DATE: 07/14/2015

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

REF - MFC-007507, MFC-007508, MFC-007509, MFC-007510 and MFC-007511

# MARTRON MTC PROCESS

PROCESS FOR WHITE TRIVALENT CHROMIUM PLATING

Martron MTC Process Excellent metal distribution across the entire current density plating range.

Martron MTC Process State of the art "Newest Generation" Trivalent chromium process provides Deepest-

Lightest-Whitest appearance.

Martron MTC Process Eliminates burning and whitewash associated with hexavalent processes.

Martron MTC Process Greatly reduces waste treatment costs.

Martron MTC Process Has excellent plating speed, allows easy conversion from existing hexavalent

processes.

# **SECTION 1: OPERATING PARAMETERS**

	RANGE	<u>OPTIMUM</u>			
Temperature	27° - 43°C (80° - 110°F)	29° - 32°C (85° - 90°F)			
pH	2.3 - 2.9	2.6 - 2.8			
Current Density	8.5 - 13.4 Amps/dm <sup>2</sup> (80 - 125 Amps/ft <sup>2</sup> )				
Martron MTC Base Compound	390 - 460 g/l (52 - 61.3 oz/gal)	415 g/l (55.3 oz/gal)			
Martron MTC Catalyst	50 - 75 ml/l (5.0-7.5% by vol.)	65 ml/l (6.5% by vol.)			
Martron MTC MS	1.0 - 4 ml/l (0.1-0.4% by vol.)	1.5 ml/l (0.15% by vol.)			
Martron MTC EXT	2.0 ml/l (0.2% by vol.)	2.0 ml/l (0.2% by vol.)			
Specific Gravity	1.220 to 1.230	1.220 to 1.230			
Chromium (Cr+3)	20 - 23 g/l (2.7 - 3.1 oz/gal)	21 g/l (2.8 oz/gal)			
Agitation	Air through low pressure blower recomme	ended.			
Anode to Cathode Ratio	1.5:1 to 2.0:1				
Current – DC	Less than 10% ripple				
Voltage	6 - 15 volts				
Deposition Rate	Approximately 0.15 - 0.25 microns at 10.8 Amps/dm <sup>2</sup> (6-10 micro inches/min at 100 Amps/ft <sup>2</sup> )				
Filtration	Usually not required, proper Ion Exchange	e equipment is needed.			

# **SECTION 2: SOLUTION MAKE UP**

Material	100 Liters	100 Gallons		
Martron MTC Base Compound	41.5 kg	346 pounds		
Martron MTC Catalyst	6.5 Liters	6.5 gallons		
Martron MTC MS	150 milliliters	0.15 gallon		
Martron MTC EXT	200 milliliters	0.2 gallon		

# **SECTION 3: SOLUTION PREPARATION**

- 1. To a clean plating tank install the special graphite anodes and titanium hangers. It is recommended that the buss bars be heavy nickel plated before installation. After the titanium hangers are installed to the buss bar, wrap the bussing with plastic tape or cover with appropriate inert material to minimize copper contamination from the copper bussing.
- 2. Install the heating and cooling coils. If the cooling coils are titanium, connect the coils through some high impedance wire so they are anodically protected.
- 3. Regenerate the Ion Exchange resin and then connect the system to the plating tank.
- 4. Fill tank full with water.
  - a) Check agitation to insure it is uniform.
  - b) Turn on the Ion Exchange system and check flow rate then turn off, and turn flow valves off.
  - c) Check heating and see what the heat up time of solution to 60 degrees Celsius is. Then turn on cooling if equipped to see if it works properly.
  - d) Lower pH to 2.5 with hydrochloric acid and then add 1ml/Liter of the Martron MTC MS.
  - e) Allow solution to stand for eight hours at operating temperature of 32°C. This will leach the equipment and tank. Run the Ion Exchange system for 1 hour.
  - f) Pump out the leach solution, drain the Ion Exchange system, and rinse the tank out.
- 5. Fill the plating tank ½ full with city water (D.I. water should be used if available).
- 6. Turn on the heating and air agitation and heat the solution to 60 65°C (140 150°F).
- 7. Using air agitation, slowly add 415 g/Liter of the Martron MTC Base Compound. Solution temperature will drop as the salts are added. Bring the temperature back up to 60 - 65°C (140 - 150°F). If the material is added too fast it may settle to the bottom and not dissolve properly. Check bottom of tank to insure all the material is dissolved before proceeding to the next step. Usually it takes 2 hours at the high temperature to completely dissolve all of the Martron MTC Base Compound.
- 8. Add 65 ml/Liter (6.5%/vol) Martron MTC Catalyst then bring tank volume up to operating level and maintain heat for 4 hours.
- 9. Allow solution to cool to operating temperature.
- 10. Add 1.5 ml/Liter of the Martron MTC MS, then add 2 ml/Liter of the Martron MTC EXT.
- 11. Allow solution to mix for 10 minutes then check pH of the solution. Adjust if necessary.
- 12. Check the concentration of the chromium metal, and the Martron MTC Catalyst. Adjust if necessary.
- 13. The solution will be ready to plate parts at this point.
- 14. If there are any HCD or LCD defects noted then the solution will need to be dummy plated for a short time. If dummy plating is needed, then heavy nickel plate a steel corrugated panel and put enough area in the tank to equal approximately 25 – 50 m<sup>2</sup>/1000 liter or 1 - 2 ft<sup>2</sup>/100 gallons. Dummy plate at 9.7 Amps/dm<sup>2</sup> or 90 Amps/ft<sup>2</sup> for 1 hour, then plate parts to see if all defects have been removed.

