PRODUCT INFORMATION

MARTRON INC.® P O BOX 309; MONROE, NC 28111 PH: (704) 289-1934; FAX: (704) 283-7400

DATE: MARCH 2017

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

REF # - MFC-003038 and 003039

MARTRON ZN370 PROCESS

Ultra-Performance Potassium Chloride Acid Zinc Process

Section 1: PRODUCT DESCRIPTION and FEATURES

The **Martron ZN370 Process** is a maximum performance plating system for the deposition of brilliant, level, ductile zinc deposits from a combination potassium and ammonium chloride zinc plating electrolyte.

- Super bright, lustrous, ductile, fine grained deposits
- No burning, staining or whiting out, over the entire plating range.
- Provides uniform deposit distribution similar to that of alkaline baths
- Requires little control
- Very tolerant to a high concentration of dissolved iron, bath impurities and general abuse
- Contains a built-in ductilizing agent making it ideal for plating heavy thickness
- Plated deposits remain ductile so there is less chance of chipping, flaking or cracking
- Accepts chromate films readily than competitive processes
- Subsequent yellow dichromate will not “slough” off as with most other chloride processes
- Allows chromate film to perform to maximum ability regarding salt spray protection
- Extremely versatile regarding bath composition allowing variety of ratios of metal to chloride
- Low foaming allows for bright, trouble-free plating even at elevated bath temperatures
- Plating additives are stable in high chloride concentrations

This process consists of the following ***Martron Inc.*** products:

Martron ZN370 MU
Martron ZN370 MA

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 ZN370 Process**.

Section 3: MAKE UP and MAINTENANCE of the MARTRON ZN370 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 line. Fiberglass is not recommended because of the possible solubility of the bonding resins.

Agitation is only required for rack plating. Barrel plating provides sufficient agitation to insure a flow of fresh solution to the parts being plated. 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.

A filter capable of turning the solution over at least once per hour (twice per hour preferable) should be used. A filter with the capability of coating the filter media with either filter aid or carbon is highly recommended.

Despite the high cathode efficiency of the **Martron ZN370 Process**, a certain amount of heat will be generated during plating. Higher temperatures generally increase brightener consumption and overall bath performance will be less than optimum. This is true of all chloride zinc processes. Therefore, a means of cooling the bath is highly recommended using Teflon or Titanium coils or heat exchangers.

Plastisol coated steel or stainless- steel racks are recommended. Copper racks, although Plastisol coated, are not recommended due to the possible introduction of copper to the solution.

Zinc ball anodes that are 99.99% pure zinc in titanium baskets are recommended. Baskets must be kept full; otherwise chemical dissolution of the basket can occur. In rack applications polypropylene anodes bags should be used to prevent shelf roughness. Anode bags must be leached prior to use for 6 - 8 hours in a hot water solution containing 5 - 10% hydrochloric acid and 4% by volume **Martron ZN370 MU**. Failure to do this will cause organic contamination from the bag sizing to enter the tank. Anode and cathode bars should be nickel plated or Plastisol coated to prevent copper from entering the plating solution.

Solution Make Up

	Optimum:	**Range:**
Zinc Chloride Concentrate*		
Rack Plating:	5% (vol)	3 – 8% (vol)
Barrell Plating:	6% (vol)	3 – 8% (vol)
Potassium Chloride		
Rack Plating:	30 oz/gal.	25 – 35 oz/gal.
Barrel Plating:	28 oz/gal.	25 – 35 oz/gal.
Ammonium Chloride:	Optional	Optional
Boric Acid:	4 oz/gal.	2 – 5 oz/gal.
Martron ZN370 MU:	4% (vol)	3 – 5% (vol)
Martron ZN370 MA:	0.1% (vol)	0.05 – 0.2% (vol)

* Zinc chloride concentrate contain 9.2 lb./gal zinc chloride, and is available through ***Martron Inc.***

Make Up Procedures

- Be sure tank is clean and free from contamination
- Fill tank to approximately 75% of the final volume with water
- Heat water to 125 – 130°F
- With agitation, add the required amount of zinc chloride concentrate
- With agitation, slowly add and dissolve the required amount of potassium chloride
- With agitation, slowly add and dissolve the required amount of boric acid
- Add the required amount of **Martron ZN370 MU** and mix well
- Add the required amount of **Martron ZN370 MA**
- Add balance of water to fill tank
- Agitate to mix uniformly
- Adjust pH and temperature to operating ranges
- Filter for approximately 6 hours to remove any impurities

Note: A small amount of hydrogen peroxide may be necessary if the potassium chloride salts contain iron.

