

SurTec® 861

Cyanide Copper Process

Properties

- deposits matt to bright copper layers, depending on the electrolyte composition
- good throwing power
- suited for barrel and rack application
- easy process handling

Application

SurTec 861 Cyanide Copper is applied as a first layer for copper-nickel-chrome coatings as well as a single coating for special applications.

The process SurTec 861 includes the following products:

- SurTec 861 I Wetting Agent contains tensides and carriers
- SurTec 861 II Brightener allows bright deposits also at high layer thickness

make-up values:

copper cyanide	70 g/l	
potassium cyanide	135 g/l	
potassium hydroxide	11 g/l	
K/Na-tartrate	10 g/l	(10-25 g/l)
SurTec 861 I Wetting Agent	4 ml/l	(4-15 ml/l)
SurTec 861 II Brightener	0.5 ml/l	(0.3-1.5 ml/l)

analytical values:

copper	50 g/l	(50-60 g/l)
free potassium cyanide	35 g/l	(25-45 g/l)
corresponds to free cyanide	14 g/l	
potassium carbonate	10 to 200 g/l (max.)	

make-up:

Steps for make-up:

Prepare a new make-up always in a coated steel tank (do not use PVC tanks for make-up because the solution gets very hot!):

1. Fill 2/3 of the deionised water into the tank.
2. Dissolve potassium hydroxide and potassium cyanide carefully, portion by portion, stirring well.
3. Mix copper cyanide with a small amount of water and add this pulp carefully and in small portions to the bath (attention: solution becomes hot!).
4. Add K/Na-tartrate and dissolve it.
5. Add the missing water and heat up to working temperature.
6. Dummy plate for 4-6 hours at 0.5 A/dm².
7. Then add the additives.

temperature: 60 °C (50-65 °C)

pH-value: iron/steel: 12 (11.0-12.8)
zinc die cast: 11 (10.5-11.5)
aluminium, magnesium: 10 (9.5-10.5)

adjust the pH-value with tartaric acid or KOH

cathodic		
current density:	0.3-1 A/dm ²	<i>barrel</i>
	0.5-4 A/dm ²	<i>rack</i>
bath voltage:	1-3 V	
current efficiency:	75 %	(65-90 %)
deposition rate:	0.35 μm/min	at 1 A/dm ²
ratio		
anode/cathode:	2:1	
anodes:	electrolytic copper as bars (99.95-99.99 %); anode bags out of resistant material (e.g. Nylon), or use diaphragma	
	If a bright copper deposit is wanted, OFHC anodes are recommended.	
	Too low anode surface leads to a brown-black oxide layer on top of the anodes and results in higher bath voltage and a higher tendency to cyanide destruction, which leads to higher carbonate contents.	
agitation:	rack agitation:	with approx. 4-12 m/min
	barrel rotation:	with approx. 2-6 rpm
tank material:	steel with rubber or plastic coating (lead will be attacked!)	
filtration:	to avoid rough deposits, continuous filtration is necessary (1-5 circles/h)	
heating:	thermostatically controlled heating of resistant material (e.g. Teflon)	
exhaust:	required for worker's protection	

Maintenance and Analysis

Check the pH-value regularly. Analyse and adjust the concentration of copper, cyanide, hydroxide and carbonate regularly.

The first rinse can be used to compensate evaporation losses (use deionised water only!)

Lack of **SurTec 861 I** leads to matt deposition in the lcd and at higher lack also in the hcd. Overdosage of SurTec 861 I leads to higher consumption of SurTec 861 II.

Lack of **SurTec 861 II** leads to general decrease of brightness, matt deposition in the low and medium current density area (lcd/mcd) and reddish brown or matt deposits in the high current density area (hcd). Overdosage is recognized by irregular brightness and dullness at the parts.

The **copper** content should be in between 50 and 60 g/l. Lower copper contents, resulting of high drag-out or too small anode surface, will be recognized by decreasing efficiency and lower deposition rate. An addition of 1 g/l Cu (= 1.43 g/l CuCN) requires an addition of 2.8 g/l KCN at the same time.

A lack of **cyanide** decreases the deep brightness and leads to cloudy depositions in the lcd and to burnings in the hcd. Also the anodes can passivate due to deposition of CuCN on top of the anodes. For binding 1 g/l free KCN, add 0.7 g/l CuCN.

For optimum working conditions, a concentration of 10 g/l **potassium carbonate** is required. The electrolyte will accumulate carbonate over the time. Concentrations above 100 g/l may lead to lower efficiency and to decreasing brightness and throwing power.