# **SECTION 4: RECOMMENDED EQUIPMENT**

Tank or Tank Liner -New PVC, polypropylene, polyethylene, ABS or Koroseal-lined steel.

Heaters/Cooling Coils -Quartz, PTFE, and titanium (must be grounded or anodic). Heaters/Chillers -Quartz, PTFE, and titanium (must be grounded or anodic).

Racks -Plastisol-coated copper.

Use Martron MTC Anodes. Consult *Martron Inc.* for recommendations. Anodes -Anode Hangers -Use Martron MTC Anode Hangers. Consult *Martron Inc.* for recommendations. Bus Bars -Copper bus that is heavily nickel plated to avoid possible copper contamination. Bus bars that are exposed should be protected from solution by a plastic shield or

by wrapping with plastic waterproof tape.

Ion Exchange -Use Martron MTC Exchange Systems.

Ion Exchange Resin -Use Martron MTC PURE Resin.

# SECTION 5: MARTRON MTC ADDITION AGENTS and REPLENISHMENT

#### **Martron MTC Base Compound**

**Martron MTC Base Compound** is used for make-up and replenishment of the solution from drag-out. It provides conductivity to the bath. Additions of **Martron MTC Base Compound** should be made slowly to minimize undissolved salts in the bath. Additions should be made in several smaller increments if the additions are over 30 g/Liter (4 oz/gallon). Large additions can also be made by simply heating the solution after the addition. The heating will properly complex the chromium whenever very large additions are required.

The addition of 21 g/Liter (2.8 oz/gallon) of the **Martron MTC Base Compound** will raise the specific gravity 0.01 units. Make the additions of **Martron MTC Base Compound** prior to adding the **Martron MTC Chromium**.

High concentration of Martron MTC Base Compound can result in crystallization if the solution temperature is too low.

Low concentration of **Martron MTC Base Compound** will result in lower conductivity, and may require use of higher voltages to maintain the same current density.

### **Martron MTC Chromium**

Martron MTC Chromium is replenished on an ampere-hour basis and replaces the chromium that is plated out of solution. Martron MTC Chromium is added at a rate of approximately 435 g/1000 amperes-hours (15.3 oz/1000 ampere-hours) and should be added at least once every 3.5 ampere-hours/Liter (13 ampere-hours/gallon) of operation.

Additions larger than 7.0 g/Liter (0.93 oz/gallon) should be made in several small increments. If a very large addition must be made then it may be helpful to heat the solution after the addition to properly complex the chromium.

#### **Martron MTC Catalyst**

Martron MTC Catalyst allows the chromium to be plated out of solution. Martron MTC Catalyst is consumed by dragout and electrolysis. High Martron MTC Catalyst can result in some precipitation of the salts. Low Martron MTC Catalyst can result in reduced plating rate. Maintain the concentration of the Martron MTC Catalyst within the specified ranges. Martron MTC Catalyst should be added at 1.52 liters (51 fl. oz) per 1000 ampere-hours and should be added at least once every 4.5 ampere-hours/Liter (17 ampere-hours/gallon) of operation.

