Non Cyanide Alkaline Copper Process SurTec[®] 864

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Why is it necessary to apply cyanide or non cyanide copper processes?

 Cu^{2+} + $Fe_{(s)}$ \longrightarrow Fe^{2+} + $Cu_{(s)}$

- out of acid electrolytes copper is precipitated without current (with amorph structure)
- in cyanide or non cyanide electrolytes the copper is complexed in a better way, so precipitation occurs only when current is applied
- normal layer sequence: alkaline copper acid copper (semi bright nickel) bright nickel chromium (brass)

2. Non cyanide copper processes

Electrolyte based on pyrophosphates (old concept)

- pyrophosphates are salts from the di-phosphoric acid
- copper is complexed by the pyrophosphate and keeps diluted at pH 8-8,5
- the oxygen links between the two phosphor atoms can be destroyed by hydrolysis
- with time, there is formed successively the normal phosphate (PO_4^{3-}), which disturbes the deposition

Electrolyte based on phosphonic acid

- copper also can be complexed by phosphonic acid
- the link between the two phosphor atoms is made by an organic group and will <u>not</u> be destroyed
- the electrolyte based on phosphonic acid keeps its good quality





Bath composition and make up values:

concentrated electrolyte (with 30 g/l Cu)30 Vol %25-60 Vol %corrector solution6.5 Vol %45% potassium hydroxide solutionto adjust the pH

A bath make up out of the salts at the customer is not possible (very exothermical reaction), it has to be made in closed reaction tanks.

Recommended: To keep clean the copper bath SurTec 864, a pre-plating in a special electrolyte is useful. The make-up values for this are:

concentrated electrolyte (with 30 g/l Cu)12.5 Vol %corrector solution7.5 Vol %

Parts should be plated there at pH 9,3 for 3 minutes with 0.5-1 A/dm²

Plating of steel parts:

temperature:	55 °C	50-70 °C	
pH-value:	9.5	9.2-9.8	
current density:	1 A/dm ²	0.1-1.5 A/dm ²	
deposition rate:	0.2 µm/min (at 1 A/dm ²)		
	Cu ¹⁺ + 1 e⁻ Cu ²⁺ + 2 e⁻	Cu(s) cyanide free process Cu(s) cyanide process	
agitation: anodes:	air agitation OFHC-anodes	(= oxygen free high conductivity)	
filtration:	contineously (1-5 bath volume/h)		

Special working conditions for zinc die-cast and aluminium parts:

pH-value:	9.2	(9.0-9.4)
contacting:	parts have to be under current while	
	into the bath	

1.) Analysis of copper

- reagents: Ammonium persulfate, concentrated ammonia solution, PAN-indicator (1-(2-Pyridylazo)-2-naphthol), 1g/l in ethanol
- process: pipette 5 ml bath solution into a 250 ml Erlenmeyer beaker, add approx. 25 ml deionised water and 2-3 g ammonium persulfate. Stirr the solution for about 15 min. Add 5 ml of the concentrated ammonia solution; the colour turns to dark blue. Add another 50 ml deionized water and 4-6 drops of the indicator (don't add more: the changing of the colour will be worse). Titrate with 0.1 N EDTA from dark blue to greenish-grey.

calculation: consumption in ml \cdot 1.27 = g/l Cu

correction: rise by 1 g/l Cu = addition of 33 ml/l SurTec 864

2.) Complexing agent SurTec 864 I

The analysis of the complexing agent is done by photometric measurement of the phosphorous content (Dr. Lange Cuvette Test LCK 350). The bath sample is diluted therefore 1:5000.

One determination is done with heat treatment for 2 hours at 100 °C, to analyse the total content of phosphorous.

Another determination is done with only storing the test tube at room temperature for 2 hours, to analyse the free phosphorous inside the bath sample.

Calculation:	measured values in mg \cdot 5 = bath concentrations in g/l	
	(Ptotal in g/l) - (Pfree phosphate in g/l) = (Pcomplexing agent in g/l)	
Desired value:	(Pcomplexing agent in g/l) / (Cu in g/l) = 4 or more	

Parameters for the Hull cell test:

volume of the bath sample:	250 ml
temperature:	the same as in the plating line (ca. 50 $^{\circ}$ C)
agitation:	no
current:	0.5 A
plating time:	15 min
type of panel:	steel panel

The plated panel should be bright and equal over the whole current density (without agitation a slight burning is normal), the back site of the panel should be covered totally with copper.

4.) Copper-(I)-content

At a high throghput in the copper bath, there will be a formation of Cu-(I). This is caused by a too low dissolvation rate of the anodes, compared with the high throghput. The Cu-(I) can not be analysed separately, a high content can only be seen in the caused effects:

Effects:

- dark red colour of the deposit
- very high Cu-(I) contents lead to a bad adhesion of the copper
- at high Cu-(I) contents the bath colour changes from blue to greenish
- Remedy: Addition of peroxide (H₂O₂), which must be diluted 1:10 with demin. water

Cyanide: Causes dark red deposits with bad adhesion in the low current density. Remedy: Addition of 5-10 ml/l H₂O₂ (1:10 prediluted).

Lead: At concentrations above 50 mg/l it also causes dark layers with a bad adhesion in the low current density. Remedy: Work out at high current densities on parts with cathode bag.

Dragged in organic:

Causes dull deposits.

Remedy: Treatment of H_2O_2 (prediluted) and active carbon afterwards.

A too low content of corrector solution SurTec 864 I can lead to aheasion problems, slight excess has no effect. The corrector solution is highly acidic, so after addition, the pH has to be controled and adjusted.

The layer properties are comparable with layers out of cyanide electrolytes:

- very good coverage
- can be soldered very well
- ductile layer
- hardness of copper layers in comparison (Vickers):

acid copper	cyanide copper	non cyanide alk. copper
2100 N/mm ²	1500 N/mm ²	500 N/mm ²

In the electrolyte are <u>no hard</u> complexing agents as EDTA, therefore the waste water treatment can be done as usual:

- addition of hydrochloric acid / sulfuric acid till pH = 1
- addition of lime milk till pH = 10
- decanting/filtrating
- (• if wanted, additional sulfide precipitation)
- copper content will be less than 0,5 mg/l

Because of the missing of cyanide and its additional property of cleaning, the parts must be pretreated more thoroughly than for the cyanide copper process.

Pretreatment for steel parts:

alkaline hot degreasing at 60 °C, for 10-20 min pickling in HCl 1:1, evtl. inhibited, for 5-10 min electrolytical (anodic) cleaning, for 2-5 min

Pretreatment for zinc die cast parts:

hot degreasing in low alkaline bath at 50 °C for 10-20 min elektrolytical (cathodic) cleaning, silicate containing, for 2-5 min acid dip containing fluoride, for 1-2 min

Pretreatment:

hot degreasing in low alkaline bath at 60 °C for 5-10 min high alkaline pickling at 50 °C for 2-5 min acid dip in nitric acid 1:1 non cyanide zincate treatment (room temperature), for 0,5-2 min Advantages and disadvantages of the non cyanide alkaline copper process in comparison to the cyanide process:

Advantages:

- free of cyanides (=> worker's protection/waste water treatment)
 - good throwing power
 - very tolerant working conditions (temperature, make up values, pH-value, types of materials which can be plated)
- tolerant vers carbonate (not necessary to freeze out)

Disadvantages: • more time or more current density is needed to reach the same layer thickness in comparison to the cyanide process

- a make up out of salts is not possible for the customer (=> high make up costs)
- plating zinc die-cast in barrel process is not quite easy till now