- Confirm solution composition by analysis and performing Hull Cell tests

Operating Conditions

	Optimum:	Range:
Zinc Metal		
Rack:	3.5 oz/gal.	2 – 6 oz/gal.
Barrel:	4 oz/gal.	2 – 6 oz/gal.
Ammonium Chloride:	Optional	Optional
Potassium Chloride:		
Rack:	30 oz/gal.	25 – 35 oz/gal.
Barrel:	28 oz/gal.	25 – 35 oz/gal.
Total Chloride		
Rack:	19 oz/gal.	16 – 24 oz/gal.
Barrel:	21 oz/gal.	16 – 24 oz/gal.
Boric Acid:	4 oz/gal.	2 – 5 oz/gal.
pH:	5.6	5.2 – 6.2
Temperature:	80°F	65 - 120°F
Cathode Current Density		
Rack:	3 – 75 ASF	0.5 – 75 ASF
Barrel:	0.5 – 30 ASF	0.5 – 75 ASF
Anode Current Density:	15 – 35 ASF	13 – 35 ASF
Voltage		
Rack:	2 – 6 volts	2 – 15 volts
Barrel:	6 – 15 volts	2 – 15 volts

Operating Notes

Temperature

The plating bath operates best when the temperature is maintained between 65 - 95°F (19 - 35°C). The **Martron ZN370 Process** has excellent tolerance to higher than normal temperatures and the process is stable at elevated temperatures. However, as with all zinc processes, the addition agents will function differently at temperatures above 100°F (38°C). More **Martron ZN370 MA** is required to maintain the same brightness and deposit uniformity at higher temperatures. If the plating bath is to be operated at elevated temperatures for extended periods of time, maintaining the pH at the lower end of the recommended range is highly recommended to improve the low current density area brightness.

pH

Lower pH maximizes brightness and leveling, and improves low current density areas while improving ductility, and uniformity of the deposit thickness. High pH improves covering power and cathode efficiency. Extremely high or low pH can cause the brighteners to “oil out”. This is a temporary situation and will return to normal as soon as the pH is corrected.

Since the anode efficiency is greater than the cathode efficiency, some hydrogen ions are neutralized during plating. This causes the pH to rise during operation. Additions of hydrochloric acid will maintain the pH in the proper range. If pH must be increased, small additions of ammonium hydroxide or potassium hydroxide can be made, or the bath can be allowed to rise to the proper level on its own. If the pH fluctuates significantly, it means that the anode area is low or the zinc metal is out of operating range. A pH meter should be used for tank side control of pH.

Current Density

Always maintain both the cathode and anode current densities within the operating range. Too high a cathode current density (too much current for the parts being plated) will cause burning and grainy deposits. Too low a current density will reduce plating speed. Too high an anode current density (too small an anode area for the current being drawn) causes anode polarization and low zinc metal concentration. Too low an anode current density causes the zinc metal to rise during operation.

Impurities

Iron

Iron builds up in the plating solution during operation and can produce blue to black stained deposits after chromating and increase deposit stress. This is due to the acidic pH of the bath and drag in of dissolved iron from the pre-treatment cycle and the parts themselves.

The **Martron ZN370 Process** has excellent tolerance to dissolved iron and does not require frequent treatment. However, the level of iron in the solution eventually reaches the point where it must be removed to prevent the co-deposition of iron. The suggested treatment is to add 0.05% by volume 35% hydrogen peroxide at the end of the plating day. In some cases, the addition of 1 – 1.5 pounds of potassium permanganate pre-dissolved in water per 1000 gallons of plating solution can also be effectively used in place of hydrogen peroxide. If added during production, good filtration is of necessity in that roughness may occur from precipitated solids unless filtered.

Heavy Metal Contamination

The presence of heavy metals in the plating solution will be apparent in the low current density areas in the form of dull to black deposits and/or skip plating in more severe contamination conditions. Low current density dummy plating is recommended, or if contamination is very severe, zinc dust treatment can be utilized. Zinc dust should be mixed in a water slurry at 16 oz/gallon and then adding 0.1% of this solution to the zinc plating solution. It should be added with agitation and then allowed to settle after 15 minutes of mixing. This typically should be done in a treatment tank and not in the plating tank. Filtration is necessary after treatment to prevent re-dissolution of the contamination.

Organic Contamination

Organic contamination detracts from the deposit brilliance and leveling, reduces chromating ability and causes brittle, burned deposits. With low levels of contamination, the solution can be circulated through a carbon packed filter; however, in more severe cases batch carbon treatment may be required.

Pretreatment is important with any zinc process to help in controlling organic contamination. Good pre-plate cleaning and pickling are also necessary to produce high quality deposits. The effectiveness of the pre-plate cycle is not always apparent simply by observing the plated finish.

Cloud Point

The “cloud point” is the temperature at which the primary organic additive, or wetter, is forced out of the bath causing the plating solution to become cloudy. The chloride zinc additives are inversely soluble with heat. Therefore, the as the plating solution temperature increases, the lower the solubility of the additives become.

