

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

29.03.2022

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
10– 16 g/L		12.5 g/L
110 – 150 g/L		120 g/L
10– 80 g/L		50 g/L
5 – 15 mL/L		10 mL/L
0.5 – 2 mL/L		1 mL/L
5 – 15 mL/L		10 mL/L
0 – 4 mL/L		If necessary
	10 – 16 g/L 110 – 150 g/L 10 – 80 g/L 5 – 15 mL/L 0.5 – 2 mL/L 5 – 15 mL/L	10 – 16 g/L 110 – 150 g/L 10 – 80 g/L 5 – 15 mL/L 0.5 – 2 mL/L 5 – 15 mL/L

Procedure for new preparation:

Fill the tank **only to 1/3 of the intended volume** with DI water, add sodium hydroxide in portions while stirring constantly and dissolve. Caution, strong heat is generated (up to 90 °C)! The calculated amount of zinc oxide is added to the hot solution and mixed until a clear, homogeneous solution is obtained. Now dissolve the prepared sodium carbonate in the electrolyte while stirring it, then fill up to the final volume with DI water and finally let everything cool down to operating temperature.

Alternative new preparation variants:

- a) The process tank is filled to 80 % with DI water and the sodium hydroxide is added slowly and carefully while stirring constantly. Then the sodium carbonate is added until a clear, homogeneous solution is obtained. Then hang the filled zinc dissolving basket into the dissolving compartment (better dissolving reaction with heated solution), activate the circuit until the desired content of dissolved zinc in the electrolyte is reached. This process is somewhat time-consuming; therefore we recommend doing this over a longer standstill period (e.g.: overnight). Accompanying analyses are recommended.
- b) We also offer you the possibility to obtain a ready-to-use potassium zincate solution (250020xxx Zinc-NaOH-electrolyte, 10 g/L zinc, 170 g/L NaOH) from us. If you are interested, please contact our sales department.

After the new preparation has been carried out, add **riag Zn 250 Carrier** and **riag Zn 250 Conditioner**. The electrolyte is worked through with low current density (0.2 A / dm²) for 8 h. Finally, **riag Zn 250 Brightener** is added.

Personal protection equipment must be worn during the addition of chemicals.

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		< 80 g/L

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

Consumption

	due to drag out*	electrolytic
	(mL per kg NaOH)	(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

To achieve good metal distribution, it is important to add **riag Zn 250 Carrier** as indicated in the instruction manual. Regular additions are important to maintain the outstanding metal distribution. Overdosing causes blistering of the deposited layers

riag Zn 250 Brightener

Used for the deposition of glossy layers. Additions should be made in steps of max. 0.2 mL/L. An overdose can only be removed by dummy plating, otherwise it causes blistering of the deposited layers.

riag Zn 250 Conditioner

Complexes the water hardness and conditions the electrolyte. Overdosing reduces the gloss level.

riag Zn 250 Purifier

Removes metallic impurities such as lead and copper. Additions should only be made when necessary, as overdosing can reduce the gloss level and even cause blistering.

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.

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 μ m 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/dm².

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 $\hat{1}$, 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/dm², the anodic current efficiency lies at 100 %. Above 3 A/dm² 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 % O₂ 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.

Liability

This instruction manual was compiled with reference to the state of the art and all current standards, and is based on the long-term knowledge and experience of riag. However, riag cannot monitor compliance with this instruction manual and the methods described herein at the customer/end-user's premises. Work carried out with riag products must be adapted accordingly to meet local conditions. In particular, riag cannot accept liability for damage, loss or cost incurred due to a failure to adhere to this instruction manual, improper application of the methods, unauthorised technical modifications, insufficient maintenance or the absence of maintenance in respect of the requisite technical hardware or equipment, or in the event of use by unqualified personnel. riag is not liable for damage or loss caused by riag or its employees except where intention or gross negligence can be proved. riag furthermore reserves the right to make changes in relation to products, methods and the instruction manual without prior notice.

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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 pretreated 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

- 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 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	5 mL 250 mL 100 mL 20 mL a spatula tip	Pipette sample into a Erlenmeyer flask, add about DI water, buffer solution and 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 sul Indicator: 0.1	phuric acid % solution of tropaeolin 0	
Process	5 mL 250 mL 100 mL 5 drops	Pipette sample into a Erlenmeyer flask, add about DI water, 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	1 mol/L hydro 1 mol/L sodiu	nitrate solution ochloric acid um hydroxide solution 4 % methyl orange solution
Process	10 mL 250 mL 50 mL 75 mL 250 mL 100 mL 20 mL 3 drops	Pipette sample into a Erlenmeyer flask, add DI water and boil the solution. Add 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 Erlenmeyer flask, add DI water, pipette 1 mol/L hydrochloric acid and heat the solution shortly. After cooling down, add of indicator and titrate excess hydrochloric acid with 1 mol/L sodium hydroxide from red to orange-yellow.
Calculation	sodium carbo	onate (g/L) = (20 – consumption in mL) x 5.3