New Concepts in Non Cyanide Alkaline Zinc Plating

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- Old Problems and Their Causes
- New Concepts:
 - 1 Zinc Process of the Third Generation
 - 2 Anodes
 - 3 Zinc Generator
 - 4 Electrochemical Process Control



Delayed Blistering

- the deposited zinc layer is correct, the parts are delivered, after two or three weeks the zinc layer bursts off in small flakes.
- wrong dosage of the additives
- **2** electrolyte temperature too low
- foreign metals embrittle zinc deposits
- **(**pretreatment)

Chromatability of Non Cyanide Zinc Deposits

spotted, yellowish blue chromating; greyish, heavily iridescent yellow chromating

Problems with Bath Control

 constant zinc content current distribution in the electrolyte tank enrichment of foreign metals bath control per Hull cell

- incorporation of foreign metals (iron!)
- **2** overdosage of the additives
- badly adjusted activation/chromating

- zinc generator not effective or too small
- anodes (soluble and inert) gets passive
- semi strong complexing agents in the bath
- misbalanced additive systems





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Throwing Power ▼ Electrolyte Conductivity ▼ Polarisation Resistance









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Delayed Blistering ▼ Layer Texture ▼ Recrystallisation

- X-ray diffraction shows that zinc crystallites from non cyanide alkaline zinc processes compared to acid zinc are strongly oriented into the direction of the electrical field during deposition.
- Even at room temperature, the orientation in the deposited layer breaks by time (some weeks or so).
- Finally, the zinc crystallites take more place and induce a pressure tension in the layer which leads to blistering.









The **sodium zincate electrolyte** is more cheap at make-up

The **potassium zincate electrolyte** offers a better electrolyte conductivity and therefore:

- better throwing power
- higher current efficiency (apprx. 80 % at 30-35 °C)
- higher burning limit
- higher deposition rate
- more ductile and whiter zinc layers
- about 0.5 to 0.75 V lower cell voltage:

Example: rack plating line with 10000 A, 10 racks per hour and 0.5 I drag out per rack

10 g/l Zinc, 120 g/l NaOH, 40 g/l Na₂CO₃ compared to 10 g/l Zinc, 170 g/l KOH, 50 g/l K₂CO₃

cost of chemicalsNa electrolyte: $10/h \cdot 0.5 \mid \cdot (0.12 + 0.03) \mid kg/l \cdot 0.51 \mid DM/kg$ = $0.38 \mid DM/h$ K electrolyte: $10/h \cdot 0.5 \mid \cdot (0.17 + 0.04) \mid kg/l \cdot 1.00 \mid DM/kg$ = $1.05 \mid DM/h$ savings of electrical energy K electrolyte: $0.5 \lor \cdot 10kAh/h \cdot 0.15 \mid DM/kWh$ = $0.75 \mid DM/h$

• potassium electrolyte for rack plating, sodium electrolyte for barrel plating





SurTec 704 – Potassium Zincate Electrolyte, 10 g/l Zinc, 170 g/l KOH, 0 to 180 g/l K₂CO₃

- ▼ Current efficiency for the anodic zinc dissolution stays about 100 % up to an anodic current density of about 3 A/dm².
- ▼ Above an anodic current density of 3 A/dm², the zinc anode is covered with a semi conductive barrier layer of zinc oxide (happens also in pure base electrolytes without organics)...
 - the cell voltage rises immediately by 3 to 4 V
 - the anode becomes black
 - the anodic current efficiency drops down to 2-5 %, in favour of 95-98 % O₂ evolution
- Therefore it is extremely hard to control the zinc content of the electrolyte by changing the anode area. The anodic c.e. is either too high or too low, there is no intermediate range of operation. This means, anodes must be removed or reinserted very frequently. This leads of course to a poor current distribution in the plating tank.
- Operation with mixed types of anodes (soluble and inert) is very problematic and at least for rack plating not suitable at all.





- ▼ Colour generally results from absorption of light at certain wave lengths.
- ▼ Certain wave lengths are absorbed because of electron transitions between discrete energy levels in the matter.
- ▼ Normally, zinc oxide is white, because there is no distance between its occupied and non occupied energy levels which fits for the range of wave lengths of visible light.
- ▼ Zinc oxide at a passive zinc anode has been running low on electrons and is therefore a p-semiconductor (positive hole conduction compared to negative electron conduction).
- ▼ These positive holes are statistically distributed, empty, intermediate energy levels.
- This results in an absorption of light at all wave lengths \rightarrow **Black!**