### **Martron MTC MS**

**Martron MTC MS** reduces the surface tension of the solution and improves the metal distribution of the deposit. Low concentrations can result in dark streaks. High concentrations can result in excessive foaming during electrolysis. **Martron MTC MS** should be added at 18 - 36 ml/1000 ampere-hours (0.6 - 1.2 fl. oz/1000 ampere-hours) and should be added at least once every 4 ampere-hours/Liter (15 ampere-hours/gallon) of operation. Concentration can be determined by measuring the surface tension.

#### **Martron MTC EXT**

**Martron MTC EXT** improves the current density range of the deposit. **Martron MTC EXT** is added at solution make-up. Further additions should only be made when advised by your Martron Inc. representative.

### **SECTION 6: TEMPERATURE**

The process operates at 27 - 43°C (80 - 110°F), heating will be required. If production is above 0.5 amperes/Liter or if ambient temperature is high, then cooling will be required. High temperature will reduce the covering power. Low temperature can result in precipitation of the salts.

# **SECTION 7: pH**

The pH should be maintained between 2.6 and 2.8. Raise the pH 0.1 unit with the addition of 2 ml/Liter (2 gallons/1000

gallons) ammonium hydroxide. Lower the pH 0.1 unit with the addition of 2 ml/Liter (2 gallons/1000 gallons) hydrochloric acid. pH adjustments will produce an artificially large change in pH that will equilibrate after a period of time. It is also recommended that pH buffers of 2.0 and 7.0 be used to calibrate the pH meter that will be used for analyzing the solution.

### **SECTION 8: EQUIPMENT**

### **Martron MTC Anodes**

Graphite anodes from Martron Inc. must be used. Anode length should be approx. 2.5 - 3.75 cm (1 - 1.5 inches) shorter than the rack package at each end when measured from the top of the top piece on the rack to the bottom of the bottom piece on the rack. The anodes should also be at least 5 cm (2 inches) below the solution level.

Generally, twice the area of anode area to cathode area should be used. The maximum current density on the anodes should be 540 amperes/m² (50 amperes/ft²). The graphite anode must be mounted below the surface of the solution. The copper bussing should be plated with a layer of nickel prior to installation; this will minimize the amount of copper contamination. Once the hangers are mounted to the buss bars, the buss bar should be wrapped with waterproof plastic tape or covered with other inert plastic material.

#### **Martron MTC Anode Hangers**

Anode hangers are available from *Martron Inc*.

#### Air Agitation

Air agitation should be as mild and uniform as possible. High agitation can result in reduced coverage while low agitation can result in uneven metal distribution. Air must be provided from an oil free blower. Perforated plastic airlines must be installed to give uniform mild agitation below the cathode area.

### **Ampere-Hour Meter**

Product additions to the solution are made by ampere-hours. A suitable ampere-hour meter should be used to ensure proper control of the process. An automatic metering pump for the **Martron MTC Catalyst** is usually recommended.

# Rectifiers

12 or 15-volt rectifiers are normally recommended however existing 6-9-volt rectifiers have been used in some installations. The **Martron MTC Process** will not burn therefore higher voltages are normally used to provide superior covering power when compared to an existing hexavalent process.

# **Martron MTC Ion Exchange Systems**

Ion Exchange equipment is available from *Martron Inc*. Consult your *Martron Inc*. representative for proper sizing of equipment.

## **Martron MTC Ion Exchange Resin**

Obtain the special Ion Exchange resin from *Martron Inc*. Consult *Martron Inc*. for specific volume recommendations.

# **SECTION 9: MARTRON MTC ANALYSIS PROCEDURES**

# **Martron MTC Catalyst**

## Reagents

5% Sodium Carbonate solution (Dissolve 50 grams Na<sub>2</sub>CO<sub>3</sub> (AR) in DI water and dilute to 1 Liter).

10% w/v Potassium Iodide solution

1:1 Sulfuric acid solution (Dilute concentrated sulfuric acid 1:1 with DI water, use caution when mixing, always add acid to water.)

