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14.12.2022

# riag Zn 231

**Cyanide bright zinc process**

## Properties

- liquid brightener
- produces brilliant deposits at low, medium, and high current densities
- suitable for both rack and particularly good for barrel operation
- 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
- its brilliant deposits and its economic use make it the outstanding cyanide zinc brightener system

## Make up

| | low | medium | high |
|---|---|---|---|
| Zinc oxide (ZnO) | 12.5 g/L | 25 g/L | 45 g/L |
| Sodium cyanide (NaCN) | 25 g/L | 60 g/L | 110 g/L |
| Sodium hydroxide (NaOH) | 70 g/L | 50 g/L | 30 g/L |
| **riag Zn 231 Brightener (3.0 x)** | 1 – 1.5 mL/L | 1 – 1.5 mL/L | 1 – 1.5 mL/L |
| **riag Zn 235 Purifier** | 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 (3.0 x)** and stir the electrolyte.

The following quantities result from the make up with zinc cyanide:

| | low | medium | high |
|---|---|---|---|
| Zinc cyanide ($Zn(CN)_2$) | 18 g/L | 36 g/L | 65 g/L |
| Sodium cyanide (NaCN) | 12 g/L | 25 g/L | 65 g/L |
| Sodium hydroxide (NaOH) | 80 g/L | 75 g/L | 70 g/L |
| **riag Zn 231 Brightener (3.0 x)** | 1 – 1.5 mL/L | 1 – 1.5 mL/L | 1 – 1.5 mL/L |
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## Desired values

| | low | medium | high |
|---|---|---|---|
| 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 |
| Ratio NaCN : Zn | 1.5 – 2.2 : 1 | 2.0 – 3.0 : 1 | 2.5 – 3.0 : 1 |

## Operating Parameters

| | |
|---|---|
| Temperature: | 18 – 40 °C<br>(at lower temperatures current densities should be lower, at higher temperatures brightness and throwing power is reduced) |
| Anodes: | Pure zinc 99.99 % or steel anodes |
| Cathodic current density: | rack: 2 – 6 A/dm$^2$<br>barrel: 0.5 – 3 A/dm$^2$ |
| Voltage: | rack: 2 – 8 V<br>barrel: 6 – 16 V |
| Deposition rate: | rack: approx. 0.6 µm/min at 3 A/dm$^2$<br>barrel: approx. 0.2 µm/min at 1 A/dm$^2$ |
| 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.<br><br>Add sodium cyanide and sodium hydroxide according analysis.<br>Add up to 0.1 L **riag Zn 235 Purifier** per added kg NaOH.<br>Freeze out excess sodium carbonate.<br>Adjust **riag Zn 231 Brightener (3.0 x)** with the aid of Hull cell tests. |
| Consumption: | **riag Zn 231 Brightener (3.0 x)** 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 (3.0 x)** | 0.3 – 1.5 L/10 kAh |
| **riag Zn 235 Purifier** | according to the drag-in of metal impurities |

To achieve uniform coating, regular additions of **riag Zn 231 Brightener (3.0 x)** are necessary. Dosing via an Ah counter and a dosing pump must be provided.
Regular control by means of lead acetate paper (must turn slightly brownish) is important; if the lead acetate paper is white, add 0.5 – 1 mL/L **riag Zn 235 Purifier** (pre-diluted 1:10).

## 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

An excess of cyanide reduces the deposition rate and increases the throwing power. Excessive concentrations should be avoided as this can lead to delayed adhesion problems. A lack of cyanide leads to reduced anode solubility and suppressed brightness- and metal throwing power.

### Sodium hydroxide

Excess of hydroxide speeds up zinc dissolution too much. Lack of hydroxide reduces the burning limit. Serves as a conducting salt and complexing agent at the same time. An excess of hydroxide speeds up zinc dissolution too much. Lack of hydroxide reduces the burning limit.

### Sodium carbonate

Excess carbonate reduces the working window of the process as well as the degree of brightener, so that more **riag Zn 231 Brightener (3.0 x)** is needed. Furthermore, this may be responsible for passive anodes, which lead to poor current distribution in the electrolyte and a too low zinc dissolution rate.

### riag Zn 231 Brightener

Excess of **riag Zn 231 Brightener (3.0 x)** 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.

### riag Zn 235 Purifier

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 235 Purifier** should be added pre-diluted (1:10) to prevent the precipitation of zinc.

## 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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## 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 $Na_2EDTA$<br>Buffer solution (100 g/L NaOH and 240 mL/L 98% acetic acid in DI water)<br>Indicator: 1 % xylenol orange blended with $KNO_3$) | |
| Process | | Pipette |
| | 5 mL | sample into a |
| | 250 mL | Erlenmeyer flask, add |
| | 100 mL | DI water, |
| | 20 mL | buffer solution **(exhaust / hydrocyanic acid)** 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<br>10 % sodium hydroxide solution<br>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<br>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 %<br>Methyl orange 0.1 % in water<br>Hydrochloric acid 1 mol/L<br>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<br>Cables<br>Hull cell 250 mL<br>Zinc anode<br>Zinc plated, steel hull cell panels |
| Process | 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.<br><br>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.<br><br>Plate for 15 min with 1 A (full voltage, current adjusted to the desired value) without agitation.<br><br>Take the panel out, rinse well and brighten in a 0.5 Vol.-% nitric acid.<br><br>If the analysis of the bath values indicated that some inorganic ingredient should be adjusted, plate a second panel with these corrections. |
| Evaluation | The correct **riag Zn 231** 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.<br><br>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.<br><br>In this case, dilute the original electrolyte 1:1 with a fresh electrolyte prepared in the laboratory and having no additives.<br><br>Plate a hull cell panel in this 50 % electrolyte and try again if the correction was now possible. |

hcd = high current density
mcd = middle current density
lcd = low current density