

# RIAG Zn 231

## Cyanide bright zinc process

### Properties

- liquid brightener
- produces brilliant deposits at low, medium, and high current densities
- for both barrel and rack operations
- excellent throwing and covering power
- plated parts can easily be chromated
- due to the variable metal and cyanide content of the solution, it may be used over a wide range of operating conditions
- contains no aldehydes - a fact which allows the plater to use operating temperatures higher than normal (up to 45 °C)
- its brilliant deposits and its economic use make it the outstanding cyanide zinc brightener system

### Bath make - up

	low cyanide	medium cyanide	high cyanide
Zinc oxide	12.5 g/L	25 g/L	45 g/L
Sodium cyanide	25 g/L	60 g/L	110 g/L
Sodium hydroxide	70 g/L	50 g/L	30 g/L
<b>RIAG Zn 231 Brightener</b>	3 – 4 mL/L	3 – 4 mL/L	3 – 4 mL/L
<b>RIAG Zn 235 Purifier</b>	0 – 1 mL/L	0 – 1 mL/L	0 – 1 mL/L

Dissolve sodium hydroxide and sodium cyanide in 2/3 of the required amount of water; considerable heat will be evolved. Add zinc oxide and stir until dissolved. Cool to room temperature. According to the amount of contaminants add the **RIAG Zn 235 Purifier** (pre-diluted 1:10), fill the tank with water to its final volume and filtrate continuously overnight. Add the required amount of **RIAG Zn 231 Brightener** and stir the electrolyte.

## Desired values

	low cyanide	medium cyanide	high cyanide
Zinc	8 - 12 g/L	15 - 25 g/L	30 - 40 g/L
Sodium cyanide	15 - 30 g/L	30 - 60 g/L	75 - 110 g/L
Sodium hydroxide	80 - 90 g/L	70 - 80 g/L	65 - 75 g/L
Sodium carbonate	max. 90 g/L	max. 80 g/L	
Ratio NaCN : Zn	1.5 – 2.2 : 1	2.0 – 3.0 : 1	2.5 – 3.0 : 1

## Operating Parameters

Temperature	18 – 40 °C (at lower temperatures current densities should be lower, at higher temperatures brightness and throwing power is reduced)
Anodes	Pure zinc 99.99 % according to DIN 1706 or steel anodes to control the zinc concentration
Cathodic current density	0.5 - 3 A/dm <sup>2</sup> (barrel) 2 - 6 A/dm <sup>2</sup> (rack)
Voltage rack	2 – 8 V
Voltage barrel	6 – 16 V
Deposition rate rack	approx. 0.6 µm/min at 3 A/dm <sup>2</sup>
Deposition rate barrel	approx. 0.2 µm/min at 1 A/dm <sup>2</sup>
Agitation	Cathode agitation (rack or barrel movement) recommended, no air agitation (to avoid cyanide mist and carbonate increase)
Tank material	Plastic or steel with plastic coating
Filtration	Recommended
Heating	If necessary, ceramic or steel immersion heaters
Cooling	Necessary for lines with high load on small volumes and/or recommended to freeze out sodium carbonate
Exhaust	Required for worker's protection
Maintenance	Analyse zinc, sodium cyanide, sodium hydroxide and sodium carbonate regularly. Zinc is controlled by changing the anodic current density or by using steel anodes. Add sodium cyanide and sodium hydroxide according analysis. Add 0.1 L <b>RIAG Zn 235 Purifier</b> per added kg NaOH. Freeze out excess sodium carbonate. Adjust <b>RIAG Zn 231 Brightener</b> with the aid of Hull cell tests.

Consumption

**RIAG Zn 231 Brightener** is consumed by drag-out as well as electrochemically, by anodic oxidation and cathodic build-in. The following values can give a range for the consumption:

**RIAG Zn 231 Brightener** 1 – 3 L / 10'000 Ah

## Effects of the electrolyte components

### Zinc

Increase of zinc increases the burning limit, but reduces the throwing power. A lack of zinc produces burnings.

### Sodium cyanide

Excess of cyanide reduces brightness, thus more **RIAG Zn 231 Brightener** is needed. Lack of cyanide produces a more brittle zinc layer. High cyanide bath types are less sensitive against impurities.

### Sodium hydroxide

Excess of hydroxide speeds up zinc dissolution too much. Lack of hydroxide reduces the burning limit.

### Sodium carbonate

Excess carbonate reduces brightness, thus more **RIAG Zn 231 Brightener** is needed. Further, it is responsible for passive anodes leading to a bad current distribution in the electrolyte and a too low zinc dissolution rate.

### Contaminating metals

Like Cu, Pb, Cd, Sn, Ni deteriorate brightness and appearance of the zinc layer and should be removed with the **RIAG Zn 235 Purifier**. Chromium(VI) reduces current efficiency and coverage in the low current density area. It affects the chromatability and appearance and must be reduced to Cr(III) with sodium dithionite.