Sample Preparation

Take a sample at a homogeneously mixed position. Let it cool down to room temperature. If the sample is turbid, let the turbidity settle down and decant or filter the solution.

Copper – Analysis by Titration

- reagents: ammonium persulfate
ammonia solution (conc.)
hydrogen peroxide H_2O_2 (30 %)
0.1 mol/l EDTA solution (Titriplex III)
indicator: PAN indicator (1-(2-Pyridylazo)-2-naphthol,
1 g/l in ethanol)
- procedure: 1. Pipette 2 ml bath sample into a 250 ml Erlenmeyer flask.
2. Dilute with approx. 25 ml deionised water.
3. Add 2 ml H_2O_2 and stir for 5 minutes.
4. Boil for 15 min until the solution becomes dark brown and dull.
5. Add 2-3 g ammonium persulfate (solution becomes clear blue).
6. Add approx. 5 ml ammonia (solution becomes deep blue).
7. Dilute with further 50 ml deionised water.
8. Add 4-6 drops PAN indicator (no more; otherwise the end point is not visible).
9. Titrate with 0.1 M EDTA solution from blue to green-grey.
- calculation: consumption in ml \cdot 3.18 = g/l Copper (Cu)
- correction: rise by 1 g/l Cu = add 1.4 g/l copper cyanide and at the same time
2.8 g/l KCN (for better dissolution/complexing of CuCN)

Free Potassium Cyanide – Analysis by Titration

- reagents: 0.1 N silver nitrate solution
potassium iodide
ammonia solution (10 %)
- procedure: 1. Pipette 10 ml bath sample into a 250 ml Erlenmeyer flask.
2. Dilute with 100 ml deionised water.
3. Add 3 drops of ammonia solution.
4. Add 1-2 g potassium iodide and wait until complete dissolution.
5. Titrate with silver nitrate until a lasting white dullness appears.
- calculation: consumption in ml \cdot 1.3 = g/l potassium cyanide (KCN)
- correction: to lower the value of the free cyanide:
to bind 1 g/l KCN = addition of 0.7 g/l copper cyanide (CuCN)

Hydroxide – Analysis by Titration

- reagents: 1 N sulfuric acid
indicator: Epsilon Blue (1 g/l in water)
- procedure: 1. Pipette 10 ml bath sample into a 250 ml Erlenmeyer flask.
2. Dilute with 50 ml water.
3. Add 4-6 drops of indicator.
4. Titrate with sulfuric acid from blue-violet to yellow-orange.
- calculation: consumption in ml \cdot 5.6 = g/l potassium hydroxide (KOH)

Carbonate – Analysis by Titration

reagents:	barium chloride solution (30 %) 1 N hydrochloric acid 1 N sodium hydroxide solution NaOH indicator: methyl orange solution (0.04 %)
procedure:	<ol style="list-style-type: none">1. Pipette 10 ml bath sample into a 250 ml Erlenmeyer flask.2. Dilute with 100 ml deionised water.3. Heat it up.4. Add 30 ml barium chloride solution to the hot solution.5. Let the precipitate settle down (for 30 min), than filtrate through a fine filter paper and wash the precipitate with hot water.6. Tear filter with deposit carefully into pieces and transfer completely into a clean Erlenmeyer flask.7. Add 100 ml deionised water.8. Add exactly 25 ml of 1 N hydrochloric acid.9. Add some drops of indicator.10. Titrate with 1 N NaOH until the colour changes.
calculation:	$(25 - \text{consumption in ml}) \cdot 6.91 = \text{g/l potassium carbonate (K}_2\text{CO}_3)$

Technical Specification

(at 20 °C)	Appearance	Density (g/ml)	pH-value (conc.)
SurTec 861 I	liquid, colourless, clear	1.000 (0.95-1.05)	7.5 (6.5-8.5)
SurTec 861 II	liquid, colourless, clear	1.015 (1.01-1.02)	7.1 (6.5-8.0)

Consumption and Stock Keeping

The consumption depends heavily on the drag-out. To determine the exact amounts of drag-out, see [SurTec Technical Letter 11](#). The following values per 10,000 Ah can be taken as estimated average consumption:

SurTec 861 I	0.5-0.75 l
SurTec 861 II	1.0-3.0 l

In order to prevent delays in the production process, per 1,000 l bath, the following amounts should be kept in stock:

SurTec 861 I	90 kg
SurTec 861 II	90 kg

Product Safety and Ecology

The safety instructions and the instructions for environmental protection have to be followed in order to avoid hazards for people and environment. The Material Safety Data Sheets (according to European legislation) contain explicit details for this.

