

riag Ni 113

Brightness preserving nickel process

The nickel process **riag Ni 113** is mainly used in technical applications. It is well-proven that barrel plating of parts for the electronic industry is successful. **riag Ni 113** produces nickel deposits with the following advantages:

Properties

- brightness preserving
- light, white deposits
- excellent metal deposit thickness distribution
- good ductility
- uniform brightness in all current densities
- ideal for technical nickel plating

Make up boric acid-free (US Patent No.: 11,396,711)

	Rack		Barrel	
	Range	Optimum	Range	Optimum
Nickel sulphate (NiSO ₄ x 6 H ₂ O)	190 – 260 g/L	220 g/L	125 – 190 g/L	145 g/L
Nickel chloride (NiCl ₂ x 6 H ₂ O)	50 – 70 g/L	60 g/L	50 – 100 g/L	85 g/L
riag Ni 149 Make up		100 mL/L		100 mL/L
riag Ni 113 Brightener	10 – 18 mL/L	15 mL/L	10 – 18 mL/L	15 mL/L
riag Ni 138 Tenside M * or riag Ni 139 Tenside L *	*1 – 10 mL/L	*2 mL/L	*1 – 10 mL/L	*3 mL/L
pH-value	3.8 – 5.2	4.9	3.8 – 5.2	4.9

* depending on customer-specific process requirements

The process is usually operated with one additive only.

Operating values

	Rack		Barrel	
	Range	Optimum	Range	Optimum
Nickel (Ni ²⁺)	60 – 80 g/L	70 g/L	50 – 75 g/L	60 g/L
Chloride (Cl ⁻)	15 – 21 g/L	18 g/L	15 – 30 g/L	25 g/L
riag Ni 149 Make up*	80 – 120 mL/L	100 mL/L	80 – 120 mL/L	100 mL/L

*corresponds to the **riag Ni 149 Buffer**

Make up

A separate tank is filled with deionised water to 3/4 of the final volume.

The water is then heated to at least 60 °C after which the chemicals are added and the tank is filled to final volume with deionised water. To remove contaminants 0.5 mL/L hydrogen peroxide is added and the solution is stirred for at least one hour. This is followed by addition of 3 g/L **riag Carb SF** activated carbon and mixing for another 30 minutes. After settling, preferably overnight, the electrolyte is transferred to the working tank by filtration. Finally, the necessary quantities of **riag Ni 149 Make up** and all other required additives are added. The electrolyte is ready for use.

It is possible to obtain ready-to-use electrolytes, e.g. **riag Ni 149 electrolyte** as a rack version.

Alternative make up containing boric acid

	Rack		Barrel	
	Range	Optimum	Range	Optimum
Nickel sulphate (NiSO ₄ x 6 H ₂ O)	220 – 290 g/L	240 g/L	150 – 220 g/L	175 g/L
Nickel chloride (NiCl ₂ x 6 H ₂ O)	50 – 70 g/L	60 g/L	50 – 100 g/L	85 g/L
Boric acid (H ₃ BO ₃)	40 – 45 g/L	42 g/L	40 – 45 g/L	42 g/L
riag Ni 113 Brightener	10 – 18 mL/L	15 mL/L	10 – 18 mL/L	15 mL/L
riag Ni 138 Tenside M* / od. riag Ni 139 Tenside L*	*1 – 10 mL/L	*2 mL/L	1 – 10 mL/L	3 mL/L
pH-value	3.8 – 4.5	4.2	3.8 – 4.5	4.2

* depending on customer-specific process requirements

Operating Values

	Rack		Barrel	
	Range	Optimum	Range	Optimum
Nickel (Ni ²⁺)	60 – 80 g/L	70 g/L	50 – 75 g/L	60 g/L
Chloride (Cl ⁻)	15 – 21 g/L	18 g/L	15 – 30 g/L	25 g/L
Boric acid (H ₃ BO ₃)	40 – 45 g/L	42 g/L	40 – 45 g/L	42 g/L

Make up

A separate tank is filled with deionised water to 3/4 of the final volume.

The water is then heated to at least 60 °C after which the chemicals are added and the tank is filled to final volume with deionised water. To remove contaminants 0.5 mL/L hydrogen peroxide is added and the solution is stirred for at least one hour. This is followed by addition of 3 – 5 g/L **riag Carb SF** activated carbon and mixing for another 30 minutes. After settling, preferably overnight, the electrolyte is transferred to the working tank by filtration. Finally, the correct undiluted volumes of **riag Ni 113 Brightener** and **riag Ni 138 Tenside M / riag Ni 139 Tenside L** are added whilst stirring.

