

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

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riag Cu 375

Acid bright copper bath for high brilliance, low-stressed and ductile deposits

Properties:

- excellent bright deposits for functional and decorative applications
- low stressed, ductile coatings, suited for plating on plastics
- high levelling and extraordinary brightness even at low coating thickness

Bath make up

	Range	Optimum
Copper sulphate (CuSO ₄ x 5 H_2O)	190 – 240 g/L	220 g/L
Sulphuric acid, 96 %, chem. pure (H_2SO_4)	50– 70 g/L	60 g/L
Sodium chloride chem. pure (NaCl)	70 – 140 mg/L	120 mg/L
riag Cu 375 Make up	8 – 12 mL/L	10 mL/L
riag Cu 375 Brightener	0.6 - 0.8 mL/L	0.7 mL/L
riag Cu 375 Leveller	0.4 - 0.6 mL/L	0.5 mL/L

Make up of 100 litres bath volume:

Dissolve copper sulphate in a separate tank in approximately 50 L of demin. water. Add approx. 0.2 kg of activated carbon and stir for about 1 hour.

Filter carefully into the working tank and fill up almost to the end volume with demin. water.

Add sulphuric acid slowly and carefully and sodium chloride, which has been dissolved in a small quantity of water, to the clear solution under stirring. After cooling down to room temperature add organic additives. Stir well again.

If basic chemicals of bad quality are used, it is recommended to dummy-plate for 2 - 3 Ah/L at 1 A/dm^2 before adding organic additives.

Attention: After make up, analysis of chloride content should take place more frequently until a stable anode- film has been formed.

Process and equipment:

Tanks	Polypropylene, PVC, rubber-lined steel		
Bath agitation	an air agitation of $10 - 20 \text{ m}^3$ /h air per meter cathode-rod is required. The used air should be oil – and dust free. In addition a mechanical agitation is recommended.		
Filtration	continuous filtration, $2 - 4$ bath volumes per hour. Porosity of filter as low as possible.		
Exhaust	recommended		
Temperature	20 – 30 °C		
pH-value	< 1.0 supervision not necessary		
Anodes	all types of anodes can be used if their purity is 99.9 % copper and if they contain 0.02 – 0.06 % phosphorus		
Current density	Cathodic: Anodic	1.0 - 6.0 1.0 0.5 - 2.5	A/dm ² (rack) A/dm ² (barrel) A/dm ²

Supervision and correction:

For maintenance of the bath supervision of the following parameters is required

Operating values

	Range	Optimum
Copper (Cu ²⁺)	50– 60 g/L	56 g/L
Sulphuric acid (H ₂ SO ₄)	60– 70 g/L	65 g/L
Chloride (Cl)	70 – 140 mg/L	75 mg/L

To **increase the copper content** by 1 g/L add 393 g of copper sulphate $x 5 H_2O$ per 100 L bath volume. Copper sulphate should be dissolved in demin. water and treated with activated carbon. At the same time **riag Cu 375 Make up** must be replenished (50 mL/kg Copper sulphate $x 5 H_2O$).

To **increase the sulphuric acid content** by 1 g/L add 100 g of sulphuric acid, density 1.84 g/cm³ chem. pure, per 100 L bath volume. Sulphuric acid must be as clear as water.

To increase the chloride content by 1 mg/L add 165 mg of sodium chloride per 100 L bath volume.

riag Cu 375 Brightener and riag Cu 375 Leveller have to be replenished at regular intervals.

Replenishing for 10'000 Ah:

riag Cu 375 Brightener	1.0 L	(0.5 – 1.5 L)
riag Cu 375 Leveller	0.9 L	(0.6 – 1.2 L)

The consumption depends on requested degree of brightness and drag out. riag Cu 375 Make up will be consumed in general by drag out. With every addition of copper sulphate add 50 ml of riag Cu 375 Make up per kg Copper sulphate – $5H_2O$.

Important: Supervision of the organic additives is done by Hull-cell testing.

Safety arrangements

We recommend wearing safety glasses, gloves and protective clothing during working with sulphuric acid.

For further information please consult the safety data sheets.

Waste water treatment / Environmental protection

The concentrates as well as their rinsing waters contain copper sulphate and sulphuric acid. They are extremely dangerous for the environment. The waste water needs to be prepared according legal regulations before getting in the canalisation.

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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riag Oberflächentechnik AG Murgstrasse 19a CH-9545 Wängi T +41 (0)52 369 70 70 F +41 (0)52 369 70 79 riag.ch info@riag.ch

Analytical instructions:

Determination of copper content:

Reagents:	EDTA-standard solution, 0.05 mol/L Ammonia solution (300 g Ammonia, 25 %/L) Indicator: Murexid, 1:100 grinded with sodium chloride		
Procedure:	10 mL 25 mL 500 mL 250 mL 0.05 mol/L	of copper bath into a 250 mL volumetric flask fill up with demin. water to the mark and stir well of this solution (1.0 mL bath solution) into a Erlenmeyer flask, add of demin. water carefully add diluted ammonia until solution turns deep-blue. Add a pinch of indicator Titrate with EDTA-standard solution until the colour changes from reddish-yellow to deep-violet	
Calculation:	Copper (g/L)	=consumed EDTA solution in mL x 3.177	
Determination of sulphuri	c acid content	::	
Reagents:	0.1 mol/L NaOH-standard solution Methylorange 0.1 %		
Procedure:	10 mL 250 mL 25 mL 250 mL 100 mL 5 drops	of copper bath into a volumetric flask. Fill up with demin. water to the mark and mix well. Put of this solution into a Erlenmeyer flask and add of demin. water. Continue with adding of Methylorange titrate with 0.1 mol/L NaOH-standard solution until the colour changes from red to yellow.	
Calculation:	Sulphuric acid (g/L) = consumed NaOH solution in mL x 4.9		
Determination of chloride	content:		
Reagents:	0.005 mol/L Mercuric(II)-nitrate-standard solution 0.1 mol/L Silver nitrate-solution diluted Nitric acid (1:1)		
Instruction:	25 mL 250mL 30 mL 30 mL 3 – 5 drops 0.005 Mol	of copper bath into a Erlenmeyer flask, add of demin. water and of diluted nitric acid, add of 0.1 mol/L Silver nitrate-solution to form a staying turbidity, titrate immediately under strong stirring with Mercuric(II)-nitrate-standard solution until turbidity clarifies	
Calculation:	Chloride (mg/L) = consumed Mercuric(II)-nitrate solution in mL x 14.2		

