shelf life in excess of two years.

### FREEZABILITY:

As with most chemical products, it is preferable that freezing be avoided. However, if freezing should occur during transportation or storage, directions for handling the products covered in this technical data sheet are as follows:

If **Martron Index Adjuster** freezes, simply allow the container to completely thaw and bring to room temperature of  $70^{\circ} - 75^{\circ}F/21^{\circ} - 24^{\circ}C$ . Thoroughly mix to bring back to original condition.

If **Martron M-1** freezes, simply allow the container to completely thaw and bring to room temperature of  $70^{\circ} - 75^{\circ}F/21^{\circ} - 24^{\circ}C$ . Thoroughly mix to bring back to original condition.

If **Martron M-2** 30 freezes, simply allow the container to completely thaw and bring to room temperature of 70° - 75°F/21° - 24°C. Thoroughly mix to bring back to original condition.

### **SECTION 18: NON-WARRANTY**

The data contained in this bulletin is believed by *Martron Inc.* to be accurate, true and complete. Since however, final methods of use of these products are in the hands of the customer and beyond our control, we cannot guarantee that the customer will obtain the results described in this bulletin, nor can we assume any responsibility for the use of this product by the customer in any process which may infringe the patents of third parties.