Operating Parameters

Temperature:	55 °C (50 – 65 °C)
pH-value:	Boric acid free: 4.9 (3.8 – 5.2) Containing boric acid: 4.2 (3.8 – 4.5) The pH-value of the boric acid-free version should always be measured at operating temperature.
Cathodic current density:	Barrel : 0.1 – 2.0 A/dm ² Rack: 2.0 – 8.0 A/dm ²
Anodic current density:	< 3.0 A/dm ²
Current efficiency:	< 100 %
Deposition rate:	Barrel: at 1 A/dm ² ca. 0.2 µm/min Rack: at 5 A/dm ² ca. 1.0 µm/min
Anodes:	Minimum purity 99.7 % Ni. We recommend polypropylene anode bags
Agitation:	Essential: Filterpump, barrel rotation or air agitation
Tanks:	Plastic or lined steel
Filtration:	It is important to use continuous filtration and we recommend using activated carbon filtration as well. The filtration rate should be two to three times the electrolyte volume per hour.
Heating:	Immersion heaters, but thermostatic control is essential
Cooling:	not required
Fume extraction:	recommended
Maintenance:	Nickel sulphate, nickel chloride and riag Ni 149 Make up respectively boric acid should be analysed and corrected regularly. To obtain uniform bright coatings, regular addition of riag Ni 113 Brightener is important. Dosing via ampere-hour meter and dosing pump in smaller but regular quantities increases the precipitation quality and reduces the consumption of riag Ni 113 Brightener .

Metallic contamination: Metallic contamination can be removed by frequent selective plating-out at 0.1 – 0.3 A/dm². The filter pump should be on with the filter outlet directed at the panels. This will ensure thorough electrolyte circulation and essential agitation at the same time.

pH-value adjustment: Adding **riag Ni 149 Buffer** lowers the pH-value. To lower the pH-value, add **riag Ni 149 Buffer** first, if necessary. Only afterwards, if necessary, use chemically pure sulphuric acid (10 %). In exceptional cases (usually for a limited time), pure hydrochloric acid is used to increase the chloride content of the electrolyte.
To increase the pH-value, only nickel carbonate must be used, never ammonia or ammonium compounds.

Additive consumption The additives are consumed during electrolytic reactions as well as drag-out losses. Consumption can therefore vary depending on the process.

riag Ni Tenside M / L **0.2 – 0.5 L/10 kAh**

riag Ni 113 Brightener **0.7 – 1.7 L/10 kAh**

The use of boric acid results in an additional consumption of 20 - 30 % of brightener.

**Operating downtimes/
Storage:** In case of longer production interruptions (e.g. company holidays), we recommend to reduce the pH-value of the electrolyte to below 4.5.

Function of electrolyte components

riag Ni 149 Make up

Contains the buffer system neutralised with nickel carbonate and purified with activated carbon. Due to the addition during preparation, as well as during maintenance, the pH value in the electrolyte changes only slightly. The buffering effect is present over a very wide range and exceeds that of boric acid.

riag Ni 149 Buffer

Is used to compensate for deficiencies in the buffer system. **riag Ni 149 Buffer** contains the same amount of active ingredient as **riag Ni 149 Make up**, but is not pH-neutral and reacts strongly acidic. It is added in aliquot quantities for drag-out, ideally when the pH should be adjusted with acid, instead of acid. By adding 5 mL/L the pH value of the nickel electrolyte drops by approx. 0.2 units. It is therefore recommended to add the buffer in small steps (empirical values). If there is a very large shortage in the buffer substance, we recommend switching to **riag Ni 149 Make up** (pH neutralised).

riag Ni 113 Brightener

For uniform bright coatings it is essential to add the **riag Ni 113 Brightener** in small doses and according to the operating instructions.

riag Ni Tenside M / L

The consumption of **riag Ni 138 Tenside M / riag Ni 139 Tenside L** is 0.2 – 0.5 L per 10 kWh and may vary due to drag out.

A minimum amount of **riag Ni 138 Tenside M / riag Ni 139 Tenside L** is recommended in barrel applications for example to avoid the formation of perforation spots on flat parts that keep "sticking" to the walls.

riag Ni 147 Oxidant

Iron contamination (pitting) can be removed effectively by additions of **riag Ni 147 Oxidant**. The maximum concentration of 0.5 g/L should not be exceeded. The salt is first dissolved in hot water and the iron is removed via the filter.

riag Ni 146 Support

The additive **riag Ni 146 Support** is used to remove dark plating in low current density areas that cannot be removed by selective plating-out. However, the maximum **riag Ni 146 Support** addition must be limited to 1 mL/L. Higher dosing reduces levelling and deposit brightness. **riag Ni 146 Support** can also be used to compensate for brightener overdosing (0.2 – 0.5 mL/L). To avoid overdosing of **riag Ni 146 Support** additions should be made in small volumes.

riag Ni 143 Purifier

Zinc-die casting processing in rack or barrel mode often leads to zinc and copper electrolyte contamination. This can be treated by additions of 0.03 – 0.1 mL/L **riag Ni 143 Purifier**. The volume **riag Ni 143 Purifier** to be added depends on contamination levels but overdosing results in loss of deposit brightness as well as levelling and must be avoided.