The following hazard designations and classifications into water hazard classes (WHC) have to be taken into account:

<u>product</u>	<u>hazard designation</u>	<u>water hazard class</u>
SurTec 861 I	-	not water hazardous
SurTec 861 II	Xi - Irritant	not water hazardous

Warranty

We are responsible for our products in the context of the valid legal regulations. The warranty exclusively accesses for the delivered state of a product. Warranties and claims for damages after the subsequent treatment of our products do not exist. For details please consider our [general terms and conditions](#).

Further Information and Contact

In our forum, you can discuss topics of the surface technology:

<http://forum.SurTec.com/>

If you have any questions concerning the process, please contact your local technical department: <http://SurTec.com/International.html>

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Trouble Shooting for the Depositions

problem	possible cause	remedy
matt Cu-layer	a) too low in free cyanide	analyse and adjust
	b) too high current density	decrease current density
	c) too low bath temperature	heat up to 70- 80 °C
	d) too low pH or too low concentration of hydroxide	adjust the pH to 11.5 with KOH
	e) brightener is consumed	add brightener
	f) wetting agent is consumed	add wetting agent
	g) too high carbonate content	analyse, freeze out or precipitate with barium sulfate
rough and red-brown Cu-layer	a) too high carbonate content	analyse, freeze out or precipitate
	b) too low in free cyanide	analyse and adjust
	c) bath impurities (e.g. anode sludge)	filtrate the electrolyte and use anode bags
no or little copper layer	a) too low in free cyanide	add cyanide
	b) too low metal concentration	add CuCN
	c) too high carbonate content	analyse, freeze out or precipitate
bath colour changes to blue-green	too low in free cyanide	analyse and adjust
strong hydrogen evolution during copper plating	a) too high current density (cathode and anode)	clean the anodes and increase the cathode surface; decrease the cathodic current density
	b) copper content is too low (low conductivity)	analyse and adjust CuCN
	c) too high in free cyanide	add CuCN
copper layer with stripes and spots	a) too low pH or too low concentration of hydroxide	adjust the pH to 11.5 with KOH
	b) too low in free cyanide	analyse and adjust
	c) electrolyte is not wetting well	add wetting agent
	d) pretreatment	check the pretreatment
relief-like Cu deposition	distance to the anode too short	increase distance
matt and hard copper layer	a) too high current density	decrease current density
	b) too low in free cyanide	add cyanide
hard, brittle copper layer	too high current density (cathode and anode)	clean the anodes and increase the cathode surface; decrease the cathodic current density
porous copper layer	a) too high carbonate content	analyse, freeze out or precipitate with barium
	b) electrolyte is not wetting well	add wetting agent
	c) pH is too high for plating Zn, base material is attacked	lower the pH using tartaric acid or KHSO_3

problem	possible cause	remedy
white spots after storing time	a) porous base material	long pickling, long anodic degreasing and good pre-dip firstly, plating a flash-copper layer with low current density pre-dip in 4-10 g/l tartaric acid
	b) included hydrogen	pickling with inhibitor (SurTec 424); long anodic degreasing
	c) pretreatment in general (especially for zinc die cast)	optimize the pretreatment
blister	a) too low pH or too low concentration of hydroxide	adjust the pH to 11.5 with KOH
	b) too high in free cyanide	analyse and adjust CuCN
	c) too low bath temperature	heat up to 70-80 °C
	d) pretreatment: base material was passive	improve the pretreatment
adhesion problems	pretreatment: base material was passive	improve the pretreatment

Trouble Shooting for the Anodes

problem	possible cause	remedy
white anode film, cell voltage rises during the deposition	a) anodes are passive	remove the anode film, evtl. increase the anode surface
	b) insufficient pretreatment (degreasing)	improve degreasing and pickling
	c) too low bath temperature	heat up the electrolyte
grey-green to black anode film	a) too low in free cyanide	analyse and adjust
	b) anodic current density is too high	remove the anode film, evtl. increase the anode surface
	c) too high salt concentration: analyse (especially carbonate content)	dilute the electrolyte or freeze out / precipitate the carbonate
	d) too low pH / hydroxide concentration	adjust the pH with KOH to 11.5
	e) low bath agitation	improve the agitation
	f) too low bath temperature	heat up the electrolyte
anodes become black	electrolyte contains silver	dummy-plate on perforated panels
no dissolution of the anodes, Cu content decreases	a) too low bath temperature	heat up the electrolyte
	b) too low concentration of free cyanide	analyse and adjust
	c) pH value too high	decrease the pH by adding tartaric acid or KHSO_3
	d) too high carbonate content	analyse and freeze out or precipitate the carbonate