The cloud point can also be influenced by the pH and the chloride concentration. In addition, as the plating solution ages and builds up impurities and brightener breakdown products, the cloud point can decrease.

Typically, the cloud point of the plating solution needs to be maintained above 120°F. If the cloud point continues to fall below 120°F, it is advisable to determine and correct the conditions or routine that is the cause of the low cloud point.

Function of Solution Components

Zinc Metal

The concentration of zinc metal will influence the maximum current density at which plating can take place without burning and/or granular deposits occurring. It also affects the covering and throwing power.

Higher concentrations of zinc metal permit higher current densities and improve covering power. However, it detracts from the throwing power (uniform deposit thickness). Normally, higher metal concentrations are used for rack plating. For barrel installations, similar metal concentrations are used, which assures the most uniform deposit thickness.

The zinc metal is maintained in the plating bath by electrochemical dissolution of zinc anodes. The proper choice of anode area will keep the concentration of metal within the proper limits, and minimize the need for additions of zinc chloride to adjust the metal concentration. Zinc metal in chloride solutions, unlike alkaline solutions, does not rise during idle periods. As a rule of thumb, a large anode is desirable to minimize the voltage necessary for maximum covering power.

Zinc chloride is used to make up a new plating solution and/or used to increase the zinc metal in the plating. Make certain that a high purity grade with a maximum of 0.009% heavy metals is used.

Chloride

Chloride is supplied by the additions of zinc chloride, potassium chloride, and the hydrochloric acid used for normal pH adjustments. Chloride provides the necessary conductivity of the plating solution. Chlorides are typically lost by dray out and are added based upon analysis.

Low chloride concentrations reduce bath conductivity causing hazy or dull zinc deposits in the low current densities, reduced low current densities coverage, reduce anode corrosion, and reduced plating rate.

High concentrations can lower the cloud point of the plating solution, increase burning in the high current densities, increase the rate of zinc dissolution, and cause some brightener systems to “oil out”.

Make sure an approved grade of potassium chloride is used that does not contain excessive amounts of anti-caking agents. The product should contain 99.5% potassium chloride.

Additions of chloride to the plating bath should never exceed 100 lb. of potassium chloride per 1000 gallons of plating solution at any one time. Large single additions of chloride can shock the plating bath by lowering the temperature of the solution and possibly breaking out some of the wetter and brightener components. Therefore, frequent small additions are preferable to single large additions.

Boric Acid

Boric acid functions as a buffer to aid in controlling the pH of the plating solution. It is also used to maintain the maximum current density to control burning of the zinc deposit. The boric acid concentration can vary within the range given. However, higher concentrations of boric acid may be harmful as it will precipitate out at lower temperatures due to its limited solubility. The precipitate will clog air spargers and in turn cause roughness in the zinc deposit.

Function of the Addition Agents

Martron ZN370 MU

Martron ZN370 MU is used at the time of bath conversion, new bath make-up, and routine maintenance of an operating solution. This addition agent establishes and maintains the proper concentration of wetter, coupler, ductilizers, and low current density brightener. A low concentration will cause burning, loss of ductility, and reduced overall brightness and grain refinement. Normally, **Martron ZN370 MU** is lost to a small degree to electrolysis, and to a larger degree through drag out.

Martron ZN370 MU should be maintained by adding 1 – 2 gallons for each 100 pounds of potassium chloride added to the plating bath.

Martron ZN370 MA

Martron ZN370 MA is the additive that provides the overall deposit luster, leveling, and brilliance. Although this process is unusually tolerant to brightener overload, high concentrations can cause random staining. This can normally by corrected by the addition of 0.2 – 0.5% by volume **Martron ZN370 MU**. Low concentrations will reduce leveling and brightness of the deposit and reduces chromate performance.

Martron ZN370 MA is maintained in the plating solution at the rate of 1 gallon per 20,000 to 25,000 amp-hours. It is highly recommended that **Martron ZN370 MA** be added by an automatic brightener feeder. Automated feeders provide uniform plating results and far lower brightener consumption.

Process Control

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. The zinc metal, total chlorides, boric acid, pH and cloud point need to be analyzed on a regular basis to maintain the quality of the zinc deposit. The addition of proprietary additives should always be confirmed by Hull Cell tests before adding to the plating solution. Frequent, small additions on a regular basis are preferred over the occasional large dose.

Analytical Methods

Determination of Zinc Metal in Chloride Zinc Plating Solution

Equipment Required

- 5.0 ml pipet
- 250 ml Erlenmeyer Flask
- 25 or 50 ml buret with stand

Reagents Required

- Xylenol-Orange Indicator
- Buffer Solution - Dissolve 90 grs of Anhydrous Sodium Acetate in 500 ml DI water. Add 15 ml Glacial Acetic Acid, reagent grade. Dilute to 1-Liter with DI water and mix well.
- 0.0575 M EDTA Solution

Procedure

- Pipet a 5.0 ml sample of the Zinc Plating solution into a 250 ml Erlenmeyer flask.
- Add 50 ml of deionized water.
- Add sufficient Buffer Solution, about 25 ml, to produce a pH of approximately 5.15 and mix the sample.