Hull-Cell instruction

Before testing in the hull-cell make sure that the contents of copper, sulphuric acid and chloride are adjusted within the prescribed limits.

Equipment:	Hull-cell 250 mL with air agitation rectifier $0 - 6 V/0 - 5 A$ test sheets of brass or copper scotch brite and abrasive powder
Instruction:	put 250 mL of bath solution into the cell clean test sheet with abrasive powder and scotch brite rinse well under flowing water dip into 10 % sulphuric acid rinse again insert test sheet in Hull-cell turn on air agitation adjust 2.0 A after 10 min switch off current and remove test panel from the cell rinse the test panel well and dry carefully

Interpretation:

With normal concentration of the constituents the test panel shows bright deposits from 0 - 100 mm. Backside totally covered.

Problems and their causes

- 1. riag Cu 375 Brightener and riag Cu 375 Leveller, shortage of both Brighteners: poor levelling at all current densities, hazyness at low current density from 85 – 100 mm
- 2. Excess of both Brighteners:

strong excess (> 2-fold conc.) shows a sharp demarcated not levelled area at low current density

riag Cu 375 Brightener Shortage: poor levelling at all current densities Excess: sharp demarcated not levelled area at low current density

- riag Cu 375 Leveller Shortage: burning at high current density Excess: strong hazyness or dull deposits at low current densities
- 5. Influence of riag Cu 375 Make up Shortage: relief deposits at high and medium current density improper reaction on dosage of brightener and leveller Excess: low current density hazy

Error	Cause	Remedy
Burning at HCD	Bath temperature too low	Increase temperature
	Copper content too low	Add copper sulphate
	Excess of riag Cu 375 Brightener	Control additions Work out excess of riag Cu 375 Brightener or destroy with H ₂ O ₂
	Shortage of riag Cu 375 Leveller	Addition of 0.2 mL/L riag Cu 375 Leveller
Relief-like deposits in HCD	Shortage of riag Cu 375 Make up	Add 5 mL/L riag Cu 375 Make up
	Shortage of chloride ions	Adjust chloride content
Dull deposits at LCD	Bath temperature too high	Cool electrolyte
	Excess of riag Cu 375 Leveller	Work out excess of riag Cu 375 Leveller
	Shortage of riag Cu 375 Make up	Add 1 – 3 mL/L riag Cu 375 Make up
	Bath is organically contaminated	Add 50 – 100 mg/L potassium persulphate
Levelling sharply reduced in LCD	Excess of riag Cu 375 Brightener	Work out excess of riag Cu 375 Brightener or destroy with H ₂ O ₂
Generally, levelling too low	Shortage of riag Cu 375 Brightener and riag Cu 375 Leveller	Add riag Cu 375 Brightener and riag Cu 375 Leveller
	Excess of chloride ions	Treat electrolyte with 1 % Silver sulphate solution. 440 mL silver sulphate solution must be added per 100 L to precipitate 10 mg/L chloride.
Electrolyte reacts badly to additions of brightener	Organic contamination	Add 50 – 100 mg/L potassium persulphate
		Clean bath with 5 – 10 g/L activated carbon, then add 50 % of new make up additives

Error	Cause	Remedy
Consumption of additives too high	Bath temperature too high.	Cool bath
	Ratio of riag Cu 375 Brightener and riag Cu 375 Leveller not correct	Adjust to correct ratio.
	Excessive sludge on anodes	Wrong anodes or anodic current density too high
Worse adhesion to nickel	Excess of brightener riag Cu 375 Brightener	Work out excess of riag Cu 375 Brightener or destroy with H ₂ O ₂ or do after copper plating electro- cleaning
Worse adhesion to nickel strike	Nickel solution contains sulphurous compounds	Use sulphur-free semi-bright nickelbath
Deposit covered with fine pores	Pump is sucking air	Remove pump suction pipes from zone of agitated air
	Air agitation incorrect	Jets of air agitation pipes too small. Diameter must be at least 3 mm.
	Shortage of riag Cu 375 Make up	Add 5 mL/L riag Cu 375 Make up
Deposit covered with particles	Particles in the bath	Filter thoroughly
	Air is contaminated	Check air-filter
	Burning of deposits	See item 1
	Impurities of copper sulphate	Filter copper sulphate solution
	Unsuitable anodes	Use suitable anodes
Anodes passive	Sulphuric acid too high	Dilute electrolyte
	Copper content too high	Dilute electrolyte
	Chloride content too high	See item 5
	Anode bags clogged or too fine	Clean anode bags
	Bath is contaminated with large amount of iron	Dilute solution