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

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CUPRO-COAT 100

Electroless plating copper electrolyte

CUPRO-COAT 100 is an electroless plating copper electrolyte which works by depositing a fine, crystalline-copper layer. It is particularly suitable for the coating of plastic materials.
The copper deposition takes place as a result of the following main reaction:

$$Cu^{2+} + 4\ OH^- + 2\ HCHO \longrightarrow Cu + 2\ HCOO^- + 2\ H_2O + H_2$$

The reducing agent is a 37 % solution of formaldehyde, while potassium hydroxide provides the alkali element.
The **CUPRO-COAT 100** can be applied both as rack or barrel plating process. The deposition rate lies within an approximate range of 1.5 µm/h to 7 µm/h.

The copper solution, complexing agent, potassium hydroxide solution and additives and formaldehyde, along with four stabilisers and a surface-active agent, are required for new or initial use. Regeneration is carried out with the copper solution (100 g/L), potassium hydroxide, formaldehyde and four stabilisers. The bath is stabilised by adding stabiliser FL 11.

Container and equipment

PE or PP tubs should be used as bath containers.

Teflon heat exchangers or Teflon bath heaters should be used for heating the bath. In order to avoid partial overheating, the air injection inlet should be located near the bath-heating device and attached to the sides of the tub to minimise the settling of hydrogen bubbles.

A suction system must be provided for the extraction of spray-mist or steam. A cover should be placed over the bath during breaks in production. This is done in order to stop evaporation loss at working or near-working temperatures, and to prevent the entry of dirt or other impurities from the surrounding air.

Operating conditions

Solution	Distilled or deionised water (conductance value < 5 µS)	
Make up:	FL 1	3.5 vol.-% (copper solution 100 g/L)
	FL 2	6.5 vol.-% (complexing agent)
	FL 3	6.5 vol.-% (complexing agent)
	FL 4	7.5 vol.-% (KOH + additives)
	FL 5 (1:10, diluted in water)	0.25 mL/L (stabiliser)
	FL 6 (1:10, diluted in water)	0.25 mL/L (stabiliser)
	FL 7 (1:10, diluted in water)	0.20 mL/L (stabiliser)
	FL 8 (1:10, diluted in water)	0.20 mL/L (stabiliser)
	FL 9	0.10 mL/L (surface-active agent)
	FL 10	6 mL/L (formalin)
		added only at beginning of bath operation
Replenishment:	FL 4	450 g/L KOH plus additives
	FL 10	37 % HCHO solution

Dosing ratio: The addition of copper solution, part FL 4 and part FL 10 carried out after analysis. Part FL 4 and FL 10 should be added via a dosing pump in order to prevent large fluctuations in parameters.
FL 7 and FL 8 (1:10 with water) should be used in the same ratio to control the electrolyte and give a deposition rate of 4 µm/h.
With 0.60 dm² surface/L electrolyte, normal practice is to add
0.15 – 0.30 mL/L FL 7 and FL 8 each.

Operating temperature:	56 – 58 °C
Copper content:	3.0 – 3.5 g/L Cu
Reducing agent:	4 – 8 mL/L
KOH content:	30 – 35 g/L
Litre charge:	max.1.25 dm²/L
Deposition rate:	0.8 – 7 µm/h

Solution make up

The first step is to pour water into the thoroughly-cleaned container. The sequence after FL 1, FL 2, FL 3 and FL 4 is then added. Once addition has taken place, the solution is replenished with distilled or deionised water to its final volume. The final step involves the addition of
0.25 mL/L FL 5 and 0.25 mL/L FL 6, plus 0.2 mL/L FL 7 and 0.2 mL/L FL 8 and 0.1 mL/L FL 9. The stabilisers FL 5, FL 6, FL 7 and FL 8 should first be diluted 1:10 with water.
The bath can now be brought up to its working temperature with the help of circulating air. The addition of FL 10 (initially 600 mL/100 L) should not take place until the start of the coating process (parts or ballast plates), followed by FL 10 - added via the dosing pump.

Working instructions

No-load running periods in excess of five minutes should be avoided. A plate can be suspended inside if required. In the case of a new or initial operation, the process can begin with a KOH content of 40 g/L in order to increase light-off performance. KOH content should be kept to approximately 30 – 35 g/L during normal operation of the bath. After overnight or weekend shutdown, the electrolyte should be pumped via a filter (size 1 µm) into a clean tub. The levels of Cu, KOH, and formaldehyde can then be adjusted as specified. At the same time the following is added:

Addition per 100 L

FL 7 (1:10 dilution)	20 mL
FL 8 (1:10 dilution)	20 mL
FL 5 (1:10 dilution)	25 mL (initial addition) mornings only
FL 6 (1:10 dilution)	25 mL (initial addition) mornings only
FL 11	10 mL (can be increased after extended shutdown)
FL 2 and 3	After analysis or approx. 5 % of initial amount for every other pump circulation cycle, to compensate drag-out losses

These additions are required because the stabilisers decompose as a result of air injection and shutdown.

Please note: These additions, which are based on previous experience with use of the electrolyte concerned, apply to single-shift electrolyte usage. In the case of two- or three-shift operation, the quantities of stabilisers added should be reduced and/or adjusted as required.