Note: The solution should be clear with no haze.

- Add a pinch of Xylenol-Orange Indicator to produce a violet color and dissolve any precipitate.
- Titrate immediately with 0.0575 M EDTA solution to a yellow or gold endpoint.
- Calculation:

  (oz/gal) Zinc Metal = ml of 0.0575 M EDTA x 0.1

Note: To raise the zinc metal by one ounce per gallon requires

1) 1.92 oz/gal of zinc chloride powder, or
2) 1.7 fl. oz./gal of 9.2 lbs./gal zinc chloride concentrate solution

Zinc metal content is normally maintained by the dissolution of the anodes as the bath operates at nearly 100% anode efficiency. If the zinc concentration must be adjusted by the use of zinc chloride, you must remember to deduct the added chloride before figuring the amount of potassium chloride to be added.

Determination of Total Chloride in Chloride Zinc Plating Solution

Equipment Required

- 5.0 ml pipet
- 10.0 ml pipet
- 100 ml volumetric flask
- 250 ml Erlenmeyer Flask
- 100 ml graduated cylinder
- 25 or 50 ml buret with stand

Reagents Required

- 4% Chromate Solution
- 0.1 N Silver Nitrate Solution

Procedure

- Pipet a 5.0 ml sample of the Zinc Plating solution into a 100 ml volumetric flask.
- Dilute to the mark with deionized water.

- Invert the stoppered flask several times to assure the solution is thoroughly mixed.
- Pipet a 10.0 ml sample of the diluted sample into a 250 ml Erlenmeyer flask.
- Add 50 ml of deionized water.
- Add 1 to 2 ml of Chromate Indicator solution to give the sample yellow color.
- Titrate with 0.1 N Silver Nitrate solution until a permanent straw coloration forms on the white silver chloride precipitate.
- Calculation:

  (oz/gal) Total Chloride = ml of 0.1 N $AgNO_3$ x 1.0

Note: The following equivalents should be noted when maintaining the chloride content of a bath:

1) Potassium chloride contains 48% chloride, and
2) Zinc chloride contains 52% chloride and 48% zinc

Therefore, to raise the chloride content in the bath by one ounce per gallon requires:

2.08 oz/gal of potassium chloride

Determination of Boric Acid in Chloride Zinc Plating Solution

Equipment Required

- 5.0 ml pipet
- 250 ml Erlenmeyer Flask
- 25 or 50 ml buret with stand

Reagents Required

- Mannitol Power, Reagent Grade
- Boric Acid Indicator Solution
- 0.1 N Sodium Hydroxide Solution

Procedure

- Pipet a 5.0 ml sample of the Zinc Plating solution into a 250 ml Erlenmeyer flask.
- Add 5 grs Mannitol Powder.
- Add 3 – 5 drops of Boric Acid Indicator solution.
- Titrate with 0.1 N Sodium Hydroxide solution to a purple endpoint.
- Calculation:

  (oz/gal) Boric Acid = ml of 0.1 N NaOH x 0.165

Determination of Cloud Point of Chloride Zinc Plating Solution

Equipment Required

- 100 ml beaker
- Thermometer
- Hot plate with stir bar capability
- Stir bar

Reagents Required

- None

Procedure

- Fill a 100 ml beaker with 60 to 80 ml of the Zinc Plating solution to be tested.
- Add stir bar to beaker.
- Place beaker on hot plate and place thermometer in the beaker.
- Turn on heat and slowly stir bar agitate the plating solution.
- Slowly heat test solution while monitoring the solution temperature with the thermometer.

- When the solution turns cloudy, record the temperature reading on the thermometer.
- Calculation:

(°F) Cloud Point = Temperature reading on thermometer when solution turns cloudy

Note: Typically, the Cloud Point of the Chloride Zinc Plating solution is maintained above 120°F. If the cloud point is below 120°F, add 0.5% by volume **Martron ZN370 MU**. Check cloud point after addition, and if necessary, continue to make additions of **Martron ZN370 MU** until desired cloud point is achieved.

Contact ***Martron Inc.*** if continued large additions are required to maintain the cloud point after the standard additions are made.

pH

The pH should be checked daily, and adjusted to maintain the solution within the proper range. For accurate results, a pH meter should be used rather than pH papers. Additions of hydrochloric acid will lower the pH to the proper range. If pH must be increased, small additions of ammonium hydroxide or potassium hydroxide can be made, or the bath can be allowed to rise to the proper level on its own.

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 ZN370 Process** components. Store the **Martron ZN370** 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.*** control, and 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.