RIAG Oberflächentechnik AG · Postfach 169 · CH-9545 Wängi TG

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RIAG Zn 250 Na

Cyanide free alkaline bright zinc process based on sodium hydroxide

Properties

- Excellent metal distribution (only about 25 % of variance on a 1 A, 30 min Hull cell panel)
- A high brilliant zinc deposit
- Easy to chromate
- Very ductile, without blistering
- Perfectly suited for rack as well as for barrel or continuous applications
- Easy plating even on parts with difficult shapes
- High burning limit, suited for high current densities
- Simple waste water treatment
- Excellently adapted for an external zinc generator

Make up

	Range	Optimum
Zinc oxide	10 – 16 g/L	12.5 g/L
Sodium hydroxide	110 – 150 g/L	120 g/L
Sodium carbonate	10 – 80 g/L	50 g/L
RIAG Zn 250 Carrier	5 – 15 mL/L	10 mL/L
RIAG Zn 250 Brightener	0.5 – 2 mL/L	1 mL/L
RIAG Zn 250 Conditioner	5 – 15 mL/L	10 mL/L
RIAG Zn 250 Purifier	0 – 4 mL/L	If necessary

Fill the tank to 1/3 with DI water, add and dissolve the sodium hydroxide in small portions while stirring the solution (attention: the solution becomes hot). Add the zinc oxide and stir until the solution is clear. Dissolve the sodium carbonate and fill the tank with DI water to its final volume. Add the **RIAG Zn 250 Carrier** and the **RIAG Zn 250 Conditioner**. Dummy plate the solution at low current density for 6 – 8 hours. Finally add the **RIAG Zn 250 Brightener**.

Analytical values and maintenance

	Range	Optimum
Zinc	8 – 13 g/L	10 g/L
Sodium hydroxide	110 – 150 g/L	120 g/L
Sodium carbonate	10 – 80 g/L	< 80 g/L

Analyse zinc and caustic soda. Keep the zinc content constant by regulation of the anode surface or by an external zinc generator. Dose caustic soda corresponding to the analysis.

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.

Consumption

	due to drag out* (mL per kg NaOH)	electrolytic (L per 10 kAh)
RIAG Zn 250 Carrier	83	0.5 – 1.5
RIAG Zn 250 Brightener	17	0.5 – 1.5
RIAG Zn 250 Conditioner	83	0

*valid only for the given make-up values

The total consumption consists of the drag out and the electrolytic consumption. For the dosage both have to be considered.

Operating parameters

Temperature:	20 – 40 °C
Cathodic current density:	0.5 – 6 A/dm^2
Current efficiency:	50 – 80 %
Deposition rate (1 A/dm^2):	0.2 µm/min.
Tank material	Plastic or steel with plastic coating
Agitation	Cathode movement with 3 – 5 m/min.
Filtration	Continuous filtration is necessary
Cooling	Necessary at high current load depending on the electrolyte volume
Exhaust	Strongly recommended, especially when using inert anodes

Function of the components

RIAG Zn 250 Carrier

The **RIAG Zn 250 Carrier** effectuates the excellent metal distribution.

RIAG Zn 250 Brightener

The **RIAG Zn 250 Brightener** is responsible for the brightness of the layer.

RIAG Zn 250 Conditioner

The **RIAG Zn 250 Conditioner** avoids negative optical influences of the layer due to water hardness or impurities of raw materials.

RIAG Zn 250 Purifier

The **RIAG Zn 250 Purifier** eliminates metal impurities as lead, cadmium or copper. Avoid overdosing of the **RIAG Zn 250 Purifier.** Test the addition of the purifier in the Hull cell before adding to the electrolyte.

Anodes

We recommend using inert anodes in combination with an external zinc generator. Despite this recommendation, **RIAG Zn 250 Na** can of course be operated with soluble zinc anodes. However, we strongly warn against mixed operation of inert and soluble anodes.

Operation with inert anodes and external zinc generator

Anodes made of expanded metal (30 mm x 8 mm piccolo mesh, rib width 6 mm, material thickness 2 mm), of mild steel (e.g. ST 38) have to be plated with 15 µm semi bright nickel. The expanded metal should be installed with the ribs horizontally oriented for driving the gas evolution to the back side.