Activated Carbon

Continuous filtration over activated carbon is recommended. This can be done via a by-pass whereby the carbon will remove organic contaminants such as oils and breakdown products. For this we recommend our **riag Carb SF** dust-free product which has an active surface area of 1500 m² /g. The additional consumption of **riag Ni 113 Brightener** should not exceed 5 %. A significant contamination of the electrolyte can be removed by filtration in the bypass (filter pump with a filled sack of **riag Carb GR**). **riag Carb GR** is ideally suited for this purpose, as such treatment may be performed during the plating process. **riag** can provide such filter system.

riag Ni 147 Oxidant

Iron contamination (pitting) can be removed effectively by additions of **riag Ni 147 Oxidant**. The maximum concentration of 0.5 g/L should not be exceeded. The salt is first dissolved in hot water and the iron is removed via the filter.

Environmental considerations and product safety

All concentrates, rinse waters and waste solution must be treated and discharged in accordance with local effluent control regulations. Information can be gleaned from the material safety data sheets. Chemicals shall not be stored below 10 °C.

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.

Our goods and services are subject to the General Terms and Conditions for Delivery of the Association of Surface Technology Suppliers (VLO), which can be viewed at www.riag.ch (link "terms and conditions" , document "General Terms and Conditions for Delivery", version 3/2018), which we gladly send you on request.

This transaction is governed by material Swiss law (Law of Obligations), excluding private international law (conflict of laws) and intergovernmental treaties, specifically the CISG.

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Analysis (Analytical Method)

Sample preparation:

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

riag Ni 149 Make up / riag Ni 149 Buffer

Reagents: bromide – bromate solution 0,05 mol/L Br₂ (0,1 N)
sodium thiosulfate solution 0.1 mol/L (0,1 N)
potassium iodide solution 100 g/L
hydrochloric acid (1:1)
starch solution 1% in deion water

Procedure:

2 mL	electrolyte are transferred via pipette into a Erlenmeyer flask, pipette
25 mL	bromide – bromate solution, add
25 mL	hydrochloric acid and immediately close the flask with the stopper mix well and place the flask in a dark place for 10 minutes, add
10 mL	potassium iodide solution, rinse the wall with deion. water and titrate with sodium thiosulfate solution to a light brown, add
5 mL	starch solution and continue to titrate until the dark blue colour disappears

Calculation: $(25 - \text{consumption in mL}) \times 13.2 = \text{mL/L riag Ni 149 Make up / riag Ni 149 Buffer}$

Replenishment of **riag Ni 149 Buffer** = $(100 - \text{value of riag Ni 149 Buffer})$ in mL/L

*Explanations for the supplement are included in the product description **riag Ni 149 Buffer**

Nickel chloride hexahydrate

Reagents: Silver nitrate solution 0.1 mol/L
Potassium dichromate solution 5 %

Procedure:

5 mL	electrolyte are transferred into a glass beaker and diluted with deionised water. 10 drops of Potassium dichromate solution are added. Titration with 0.1 mol/L Silver nitrate solution from white yellow to a light brown end point.
250 mL	
50 mL	
10 drops	

Calculation: Nickel chloride hexahydrate (g/L) = consumption of mL AgNO₃ x 2.380

Chloride (g/L) = consumption of mL AgNO₃ x 0.709

Nickel

Reagents: Buffer solution pH 10
 Na₂EDTA 0.1 mol/L
 Murexide (Sodium chloride 1: 100)

Procedure: 10 mL electrolyte are transferred via pipette into a
 100 mL measuring flask and filled- up to the mark with deionised
 water and mixed well
 10 mL of this mixture is given into a 250 mL glass beaker by
 pipette followed by
 15 mL Buffer solution addition
 100 mL deionised water and
 1 spatula tip of Murexide are added The sample colour should then be
 deep yellow
 Titrate immediately with Na₂EDTA 0.1 mol/L to a blue-
 end- point

Calculation: Nickel (g/L) = consumption of mL Na₂EDTA 0.1 mol/L x 5.869

Nickel sulphate hexahydrate (g/L) = [A – (B x 0.247)] x 4.48

A = Nickel concentration in g/L

B = Nickel chloride conc. in g/L

riag Ni 138 Tenside M

Reagents: Glycerine
 Butyl phosphate solution:
 Mix 5 mL Tri-n-Butyl phosphate
 500 mL Methanol
 500 mL water DI

Procedure: 25 mL electrolyte are transferred via pipette into a 300 mL
 Erlenmeyer flask, add
 3 drops glycerine, shake well, to form a foam cover. Add in steps
 of
 0.5 mL butyl phosphate solution,
 shake well after each addition, until the foam cover
 disappears within 10 seconds

Calculation: consumption in mL = mL/L **riag Ni 138 Tenside M**

Boric acid

Reagents:	Sodium hydroxide solution 0.1 mol/L Bromcresol purple (1 % in Ethanol) Mannitol
Procedure:	10 mL electrolyte are transferred via pipette into a 100 mL measuring flask and filled up to the mark with deionised water followed by mixing well. 10 mL of this mixture is given into a 250 mL beaker via pipette followed by 100 mL deionised water addition. 2 – 3 g Mannitol is added followed by addition of 10 drops Bromcresol purple. Titration with 0.1 mol/L Sodium hydroxide from yellow to green, to dark green and finally to blue-violet.
Calculation:	Boric acid (g/L) = consumption of mL NaOH x 6.18