- Usually non cyanide alkaline zinc processes are driven with inert anodes in combination with an external zinc generator for the replenishment of zinc.
- ▼ "Inert" steel anodes are most commonly used.
- ▼ But steel anodes are, in contrary to common belief, not 100 % stable. This means, iron is dissolved!
- ▼ There are some cyanide free zinc electrolytes which contain more iron than some standard zinc/iron electrolytes.
- ▼ Of course, dissolved iron is co-deposited with the zinc. Dependent on the amount, the troublesome discolouration of the chromating layer occurs.
- Steel anodes are fairly unsuitable for non cyanide alkaline zinc plating. <u>Coated</u> steel anodes are much superior.
- Stainless steel anodes are totally unsuitable, because it anodically releases chromium(VI) into the electrolyte.

 non cyanide alkaline zinc electrolyte: 10 g/l Zn, 120 g/l NaOH with SurTec 702 (old generation process)
 cell voltage in a Hull cell at 1 A: 3.21 V (steel anode)

(freshly prepared electrolytes, new anodes) 3.39 V (coated anode)

iron content of the electrolytes in mg/l (1.8 l volume, operation with 1 A at 25 °C)

	start	16 h	40 h	64 h	88 h
steel anode	< 0.5	2.5	5.0	6.0	7.1
coated anode	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5

cell voltage at 1 A:

(used electrolyte, used anodes)

3.39 V (steel anode, brown-black coating)3.32 V (coated anode, blank)



Minimal requirement:15 μm semi bright nickel plated steelBetter:15 μm semi bright nickel + SurTec Catalyst coating on steel

The catalytic coating decreases the oxygen overvoltage, therefore:

- ✓ better current distribution in the plating tank
- ✓ lower cell voltage (energy savings)
- lower consumption of organics

Optimum:

Anodes made of expanded metal (30 mm \times 8 piccolo mesh, rib width 6 mm material thickness 2 mm) of mild steel (e.g. ST 37) plated with 15 µm semi bright nickel + a SurTec Catalyst finish.



Flow of the gas evolution when anodes are correctly installed



The expanded metal should be installed with the ribs horizontally oriented for driving the gas evolution to the back side. By this way, a better electrolyte conductivity in front of the anode is achieved. Anodic current density up to 20 A/dm².

- Why are most zinc generators not effective enough?
- ▼ Zinc appears in the electrochemical series of elements more negative than hydrogen, and zinc is an amphoteric element:

 $Zn + 2H_2O + 2OH^- \rightarrow [Zn(OH)_4]^{2-} + H_2^{\uparrow}$

- ▼ This is a typical redox reaction which can be divided into an anodic oxidation step and an cathodic reduction step:
- anodic oxidation

 $Zn + 4 OH^{-} \rightarrow [Zn(OH)_{4}]^{2-} + 2 e^{-}$

cathodic reduction

 $2 H_2O + 2 e^- \rightarrow H_2\uparrow + 2 OH^-$

• The two partial reactions depend on each other, both reactions must occur at the same time with the same speed. That means, the zinc dissolution cannot be any faster than the hydrogen evolution.

- ▼ The hydrogen overvoltage on zinc is very high or in other words, the evolution of hydrogen at zinc is very slow. This means that the zinc dissolution is very slow too.
- Contacting zinc with a metal which has a small hydrogen overvoltage will lead to a much faster hydrogen evolution on that metal compared to the evolution at zinc.
- Conventionally, zinc dissolution baskets are made out of steel. The zinc is placed into these baskets and immersed into the alkaline electrolyte where a slow dissolution occurs because iron compared to zinc exhibits a lower (though significant) hydrogen overvoltage.
- Hydrogen catalysts are much better suited as basket material than iron because their hydrogen overvoltage is very low and they enhance the hydrogen evolution by far.









 In contact with the SurTec Catalyst zinc, is dissolved in average with 1.5 A/dm² (catalyst area). The dissolution rate is at least 10 times higher than at steel.





SurTec[®] 704, 712 and 715 Size of Zinc Generators with Catalytically Plated Baskets for Cyanidefree Alkaline Zincand Zinc Alloy Processes



Input data

Data for determination of the zinc consumption of the line

totally installed rectifier capacity:

current efficiency:

load of the plating line and the rectifiers:

Data for sizing the catalytical zinc baskets and the generator tanl

depth of the zinc generator tank:

length of one side of the tank; result is length of 2. side:

(input of zero results in a generator tank with a quadratic cross section) basket width (quadratic cross section):

bulk density of zinc pieces

Do the Calculation Reset Data

ator tank	
1200	mm
0	mm
62.5	mm
5	kg/l

12000 A

70

75

%

%

SurTec[®] 704, 712 und 715 Size of Zinc Generators width Catalytically Plated Baskets for Cyanidefree Alkaline Zincand Zinc Alloy Processes



