

riag Ni 149

Boric acid-free nickel processes (US Patent No.: 11,396,711)

The **riag Ni 149** process is a boric acid-free, optimally buffered nickel process which can be used in various process variants.

Properties

1. Watts electrolyte gloss preserving
2. Watts electrolyte gloss to high gloss
3. Sulphamate electrolyte

Examples for electrolyte versions

Gloss systems are mentioned as examples for all electrolyte versions. For other specific requirements/gloss systems, please contact a riag technical advisor.

1. Watts electrolyte gloss preserving

	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

2. Watts electrolyte gloss to high gloss

	Rack		Barrel	
	Range	Optimum	Range	Optimum
Nickel sulphate ($\text{NiSO}_4 \times 6 \text{H}_2\text{O}$)	190 – 260 g/L	220 g/L	125 – 190 g/L	145 g/L
Nickel chloride ($\text{NiCl}_2 \times 6 \text{H}_2\text{O}$)	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 132 Make up	10 – 15 mL/L	12 mL/L	10 – 15 mL/L	12 mL/L
riag Ni 135 Carrier	2 – 5 mL/L	3 mL/L	2 – 5 mL/L	3 mL/L
riag Ni 118 Brightener	0.1 – 0.3 mL/L	0.2 mL/L		
riag Ni 120 Brightener			0.1 – 0.3 mL/L	0.2 mL/L
riag Ni 138 Tenside M * or riag Ni 139 Tenside L *	*1 – 10 mL/L	*2 mL/L	*1 – 10 mL/L	*2 mL/L
pH – value	3.8 – 5.2	4.9	3.8 – 5.2	4.9

* depending on customer-specific process requirements

Make up

The nickel salts are dissolved in hot deionised water, the solution is filtered clear and the appropriate amounts of **riag Ni 149 Make up** and any other additives required are added. The electrolyte is ready for use.

It is possible to get ready-to-use electrolytes, e.g. **riag Ni 149 electrolyte** as rack/ or barrel variant.

Watts electrolyte tolerances

	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 – 110 mL/L	100 mL/L	80 – 110 mL/L	100 mL/L

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

Operating parameters

Temperature:	55 °C (50 – 60 °C)
pH-value:	4.9 (3.8 – 5.2); measured at working temperature
Cathodic current density:	0.1 – 10.0 A/dm ²
Anodic current density:	< 3.0 A/dm ²
Current efficiency:	< 100 %
Deposition rate:	at 1 A/dm ² ca. 0.2 µm/min
Anodes:	Minimum purity 99.7 % Ni. We recommend polypropylene anode bags
Agitation:	Electrolyte movement by filter pump, cathode movement 2 – 3 m/min or air agitation (depending on tenside), suitable barrel rotation
Tanks:	Plastic or lined steel
Filtration:	It is important to use continuous filtration. The filtration rate should be two to three times electrolyte volume per hour.
Heating:	Immersion heaters, but thermostatic control is essential
Cooling:	not required
Fume extraction:	Recommended
Metallic contamination:	<p>Metallic contamination can be removed by frequent selective plating-out at 0.1 – 0.5 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. In any case, the electrolyte should be strongly moved around the panels.</p> <p>Iron contamination leads to discoloration of the electrolyte. Note: The base colour of the electrolyte tends towards olive green. The colour should therefore not be used as a qualitative measure for metallic impurities.</p>
pH-value adjustment:	Additions of riag Ni 149 Buffer reduce the pH value. To lower the pH, add, if necessary, riag Ni 149 Buffer first, than chem. pure sulphuric acid (10 %) is added. In exceptional cases (usually temporary) pure hydrochloric acid is used to increase the chloride content of the electrolyte. To increase the pH value, use only nickel carbonate, never ammonia or ammonium compounds.
Maintenance:	Nickel sulphate, nickel chloride and riag Ni 149 Buffer should be analysed and corrected regularly. Additions of riag Ni Brightener , riag Ni 133 Carrier and riag Ni 135 Carrier are made via Ampere-hour consumption.

