

riag Zn 270

Acid bright zinc plating process for high temperature application

Properties

- Excellent for barrel plating with high temperature stability
- Can be operated with air or cathode movement
- Stable over a wide metal ion concentration and temperature range (high cloud point)
- Deposits soft ductile, bright coatings with excellent levelling
- Very good covering power and brightness range in recesses
- The deposits can be easily conversion coated in all common processes
- Suitable for ammonia as well as ammonia free electrolytes

Electrolyte make - up

	Potassium electrolyte	
	Range	Optimum
Zinc chloride ($\text{ZnCl}_2 \times 1.5 \text{ H}_2\text{O}$)	50 – 150 g/L	60 g/L
Potassium chloride (KCl)	180 – 240 g/L	210 g/L
Boric acid (H_3BO_3)	18 – 25 g/L	22 g/L
riag Zn 270 Carrier	30 mL/L	30 mL/L
riag Zn 270 Brightener	2 mL/L	2 mL/L
pH – value	5.4 – 5.7	5.5

Electrolyte values

	Potassium electrolyte	
	Range	Optimum
Zinc (Zn^{2+})	25 – 70 g/L	30 g/L
Chloride (Cl^-)	Zn+ 100 g/L	130 g/L

Electrolyte make - up

Zinc chloride ($\text{ZnCl}_2 \times 1.5 \text{ H}_2\text{O}$)Ammonia chloride (NH_4Cl)Potassium chloride (KCl)Boric acid (H_3BO_3)**riag Zn 270 Carrier****riag Zn 270 Brightener**

pH – value

Mixed electrolyte

Range	Optimum
40 – 150 g/L	60 g/L
0 – 60 g/L	30 g/L
100 – 240 g/L	110 g/L
18 – 25 g/L	22 g/L
40 mL/L	40 mL/L
2 mL/L	2 mL/L
5.4 – 5.7	5.5

Electrolyte values

Mixed electrolyte

Zinc (Zn^{2+})Ammonia (NH_4^+)Chloride (Cl^-)

Range	Optimum
20 – 70 g/L	30 g/L
0 – 20 g/L	10 g/L
85 – 150 g/L	100 g/L

Electrolyte make - up

Zinc chloride ($\text{ZnCl}_2 \times 1.5 \text{ H}_2\text{O}$)Ammonia chloride (NH_4Cl)Boric acid (H_3BO_3)**riag Zn 270 Carrier****riag Zn 270 Brightener**

pH – value

Ammonia electrolyte

Range	Optimum
40 – 150 g/L	60 g/L
130 – 170 g/L	150 g/L
18 – 25 g/L	22 g/L
40 mL/L	40 mL/L
2 mL/L	2 mL/L
5.4 – 5.7	5.5

Electrolyte values

Ammonia electrolyte

Zinc (Zn^{2+})Ammonia (NH_4^+)Chloride (Cl^-)

Range	Optimum
20 – 70 g/L	30 g/L
45 – 60 g/L	50 g/L
85 – 115 g/L	100 g/L

Make up

Zinc chloride and boric acid are dissolved in deionised warm water (50 % of final volume). The volume is increased to 90% after the addition of potassium chloride and/or ammonia chloride. This is followed by pH adjustment using hydrochloric acid. The additives are added in the following order **riag Zn 270 Carrier**, **riag Zn 270 Brightener** followed by water addition to final volume. The electrolyte should be filtered prior to initial electrolyte use to prevent deposit roughness.