Input Data

total current:	12000	A
current efficiency:	70	%
load of the plating line and the rectifiers:	75	%
depth of the generator tank:	1200	mm
length of one side:	0	mm
width of the baskets:	62.5	mm
bulk density of the zinc pieces:	5.00	kg/l

Calculation Results

zinc consumption of the plating line:	7.7	kg/h
length of the zinc baskets:	1000	mm
surface area of one basket (inner + outer):	50.8	dm ²
necessary total catalytical surface area:	4200	dm ²
number of catalytical baskets:	83	piece
dimensions of the generator (w x I x h):	925 x 925 x 1200	in mm
stored zinc metal in the generator:	1621	kg
volume of the electrolyte in the generator:	714	Ι

• The performance properties and the influences for a zinc electrolyte are:

Properties	Relations	Influences		
throwing power		carrier (SurTec 704 I)	С	
brightness		brightener (SurTec 704 II)	С	
distribution of brightness		zinc concentration	С	
ductility		NaOH or KOH content	С	
adherence/blistering		carbonate concentration	I	
deposition rate		foreign metals (iron, lead)	I	
current efficiency		current density	Ρ	
chromatability		temperature	Ρ	
		agitation	Ρ	
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C = Chemical parameter

P = Physical Parameter

I = Interference



- Physical process parameters like current density, temperature, agitation and time can be held constant easily by relatively simple standard equipment.
- Interfering foreign metals can be avoided by using really inert anodes (no steel anodes!) in combination with an external zinc generator. Lead begins to interfere above 1 mg/l. It comes into the electrolyte because zinc metal is always contaminated with lead. It must be precipitated with suitable sulfur compounds like SurTec 701.
- Sodium carbonate interferes only above 70-80 g/l. Almost no conventional non cyanide alkaline installation has ever reached this value. Though it might be possible with heavy rinse water recycling. However, sodium carbonate can be "frozen out".
 Potassium carbonate does not interfere up to 180 g/l.



- Sodium or potassium hydroxide could be titrated automatically. Hydroxide is consumed by drag-out and generation of carbonate. Continuous dosage is necessary for maintaining the electrolyte conductivity.
- ▼ The concentration of **zinc** could be determined automatically by complexometric titration. Zinc is consumed by drag-out and of course mainly for the desired zinc deposition. It is replenished preferably by a zinc generator.
- ▼ The additives carrier and brightener are adjusted with respect to their effect on the zinc deposition (e. g. with the aid of Hull cell tests). But, Hull cell tests are hardly automisable.
- ▼ With exception of the organic additives, all process parameters can be automatically controlled by conventional technics and equipment.
- For automatic adjustment of the organic additives new different methods must be found.

Electrochemical Process Control: Electronic Hull cell panel



Current voltage curves, 20 mV/s, rotating Au disk electrode, 0.196 cm², 1600 rpm, non cyanide alkaline zinc electrolyte (10 g/l Zn, 120 g/l NaOH)

- Current voltage curves are a **direct** measure for the deposition conditions in an electrolyte and only a **indirect** measure for the concentrations of its ingredients.
- ▼ The deposition conditions are the target measure, not the concentrations.
- Therefore, an automatic control of electrolytes on the basis of current voltage curves seems to be possible.
- ▼ The idea behind this is to measure current voltage curves which characterise the actual electrolyte conditions and to compare them with a desired current voltage curve.
- ▼ By the way of test injections of the additives into the measuring cell, it is possible to approach stepwise iteratively the desired conditions.



Automation: Test Injections into a Measuring Cell





- ▼ The electrolyte conductivity is mainly determined by sodium or potassium hydroxide.
- ▼ The electrolyte conductivity is the aim for the bath control, not the concentrations.



• The device doses conc. caustic soda or potash solution for maintaining the electrolyte conductivity.



- Current voltage curves are a **direct** measure for the deposition conditions in an electrolyte and only an **indirect** measure of the concentrations of the individual bath components. Important are the deposition conditions and not the concentrations.
- ➡ SurTec[®] 704 ZincOperator
- controls the status of the electrolyte in total, not only individual factors
- doses all organic additives
- controls the zinc generator and the alkalinity
- documents

The SurTec 4x Concept for the non cyanide alkaline zinc plating comprises:

- the **optimal additive system SurTec**[®] **704** for best throwing power with lowest affinity to blistering and to the respective task adapted composition
- really inert anodes with additional SurTec Catalyst coating
- small and highly effective zinc generators because of the SurTec[®] Hydrogen
 Catalyst
- **2 ZinkOperator** automatic electrochemical process control