Additive consumption: The additives are consumed both by drag-out losses and electrolytic reactions, i.e. by anodic and cathodic processes. The consumptions of 10 kAh each can therefore vary due to the process.

riag Ni Brightener 0.7 – 1.5 L/10 kAh

riag Ni 135 Carrier 0.5 – 1.2 L/10 kAh

riag Ni 133 Carrier 0.3 – 0.7 L/10 kAh

riag Ni Tenside M / L* 0.1 – 0.3 L/10 kAh

* depending on customer-specific process requirements

Operating downtimes/
Storage: In case of longer production interruptions (e.g. company holidays) it is recommended to reduce the pH of the electrolyte below 4.5.

Function of electrolyte components

riag Ni 149 Make up

Contains the buffer system neutralised with nickel carbonate. 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. The addition is made in aliquot quantities to the drag out. In the first days after new preparation, the analysable concentration of **riag Ni 149 Make up** is reduced by up to approx. 10 %. This is due to the adjustment of the equilibrium in the solution and is a normal feature of the electrolyte.

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. When

5 mL/L is added 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 Brightener

For uniform bright layers it is essential to add the **riag Ni Brightener** in small doses and according to the operating instructions. Smaller more frequent additions are important for optimal brightness and high levelling. Regular pH-control and correction reduce the **riag Ni Brightener** consumption as well.

riag Ni 135 Carrier

riag Ni 135 Carrier are responsible for uniform bright deposits over a wide current density range (especially for low current density). In the presence of **riag Ni 149 Make up**, the **riag Ni 135 Carrier** content can currently only be determined analytically with ion chromatography.

riag Ni 132 Make up / riag Ni 133 Carrier

The **riag Ni 132 Make up / riag Ni 133 Carrier** provide a base brightness. To get ductile deposits, we recommend not to fall below the operating value. A lack of **riag Ni 132 Make up / riag Ni 133 Carrier** is indicated by shadows at medium to high current densities. In this case, 3 – 8 mL/L **riag Ni 132 Make up** must be added. The **riag Ni 132 Make up / riag Ni 133 Carrier** content can be determined analytically.

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.

riag Ni Tenside M / L

The consumption of **riag Ni Tenside M / L** may vary due to the drag out. A minimum content of **riag Ni Tenside M / L** in barrel nickel application is necessary to avoid, for example, the formation of perforation stains on flat parts, which repeatedly stick on the barrel wall.

Activated Carbon

Discontinuous filtration via activated carbon is necessary (possibly by-pass). This absorbs disturbing influences such as organic impurities, drag in of oils or fats. For this purpose, we recommend our dust-free activated carbon **riag Carb SF** with a surface area of 1500 m²/g.

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.

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.

3. Sulphamate electrolyte

Make up values

	Range	Optimum
Nickel sulphamate concentrate (185 g/L Ni)	270 – 450 mL/L	350 mL/L
Nickel chloride (NiCl ₂ x 6 H ₂ O)	7 – 17 g/L	12 g/L
riag Ni 149 Make up	80 – 110 mL/L	100 mL/L
riag Ni 113 Brightener* / riag Ni 141 Additive*	0 – 15 mL/L	10 mL/L
riag Ni 138 Tenside M* / riag Ni 139 Tenside L*	1 – 10 mL/L	2 mL/L

* depending on customer-specific process requirements

riag Ni 113 Brightener and **riag Ni 141 Additive** are additives to reduce internal stresses in sulphamate nickel electrolytes and are therefore especially suitable for use in nickel plating of electronic components including printed circuits, as well as for "electroforming". Any pore formation is controlled by the addition of wetting agent. The electrolyte can be used for rack or barrel plating.