Before plating the expanded metal with semi bright nickel, it should be vertically stiffened with flat irons leading to the anode hooks. For optimal current distribution, the anodes should be placed at both sides of the cathode along the full width of the plating tank. Anodic current density up to 20 A/dm^2.

Zinc generator with baskets (optimal: 62.5 mm x 62.5 mm x 1000 mm of 1.5 mm perforated mild sheet DD 11 GK according to DIN 10111/10051; perforation Rv 3 – 5 DIN 24041) plated with semi bright nickel (**RIAG Ni 140**). Fill the baskets with zinc clippings (approx. 100 mm ⇑, lead content <0.002 %). Control the zinc concentration in the electrolyte adjusting the exchange rate between plating cell and zinc generator. For an online calculation of the necessary number of catalytically baskets and for determination of the size of the zinc generator, please consult RIAG.

Operation with soluble anodes

Soluble zinc anode pieces, clippings, drops or balls in titanium baskets as usual in the trade, or zinc anode panels at titanium hooks (the lead content of the zinc anodes must be generally <0.002 %). Up to a current density of about 3 A/dm^2, the anodic current efficiency lies at 100 %. Above 3 A/dm^2 the anode gets covered with a semi conductive zinc oxide parting layer, the anode becomes black, the cell voltage increases abruptly by 3 to 4 V, and the anodic current efficiency drops down to 2 – 5 % in favour of 95 – 98 % O_2 evolution. However, it is not impossible, but it is hard to control the zinc content of the electrolyte by adjusting the anode surface. Anodes must be removed and placed back frequently. Consequently, the current in the plating cell is of course very unevenly distributed.

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Trouble Shooting

Before consulting the following list, it should be verified that temperature, current density and analytical values stay within the above limit values. Hull cell tests should be done with a 250 mL Hull cell at 1 A, 15 min on thorough fully pre-treated steel panels. The plated Hull cell panel should be rinsed in 0.5 vol % nitric acid for 15 s, rinsed again with tap water and dried with hot air.

Error	Cause	Remedy
bright uniform layer within the whole current density range	electrolyte is ok	none
bad throwing power	concentration of **RIAG Zn 250 Carrier** is too low	add **RIAG Zn 250 Carrier** in steps of 2 – 5 mL/L, confirm each step by the way of Hull cell tests before addition to the bath
low but uniform brightness within the whole current density range	concentration of **RIAG Zn 250 Brightener** too low	add **RIAG Zn 250 Brightener** in steps of 0.25 mL/L, confirm each step by the way of Hull cell tests before addition to the bath
dull irregular regions in the zinc deposit	a) bad pre-treatment	improve the pre-treatment (note: pre-treatment of Hull cell panels is also very important for good test deposits)
	b) water hardness too high	for water conditioning, add **RIAG Zn 250 Conditioner** to the electrolyte in steps of 3 – 5 mL/L, confirm each step by the way of Hull cell tests before addition to the bath
dentrites, distributed in all current density regions	over dosage of **RIAG Zn 250 Brightener**	work out
bad current efficiency, no deposits in low current density area	a) over dosage of **RIAG Zn 250 Carrier**	work out
	b) impurities of chromium (VI)	add reduction agent sodium dithionite according to hull cell tests
discoloured chromating layers	a) chromating bath wrongly adjusted	check chromating bath and activation
	b) metal impurities in the zinc electrolyte	close the source of the impurities; dummy plate at low current densities
dull grey low current density area	lead impurities (about 1 ppm and higher)	a) treatment of the electrolyte with 1 g/L zinc dust
		b) add **RIAG Zn 250 Purifier**

Conversion of a strange electrolyte to RIAG Zn 250 Na

For a complete conversion test, at least 3 L original electrolyte are necessary.
First indication:

1. Plate a Hull cell panel in a freshly prepared **RIAG Zn 250 Na** electrolyte according to the instructions of the chapter “Trouble shooting”.

2. Plate an “original” panel in the strange electrolyte without any additions. If the original panel is already bright, you can only try the over dosage effect, if it is less bright than panel 1, you can already get an indication on the receptivity of the old system for **RIAG Zn 250 Na**.