Operating parameters

Temperature	RT (20 – 60 °C)		
pH – value	5.4 – 5.7		
Cathodic current density	Current density	Barrel : Rack:	0.5 – 3.0 A/dm ² 0.5 – 3.0 A/dm ²
Anodic current density	< 3.0 A /dm ²		
Current efficiency	< 100 %		
Deposit rate	Barrel: Rack:	at 1 A/dm ² ca. 0.25 µm/min. at 1 A/dm ² ca. 0.25 µm/min.	
Anodes	Zinc anodes acc. to DIN 1706 with 99.99 % Zinc		
Agitation	Cathode movement (ca. 3 – 6 m/min.) or air (oil free compressed air is required)		
Tanks	Plastic or lined steel tanks		
Filtration	Recommended (1 – 5 turnovers/ h)		
Heating	Only for continuous warm zinc plating		
Cooling	Not required due to the temperature tolerance of this process (max. 60 °C)		
Fume extraction	Recommended		
Electrolyte maintenance	Zinc, boric acid and conducting salts should be routinely analysed and corrected.		
Consumption	The additive consumption can vary according to drag out as well as electro chemical reactions and the value serves only as guide line. riag Zn 270 Carrier 1.5 L je 10 kg KCl or 2.5 L je 10 kg NH ₄ Cl riag Zn 270 Brightener 1.0 – 2.5 L/10kAh + 2 mL per liter drag out. The required dosing for drag out losses can be estimated by conducting salt consumption.		

Function of the various additives

Zinc

Increasing the zinc concentration lowers the burning effect risk but also reduces the metal distribution. A too low zinc value can result in deposit burning. The **riag Zn 271 Carrier** must be added for correction.

Chloride

Too high chloride concentrations result in excessive zinc and iron dissolution. Low chloride levels promote deposit burning and decreasing zinc concentration.

Boric acid

Over dosing results in incomplete dissolution and subsequent deposit roughness. The excess boric acid can be removed by filtration. The effect of too low boric acid concentrations results in deposit burning in high current density areas.

pH - value

A too low pH – value leads to rapid iron build up and deterioration in covering and metal distribution. Higher pH – value result in deposit burning in high current density areas. The zinc concentration decreases and the metal hydroxide inclusion can lead to deposit roughness.

Iron

Concentration from approximately 300 ppm iron become visible in high current density areas, especially on blue chromate passivated parts, and must therefore be reduced. The iron is precipitated by raising the pH – value to 5,8 – 6,0 with weak potassium hydroxide solution. The iron is then oxidised by adding 0,1 – 0,3 mL/L hydrogen peroxide solution. As a result iron (III) hydroxide is then removed by filtration. However, overdosing of hydrogen peroxide results in rough deposits and should be avoided. A better iron removal method is the continuous oxidation with oxygen gas purging combined with filtration.

riag Zn 270 Carrier

riag Zn 270 Carrier is only used for new electrolyte make up and replenishing of drag out losses. The electrolyte changes resulting from a too low **riag Zn 270 Carrier** concentration include roughness, metal flitter and turbidity. Overdosing of the **riag Zn 270 Carrier** has no disadvantages except for increased brightener consumption.

riag Zn 270 Brightener

riag Zn 270 Brightener is the main consumable during plating. A drop in the concentration shows a loss of brightness which can be restored by additions of **riag Zn 270 Brightener**. Overdosing of the **riag Zn 270 Brightener** results in „spotty” brightness that is normally not critical but a simultaneous lack of the basic additive **riag Zn 270 Carrier** could lead to brittle plating.

Activated Carbon

Is not recommended.