Tolerances

	Range	Optimum
Nickel (Ni ²⁺)	60 – 90 g/L	75 g/L
Chlorid (Cl ⁻)	2 – 5 g/L	3,5 g/L
riag Ni 149 Make up	80 – 110 mL/L	100 mL/L
pH-value	3.8 – 5.2	4.9

Make up

The tank is filled with deionised water to 1/3 of the final volume, the nickel chloride is added and solved in water. Afterwards the nickel sulfamate solution and **riag Ni 149 Make up** are added. The tank is filled with deionised water up to 95 % of its final volume and stirred. After adding **riag Ni 113 Brightener / riag Ni 141 Additive** and **riag Ni 138 Tenside M / riag Ni 139 Tenside L** we recommend a filtration of the electrolyte during 2 – 4 hours.

Operating parameters (only different from Watts variants)

Cathodic current density:	Rack: 4 A/dm ² (1 – 10 A/dm ²) Barrel: 0.75 A/dm ² (0.5 – 1.0 A/dm ²)
Anodes:	„S“ Nickel with polypropylene bags. Titanium baskets may be used.
pH-value adjustment:	Additions of riag Ni 149 Buffer reduce the pH-value. To lower the pH, add riag Ni 149 Buffer first, then chem. pure sulphamic acid is added. To increase the pH-value, use only nickel carbonate, never ammonia or ammonium compounds.

Maintenance: Nickel sulphamate, nickel chloride and **riag Ni 149 Buffer** should be analysed and corrected regularly.

Additive consumption: The additives are consumed both electrochemically, i.e. by anodic and cathodic processes, and by drag-out. The consumption is therefore process-related.

riag Ni 113 Brightener* 1.0 – 1.5 L pro 10 kWh

riag Ni 141 Additive* 1.0 – 1.5 L pro 10 kWh

riag Ni Tenside M* / L* 0.1 – 0.3 L pro 10 kWh

* depending on customer-specific process requirements

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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Analysis (Analytical Methods)

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: $(25 - \text{consumption in mL}) \times 12.0 = \text{mL/L riag Ni 149 Make up / riag Ni 149 Buffer}$

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
250 mL	glass beaker and diluted with
50 mL	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.

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

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

Nickel

Reagents:	Buffer solution pH 10 Na ₂ EDTA 0.1 mol/L Murexide (Sodium chloride 1:100)
Procedure:	<p>10 mL electrolyte are transferred via pipette into a</p> <p>100 mL measuring flask and filled- up to the mark with deionised water and mixed well</p> <p>10 mL of this mixture is given into a 250 mL glass beaker by pipette followed by</p> <p>15 mL Buffer solution addition</p> <p>100 mL deionised water and</p> <p>1 spatula tip of Murexide are added The sample colour should then be deep yellow</p> <p>Titrate immediately with Na₂EDTA 0.1 mol/L to a blue-end- point</p>
Calculation:	<p>Nickel (g/L) = consumption of mL Na₂EDTA 0.1 mol/L x 5.869</p> <p>Nickel sulphate hexahydrate (g/L) = [A – (B x 0.247)] x 4.48</p> <p>A = Nickel concentration in g/L</p> <p>B = Nickel chloride conc. in g/L</p>

riag Ni 138 Tenside M

Reagents:	<p>Glycerine</p> <p>Butyl phosphate solution:</p> <p>Mix 5 mL Tri-n-Butyl phosphate</p> <p>500 mL Methanol</p> <p>500 mL water DI</p>
Procedure:	<p>25 mL electrolyte are transferred via pipette into a 300 mL Erlenmeyer flask, add</p> <p>3 drops glycerine, shake well, to form a foam cover. Add in steps of</p> <p>0.5 mL butyl phosphate solution, shake well after each addition, until the foam cover disappears within 10 seconds</p>

Nickel sulphamate $\text{Ni}(\text{NH}_2\text{SO}_3)_2 \times 4 \text{H}_2\text{O}$

Reagents: Buffer solution pH 10
 Na_2EDTA 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 the Na_2EDTA 0.1 mol/L to a blue-
 end- point

Calculation: Consumption of mL Na_2EDTA 0.1 mol/L x 5.869 = Nickel (g/L) = **A**
 $[A - (B \times 0.247)] \times 5.41$ = mL/L Nickel sulphamate solution
 A = Nickel concentration in g/L
 B = Nickel chloride conc. in g/L