0.100 N Sodium Thiosulfate solution.

0.100 N Potassium Permanganate solution.1% Starch Indicator solution

#### **Apparatus**

1 mL Pipette, volumetric 5 mL Pipette, volumetric 25 mL Pipette, volumetric 250 mL Erlenmeyer flask

#### **Procedure**

- 1. Pipette 1.0 mL of filtered solution into a 250 mL Erlenmeyer flask. Run a blank using water in place of the plating solution. It is suggested that a blank be run at least monthly until experience dictates otherwise.
- 2. Add 5 mL of 5% Sodium Carbonate solution.
- 3. Place the flask in a boiling water bath so that the flask is generally upright and the liquid in the flask is covered by the boiling water. Heat for 15 minutes. After this time, carefully remove the flask and check for the odor of ammonia. All ammonia should be driven off but if an odor of ammonia can still be detected then reheat for another 2-3 minutes. In any event, all ammonia must be removed before continuing.
- 4. Remove the flask from the water bath and wash down the sides of the flask with 5 mL DI water. Cool to room temperature.
- 5. Pipet 25 mL of 0.100 N KMnO<sub>4</sub> solution into the flask. Swirl to coat any precipitate on the flask walls with the mixture.
- 6. Again, place the flask into the boiling water bath for 5 minutes. The purple permanganate should change to brown shortly after heating.
- 7. Cool to room temperature.
- 8. Add 5 mL of 10% w/v Potassium lodide solution.
- 9. Add 5 mL of 1:1 H<sub>2</sub>SO<sub>4</sub> and immediately titrate with 0.100 N Sodium Thiosulfate solution until the solution turns a light yellow. Add 10 drops of starch indicator and titrate to the point where the dark iodine/starch color disappears and the solution is a clear light blue.
- 10. Calculate as follows:

Martron MTC Catalyst (%/vol) = 0.606 X (mL B - mL A) where A = mL 0.1N Sodium Thiosulfate for the sample, B = mL 0.1N Sodium Thiosulfate for blank.

# **Trivalent Chromium**

# Reagents

30% Hydrogen Peroxide solution, AR (see Note)

50% Sodium Hydroxide Solution 10% w/v Potassium Iodide solution

1:1 Sulfuric acid solution (Dilute concentrated sulfuric acid 1:1 with DI water, use caution when mixing, always add acid to water.)

1% Starch Indicator solution

0.100 N Sodium Thiosulfate solution

# **Apparatus**

5 mL Pipette, volumetric 100 mL Volumetric flask 250 mL Erlenmeyer flask

#### **Procedure**

- 1. Pipette 5.0 mL of filtered solution into a 100-mL volumetric flask and dilute to volume.
- 2. Pipette 5.0 mL of the solution from the volumetric flask directly to the Erlenmeyer flask.
- 3. Add 6 drops of 30% Hydrogen Peroxide.
- 4. Add 4 drops of the 50% Sodium Hydroxide solution.
- 5. Swirl lightly and insert into the boiling water bath. Maintain heat for 10 minutes. All traces of gassing should be removed.

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- 6. Add 5 mL 10% Potassium Iodide solution and mix.
- 7. Add 10 mL 1:1 Sulfuric acid and immediately titrate with 0.1 N Sodium Thiosulfate solution until the solution turns a light-yellow color.
- 8. Add 1 mL of 1% starch solution and again titrate to the disappearance of the dark blue starch/iodine color. Calculate the concentration as follows:

oz/gal 
$$Cr^{+3} = mL \ 0.1 \ N \ Na_2S_2O_3 \ X \ 0.904$$
  
g/L  $Cr^{+3} = oz/gal \ X \ 7.5$ 

#### **DETERMINATION OF SURFACE TENSION**

#### **Apparatus**

Stalagmometer: Available from Martron Inc.

# **Procedure**

The **Martron MTC MS** concentration 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 Martron MTC MS.

Standards should be made at 0.0,1.0, 2.0 and 3 ml/Liter of **Martron MTC MS** to prepare a concentration versus surface tension graph. Take an average of three readings for each standard.

Calculate surface tension as:

Surface Tension (Dynes/cm) = 
$$\frac{SW \times NW \times D}{N \times DW}$$

D= Density of the Sample in grams/ml
DW= Density of the water in grams/ml
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)

### **Martron MTC Solution Control**

# Overview

**Martron MTC** plating solutions utilize a weak complex to deposit trivalent chromium. Trivalent chromium solution must be properly maintained to provide the correct amount of complex chromium. Additions should be made frequently to provide consistent concentration of the constituents.