Removal of metallic contaminations in acid zinc electrolytes

- Iron:** Oxidizing of iron with 1 – 2 mL/L hydrogen peroxide (H_2O_2 diluted 1 : 10). Iron 3^+ begins to precipitate at pH 4.8 as ferric hydroxide ($\text{Fe}(\text{OH})_3$) so that the precipitated iron can be filtered at a pH value of approx. 5.5.
- Copper:** Copper can be removed by dummy plating at 0.1 to 0.3 A/dm². With much contamination finely pulverised zinc dust (1 – 2 g/L) can as well be added to the electrolyte.
- **Important** in that case: to keep the electrolyte in agitation during about 1 hour by stirring. By charge exchange the copper is reduced. ($\text{Zn}^0 + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu}^0$). Subsequently the electrolyte must be filtered thoroughly.
- Nickel:** Nickel can be removed from the electrolyte by dummy plating at 0.3 – 0.4 A/dm².
- Chrome:** By means of sodium hydrosulphite chrome VI can be reduced to chrome III which precipitates at a pH value of about 5.7 and can so be filtered out. The required quantity of sodium hydrosulphite can previously be determined stoichiometric by chromium analysis. In case that the chrome cannot be analysed the following proceeding is recommended:
- Take 1 litre from the electrolyte.
 - Add 20 mg of sodium hydrosulphite.
 - 10 mL of it are then to pour into a test tube.
 - Addition of 4 drops Solution A → shake
 - Addition of 3 drops Solution B → shake.
- If a violet colour develops, there is still chrome VI existing.
- Add again some mg of sodium hydrosulphite into the beaker (continuously stirring). Repeat this step as often until no violet coloration comes into being. (Make up a dummy test for colour comparison!)
- Solution A: 50 mL/L H_2SO_4 conc., fill up to 1 litre with water
 Solution B: Cold saturated alcoholic solution with diphenylcarbazide

Lead, Cadmium, Cobalt Removal by dummy plating at 0.2 – 0.4 A/dm².

Liability

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riag Oberflächentechnik AG
Murgstrasse 19a
CH-9545 Wängi
T +41 (0)52 369 70 70
F +41 (0)52 369 70 79
riag.ch
info@riag.ch

Analysis (Analytical Methods)

Sample Preparation:

The sample must be taken from a well-mixed point and allowed to cool down to 25 °C.

Boric acid

Reagents	Sodium hydroxide solution 0.1 mol/L Sorbitol solution 20 %V or Mannitol Indicator: Bromcresol purple (1 % in Ethanol)	
Process	5 mL 250 mL 50 mL 5 drops	Pipette sample into a Erlenmeyer flask, add about Sorbitol solution 20%V, add of indicator and titrate with Sodium hydroxide solution from yellow to violett.
Calculation	Consumption of mL NaOH x 1.236 = g/L Boric Acid (H₃BO₃)	

Chloride

Reagents	Silver nitrate solution 0.1 mol/L Indicator: Potassium chromate solution 5 %	
Process	1 mL 250 mL 100 mL 5 drops	Pipette sample into a Erlenmeyer flask, add about deionised water, add of indicator and titrate with 0.1 mol Silver nitrate solution from yellow to a brown end point.
Calculation	Consumption of mL AgNO ₃ x 3.545 = g/L Chloride (Cl⁻)	
Correction	Addition of 1 g/L Chloride = 2 g/L Potassium chloride	

Zinc

Reagents	0.1 mol/L Na ₂ EDTA Buffer solution (100 g/L NaOH and 240 mL/L 98 % acetic acid in DI water) Indicator: Xylenol orange, (mixture of 1 % in KNO ₃).												
Process	<table><tr><td>5 mL</td><td>Pipette</td></tr><tr><td>250 mL</td><td>sample into a</td></tr><tr><td>100 mL</td><td>Erlenmeyer flask, add about</td></tr><tr><td>20 mL</td><td>DI water,</td></tr><tr><td>a spatula tip</td><td>buffer solution and</td></tr><tr><td></td><td>of indicator. Titrate with 0.1 mol/L EDTA from red to yellow.</td></tr></table>	5 mL	Pipette	250 mL	sample into a	100 mL	Erlenmeyer flask, add about	20 mL	DI water,	a spatula tip	buffer solution and		of indicator. Titrate with 0.1 mol/L EDTA from red to yellow.
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250 mL	sample into a												
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20 mL	DI water,												
a spatula tip	buffer solution and												
	of indicator. Titrate with 0.1 mol/L EDTA from red to yellow.												
Calculation	Consumption of ml EDTA x 1.3074 = g/l Zinc (Zn²⁺)												
Correction	Addition of 1 g/L Zinc = 2 g/L Zinc chloride												