3. Add 5 mL/L **RIAG Zn 250 Carrier** and 0.5 mL/L **RIAG Zn 250 Brightener** to the 250 mL Hull cell 2 and plate again. If there is a positive effect (panel 3 is the same as or better than panel 2), a conversion is possible without an immediate problem.

Middle term compatibility

1. Fill 1.8 L original bath into a 2 L beaker, hang in a small hull cell soluble zinc anode an a pre-treated Jiggle cell panel (or, if not available, a 15 cm long and about 4 cm wide steel sheet) as a cathode, put it onto a magnetic stirrer and stir slowly, connect anode and cathode to the rectifier and plate with 1 A for 8 h.

2. Fill 250 mL of this treated electrolyte into a Hull cell and plate a Hull cell panel according the instructions of the chapter “Trouble Shooting”.

3. Add 5 mL **RIAG Zn 250 Carrier** and 0.5 mL **RIAG Zn 250 Brightener** to the Hull cell and repeat the test.

4. Repeat (3) until a good result is achieved.

Long term compatibility

1. Prepare 1 L of a fresh **RIAG Zn 250 Na** electrolyte with the desired concentrations of zinc and NaOH or KOH and add 10 mL/L **RIAG Zn 250 Carrier**, 1 mL/L **RIAG Zn 250 Brightener**, 10 mL/L **RIAG Zn 250 Conditioner** and 1 mL/L **RIAG Zn 250 Purifier**.

2. If the first indication test (see above) had shown a lack of brightness in the original bath, then add 0.5 mL/L **RIAG Zn 250 Brightener** to the untreated strange electrolyte.

3. Prepare 5 dilutions with a total volume of 250 mL each of the strange electrolyte (if necessary + **RIAG Zn 250 Brightener**) with the **RIAG Zn 250 Na** electrolyte mentioned above.

a) 225 mL original bath + 25 mL RIAG Zn 250 Na electrolyte
b) 175 mL original bath + 75 mL RIAG Zn 250 Na electrolyte
c) 125 mL original bath + 125 mL RIAG Zn 250 Na electrolyte
d) 75 mL original bath + 175 mL RIAG Zn 250 Na electrolyte
e) 25 mL original bath + 225 mL RIAG Zn 250 Na electrolyte

Plate a Hull cell panel in each electrolyte mixture.
There should not be any negative effect in any dilution. If e.g. the panel plated in bath c) had an unexpected e.g. uncorrectable spottiness, possible problems must be expected after about 5 weeks of conversion (barrel application) resp. 15 – 20 weeks (rack application).
If every dilution can be adjusted to a good panel, no problems are expected by the conversion itself.

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 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		Pipette
	5 mL	sample into a
	250 mL	Erlenmeyer flask, add about
	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 1.3078	

Sodium hydroxide

Reagents	0.5 mol/L sulphuric acid Indicator: 0.1 % solution of tropaeolin 0	
Process		Pipette
	5 mL	sample into a
	250 mL	Erlenmeyer flask, add about
	100 mL	DI water,
	5 drops	of indicator and titrate with 0.5 mol/L sulphuric acid from orange-brown to yellow.
Calculation	NaOH (g/L) = Consumption in mL x 8.00	

Sodium carbonate

Reagents	5 % barium nitrate solution 1 mol/L hydrochloric acid 1 mol/L sodium hydroxide solution Indicator: 0.04 % methyl orange solution	
Process		Pipette
	10 mL	sample into a
	250 mL	Erlenmeyer flask, add
	50 mL	DI water and boil the solution. Add
	75 mL	barium nitrate solution. After settle down of the precipitate, filtrate with a fine grained filter paper and wash with hot DI water. Put the filter into a
	250 mL	Erlenmeyer flask, add
	100 mL	DI water, pipette
	20 mL	1 mol/L hydrochloric acid and heat the solution shortly. After cooling down, add
	3 drops	of indicator and titrate excess hydrochloric acid with 1 mol/L sodium hydroxide from red to orange-yellow.
Calculation	sodium carbonate (g/L) = (20 – consumption in mL) x 5.3	