### RIAG Zn 231

Excess of **RIAG Zn 231 Brightener** causes a spotted dull zinc deposition in the low to medium current density area, current efficiency is reduced and in extreme cases, blistering may occur. Lack of additive results into lack of brightness and throwing power.

## Environmental considerations

All concentrates, rinse waters and waste solution must be treated and discharged according to local effluent control regulations. Chemicals shall not be stored below 10 °C.

## Liability

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RIAG Oberflächentechnik AG  
Murgstrasse 19a  
CH- 9545 Wängi  
Tel. + 41 (0) 52 / 369 70 70  
Fax + 41 (0) 52 / 369 70 79  
[www.riag.ch](http://www.riag.ch)  
[info@riag.ch](mailto:info@riag.ch)

## Analysis

### Sample preparation

Take the sample at a homogeneously mixed position and let it cool down to room temperature. If turbid, allow to settle and decant or filter.

### Zinc

Reagents                      0.1 mol/L Na<sub>2</sub>EDTA  
Buffer solution (100 g/L NaOH and 240 mL/L 98% acetic acid in DI water)  
Indicator: 1 % xylenol orange blended with KNO<sub>3</sub>)

Process                                      Pipette  
5 mL                                      sample into a  
250 mL                                    Erlenmeyer flask, add  
100 mL                                    DI water,  
20 mL                                    buffer solution and  
a spatula tip                          of indicator. Titrate with 0.1 mol/L EDTA from red to  
yellow.

Calculation                                zinc (g/L) = Consumption in mL x 1.3074

### Sodium cyanide

Reagents                                0.1 mol/L silver nitrate solution  
10 % sodium hydroxide solution  
2 % potassium iodide solution

Process                                      Pipette  
5 mL                                      sample into a  
250 mL                                    Erlenmeyer flask, add  
100 mL                                    DI water,  
10 mL                                    10 % sodium hydroxide solution  
6 drops                                    of potassium iodide solution and titrate with 0.1 mol/L  
silver nitrate solution until lasting turbidity.

Calculation                                sodium cyanide (g/L) = Consumption in mL x 1.96

## Sodium hydroxide

Reagents	0.5 mol/L sulphuric acid Indicator: sat alcoholic solution of tropaeolin 0
Process	Pipette 5 mL sample into a 250 mL Erlenmeyer flask, add 100 mL DI water, 5 drops of indicator and titrate with 0.5 mol/L sulphuric acid from orange to light yellow.
Calculation	sodium hydroxide (g/L) = Consumption in mL x 7.98

## Sodium carbonate

Reagents:	Barium chloride 10 % Methyl orange 0.1 % in water Hydrochloric acid 1 mol/L Sodium hydroxide 1 mol/L
Procedure:	pipette 10 mL electrolyte in a 250 mL beaker, add 100 mL deion. water and heat until boiling, add 50 mL Barium chloride solution and stir for another 30 s. Filter by suction and rinse with hot deion. water until the rinse water is neutral. Put the filter in a 250 mL beaker and add 150 mL hot deion. water, add 30.0 mL Hydrochloric acid 1 mol/L, stir, add 5 drops Methyl orange solution  Titrate with sodium hydroxide 1 mol/L until the colour turns from pink to yellow.
Calculation:	Sodium carbonate g/L = (30 - mL NaOH 1 mol/L) x 5.3

## Hull Cell Test

Equipment	Rectifier with 10 V and 10 A Cables Hull cell 250 mL Zinc anode Zinc plated, steel hull cell panels
Process	<p>Put the anode into the Hull cell and connect with the cable to the (+) pole of the rectifier; fill the cell with the original zinc bath up to the Hull cell's mark.</p> <p>Remove the zinc coating of the Hull cell panel in 1:1 hydrochloric acid, rinse, clean the panel electrolytic, rinse well and put into the cell. Move slightly to and from in order to wet the panel properly. Then connect with the cable to the (-) pole of the rectifier.</p> <p>Plate for 15 min with 1 A (full voltage, current adjusted to the desired value) without agitation.</p> <p>Take the panel out, rinse well and brighten in a 0.5 Vol.-% nitric acid.</p> <p>If the analysis of the bath values indicated that some inorganic ingredient should be adjusted, plate a second panel with these corrections.</p>
Evaluation	<p>The correct <b>RIAG Zn 231</b> panel should be completely bright and uniform; a slight haziness in the hcd area is normal, vertical hydrogen marks (stripes) also. There should be no dullness in mcd and lcd area and the panel should be coated completely.</p> <p>Correct according the information under "Effect of the electrolyte components". If the organic additives have no positive effect but the panel is still dull, it might be a strong overdose.</p> <p>In this case, dilute the original electrolyte 1:1 with a fresh electrolyte prepared in the laboratory and having no additives.</p> <p>Plate a hull cell panel in this 50 % electrolyte and try again if the correction was now possible.</p>

hcd = high current density

mcd = middle current density

lcd = low current density