At the end of each shift, the electrolyte should be stabilised by the addition of 40 mL/100 L of stabiliser FL 11 and, before the weekend, with the addition of 80 mL/100 L of stabiliser FL 11.
The hourly deposition rate of the electrolyte is to be determined by means of X-ray examination of freshly copper-coated test plates, or by examining the actual coated parts.
When coating is carried out on palladium-compound LCP parts, the reaction should start on the parts with the electrolyte after about 15 – 25 min. An intact copper layer must be formed by the end of the coating period. (Microscope)
The service life of the electrolyte is limited by the occurrence of the Cannizarro reaction (reduction of the HCHO and KOH content at a constant level of copper content). When the Cannizarro reaction occurs, 2/3 of the electrolyte must be discarded. It is then replenished with new solution until the original electrolyte volume is reached.

Function of the individual constituents

FL 4 contains stabiliser FL 5 and FL 6, along with stabiliser FL 11.
Stabilisers FL 5 and FL 6 stabilise the Cu^{+} and act on the particle size of the crystals (particle-size reducer). They also have an influence on the colour of the copper coating. Stabilisers FL 7 and FL 8 act on the redox potential of Cu^{2+}/Cu^{+} and/or Cu^{+}/Cu. FL 8 is a pyridine derivate, and can give the copper coating a violet-coloured tinge. This violet-coloured tinge to the copper coating has no influence on the quality of finish.
If dried remains of electrolyte solidify in the barrel body after copper-plating with Cu electrolyte, the system is operating with clearly excessive doses of FL 7 und FL 8. These deposits are extremely difficult to remove.
Stabiliser FL 11 hinders the depositing of copper through complex formation of Cu^{+}, and influences the coloration of the precipitated copper layer.
The following section summarises how to proceed in the event of problems with electrolyte:

Lack of selectivity

Increase the hourly addition of FL 7 (1:10 dilution) and FL 8 (1:10 dilution) up to max. 40 mL/100 L. In the event of an overdose of FL 7 and FL 8, the reaction of Cu to Vectra E820 i Pd is slowed down or will no longer take place. The electrolyte should then be used, with ballast plates and without the dosed addition of FL 7 and FL 8, until the typical reactive behaviour on Vectra E820 i Pd can be observed.
FL 7 and FL 8 can also decompose as a result of overnight shutdown of the electrolyte system and air injection.

Reduction in the deposition rate

Increase the hourly addition of FL 11 to max. 5 mL/100 L.
Excess doses of FL 11 can disrupt the reactive process. If this occurs, the electrolyte should be used, without any addition of FL 11, until typical reactive behaviour is observed. Air injection during system shutdown can also destroy stabiliser FL 11 by oxidation.

The deposited copper is brown to dark brown in colour

Remedy by adding FL 11 (2 – 4 mL/100 L) until the coating takes on a pink tinge.

The deposited copper is glossy metallic red in colour

The electrolyte contains too much reducing agent FL 10 (formalin).

Incorrect reactive behaviour

Increase KOH content to 40 g/L; run bath with ballast plate. The air injection quantity may have to be reduced.
The cause of an incorrect reaction could also be excessive dosing of FL 7, FL 8 or FL 11. The electrolyte should be used with ballast material, without the addition of stabiliser, until typical reactive behaviour can be observed.
Stabilisers also decompose as a result of electrolyte system shutdown and air injection.

Particles in electrolyte (electrolyte appears grey in colour), foreign deposits on part

Stabilise electrolyte with FL 11 (approx. 5 - 10 mL auf 100 L), increase the rate of air injection. Filter the electrolyte into a clean tub.
The chemical-copper tub is cleaned with a solution consisting of 10 – 15 vol.-% conc. H_2SO_4 and 5 – 10 vol.-% H_2O_2. This solution can be reused several times (adding further H_2O_2 as required).
When reusing electrolyte, add FL 1, FL 4 and FL 10 after analysis.

Base materials

CUPRO-COAT 100 can be used on both metallic and plastic base materials (LCP (Vectra E820 i Pd) and PA). The LCP coating sequence should not be interrupted after pre-treatment. Wait until the parts have been copper-plated. Copper-coated parts can also, after storage, be plated again with e.g. nickel or gold.

Temperature

Normal operating temperature lies between 56 °C and 58 °C.
The finished bath solution should be injected with air during the warm-up and cooling phases to prevent the formation of localised hot-spots.

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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

Analysis – methods of analysis

Copper

Target value:	3.5 g/L copper
Method:	AAS, dilution 1000 times

Formaldehyde and potassium hydroxide content

Target value:	4 – 8 mL/L	Formaldehyde
	30 – 35 g/L	KOH
Method:	5 mL	the bath solution being examined is placed in a
	400 mL	beaker with a pipette, along with
	150 mL	of distilled water and titrated, with constant stirring, with
	0.1 mol/L HCl	to pH 10.0. Consumption is **a** mL
		Now, while still stirring constantly, add
	25 mL	1.0 mol/L sodium sulphite solution (126 g/L water-free sodium sulphite). The pH-value climbs back up to 10.5. The burette is now refilled and titrated, still constantly stirring, with
	0.1 mol/L HCl	to pH 10.0. Consumption is **b** mL

Calculation:	KOH content (g/L)	= consumption **a** mL HCl x 1.12
Calculation:	Formaldehyde content (g/L)	= consumption **b** mL HCl x 3