#### **Martron MTC Addition Agent Consumption**

Martron MTC plating solutions are consumed by electrolysis and by drag-out. Drag-out affects all the addition agents but electrolysis only affects certain addition agents.

### **Electrolysis and Drag-out**

**Drag-out** 

Martron MTC Chromium Martron MTC Catalyst Martron MTC MS **Martron MTC Base Compound** 

Addition agents that are lost by electrolysis can be replaced by ampere-hour determination. Materials that are lost by drag-out can be replaced by checking the specific gravity of the plating bath. Use the log sheet provided on the following page to determine the appropriate additions to the **Martron MTC** plating solution. High drag-out or low drag-out may require adjustment to the addition rates for the **Martron MTC** process.

# Martron MTC Process

LOG SHEET	TANK #:		OPERATING TEMPERATURE:		
	VOLUME:	GALLON	PAGE #:		

	STD=1.19	DIFFERENCE (D)	POUNDS OF MARTRON MTC BASE COMPOUND				(RP200=0.00096) POUNDS MARTRON MTC CHROMIUM COMPOUND	(RP2300=.000398) GALLONS MARTRON MTC CATALYST	(AM400=0.000007) GALLONS MARTRON MTC-MS		
DATE	SPECIFIC GRAVITY (SG)	DIFFERENCE BETWEEN SG AND STD	=D x 280 x TANK VOLUME /16	LAST AMP.HR METER READING	CURRENT AMP.HR METER READING	CHANGE IN AMP. HRS D (AH)	D(AH) x RP200	D(AH) x RP300	D(AH)Xam400	рН	REMARKS/ ADDITIONS
EX:	1.17	.02	.02 x 280 x 750/ 16= 262.5 lbs.	40	50	+10	.0096 lbs.	.0398 gals.	.00007 gals.	3.0	-

# **SECTION 10: TROUBLESHOOTING**

#### **DARK STREAKS**

<u>Cause</u> <u>Remedy</u>

Low Martron MTC Catalyst
Low specific gravity

Add Martron MTC Catalyst
Add Martron Base Compound

Metallic contamination

Turn on **Martron MTC PURE** or dummy-plate at 20 - 40 Amps/ft<sup>2</sup>

Contaminated nickel-plated surface

Improve rinsing after nickel or delay plating in the **Martron MTC** bath

Organic contamination Carbon Treat

Low Martron MTC MS Add Martron MTC MS

**POOR COVERAGE** 

<u>Cause</u> <u>Remedy</u>

Low specific gravity Check and adjust with Martron MTC Base Compound

Low pH Adjust with ammonium hydroxide

High temperature Reduce temperature to 85° - 90°F (29° - 32°C)

Low Martron MTC EXT
Low Current Density
High agitation

Add Martron MTC EXT
Increase Current Density
Reduce agitation

PATCHY WHITE DEPOSIT

<u>Cause</u> <u>Remedy</u>

Organic contamination Carbon Treat

Dry-on of nickel-plating solution Transfer racks faster, increase rinsing time, lower nickel temperature

Delay current initiation in **Martron MTC** plating bath

Organic contamination Carbon treat

Contaminated nickel rinses Dump and refill rinse tanks

Zinc contamination Dummy plate at 20 - 40 Amps/ft² or purify

**LOW PLATING RATE** 

<u>Cause</u> <u>Remedy</u>

Low current density Increase current applied

Low specific gravity Add Martron MTC Base Compound

Anodes coated Check anodes and clean

High pH Lower pH in 0.2 pH unit increments

Low Martron MTC Catalyst Add Martron MTC Catalyst

**NON-UNIFORM THICKNESS** 

<u>Cause</u> <u>Remedy</u>

Low agitation
Low Martron MTC MS
Low Martron MTC Catalyst
High Martron MTC Catalyst
Allow concentration to fall

Poor anode spacing Check length to anode length and adjust

# **SECTION 11: HANDLING and STORAGE**

**Martron MTC** 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

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should be worn when handling **Martron MTC** additives. In case of contact, immediately flush with copious amounts of water and scrub well with soap and water. **Martron MTC** 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 MTC Catalyst** 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.

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

If **Martron MTC EXT** 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 12: 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.