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SLOTOLOY ZN „Generation VX"

SLOTOLOY ZN 80 VX - SLOTOLOY ZN 210 VX

A new technology for alkaline zinc-nickel electrolytes of the future.

The formation of cyanide and organic breakdown products in alkaline Zn-Ni electrolytes is a well-known problem. With the new processes SLOTOLOY ZN "Generation VX", a patent has been applied for by Schlötter, these undesired effects will be reduced to a minimum or even don't appear any more. The efficiency of the electrolyte will remain constantly. This effect is achieved by the use of a new additive system in conjunction with an innovative anode.

1 Motivation

When operating an alkaline zinc-nickel electrolyte with insoluble anodes there's an unavoidable decomposition of organic additives due to the anodic partial reaction. Here, the organic additives can incrementally oxidize until cyanide is formed. The rising demand of organic additives as a result is disadvantageous. There's additionally the danger of a decreasing current efficiency caused by the enrichment of breakdown products which in total negatively influences the economic efficiency of the process.
By the formation of cyanide a part of nickel in the electrolyte is transferred in an extremely stable Tetracyanonickelate complex. The complexed nickel is then not available for the plating and deposition on the cathode. Therefore an increased demand for expensive nickel is required. Furthermore, the effluent treatment of cyanide charged rinse water is significantly more complex (image 1).

In the field of electroplating, different approaches have already been developed in order to reduce the decomposition of organic additives in alkaline zinc-nickel processes. This includes the application of the relative elaborately membrane technology. With this technology the anode compartment is separated by a membrane from the cathode compartment. Normally, the anolyte is a sodium hydroxide- or a sulphuric acid solution. This is associated with high investment costs and due to lack of space conversion of older plant installations to this technology isn't possible. Additionally the effectivity of rack installations is restricted since rack installations are often operated with internal anodes which cannot be protected by a membrane.
Another technology presents the subsequent removal of the Tetracyanonickelate complex formed by a selective special ion exchanger resin. The current costs are extremely high since the resin is expensive and a simple possibility of a resin regeneration isn't possible. This process cannot prevent new formation of cyanide in the electrolyte but can only remove already formed cyanide.

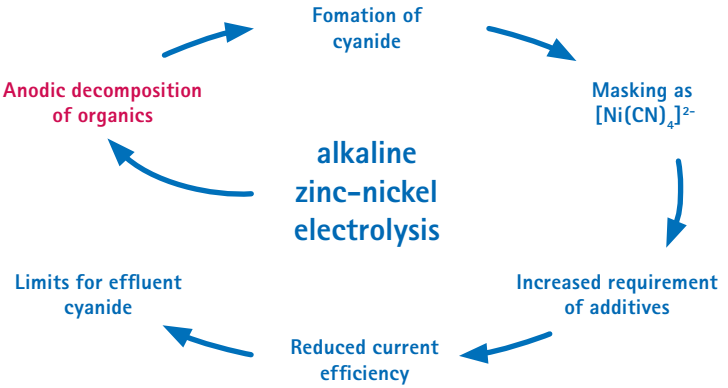


Image 1: Schematic cycle of the cyanide development

2 New development SLOTOLOY ZN VX process

Therefore, the R&D team of Dr.-Ing. Max Schlötter GmbH & Co. KG chose a different way and put the focus on the anode itself. Is it possible to inhibit the formation of cyanide by the choice of the anode material? The developers tested several materials and finally achieved with a new anode, distributed under the name Special Anode VX 1, providing very promising results so that in February 2017 a patent was applied for. The alkaline zinc-nickel electrolytes traded under the name SLOTOLOY ZN 80 VX (rack process) and SLOTOLOY ZN 210 VX (barrel process) are offered with special anodes (Special Anode VX 1) and an optimized matched organic additive system.
With this concept the significantly lower decomposition of single organic additives could be verified. So, the formation of cyanide in the electrolyte was decreased to an extremely low level.

3 Advantages by an innovative troubleshooting

The resulting advantages have been practically demonstrated for over one year providing:

- lower formation of cyanide
- reduced organic requirement/saving of chemical costs
- reduced nickel requirement/saving of chemical costs
- consistent high current efficiency and process stability
- constant high deposition rate and productivity
- simplified effluent treatment and better
- environmental compatibility

Comparative endurance tests in the Schlötter technology center showed after an electrolyte load of 1000 Ah/l different electrolyte colours. While the innovative SLOTOLOY ZN 210 VX electrolyte showed only a slight change of the colour, the conventional operated SLOTOLOY ZN 210 electrolyte showed already a clear brownish discolouration. This shows visually that in the new SLOTOLOY ZN VX processes produce less organic breakdown products (image 2).
Tests showed that with the new barrel plating process SLOTOLOY ZN 210 VX, during a load up to 1000 Ah/l, a consistently higher current efficiency was achieved.

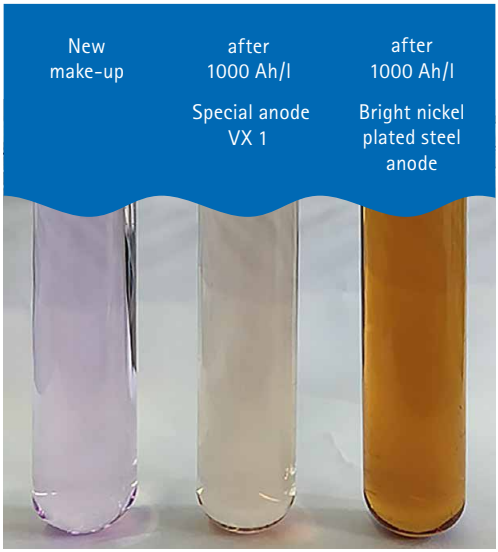


Image 2: For better visibility, electrolyte samples are diluted 1: 10 aqueous.

The effective deposition rate can be raised at 1 A/dm² cathodic current density by app. 10 %. This confirms the productivity of the new process (image 3).

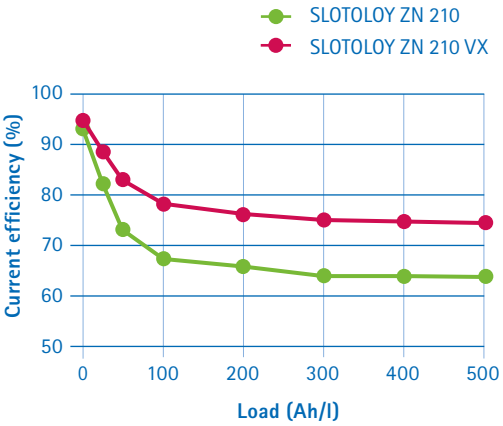


Image 3: Comparative current efficiency at ik = 1 A/dm² (8 g/l Zn, 1 g/l Ni, 110 g/l NaOH)

In comparative endurance tests carried out in the Schlötter technology center with rack electrolyte SLOTOLOY ZN 80 VX a significantly brighter deposition could be acheived in the medium to higher current density areas. This is due to the reduced quantity of cyanide and the lower organic consumption after an electrolyte load of 100 Ah/l (image 4 and 5).

The tolerance/reduction of burning on components with a complex geometry is significantly enhanced with the newly developed rack electrolyte throughout the solutions life.

Image 4: Comparative lab panel series after an electrolyte load of 100 Ah/l.

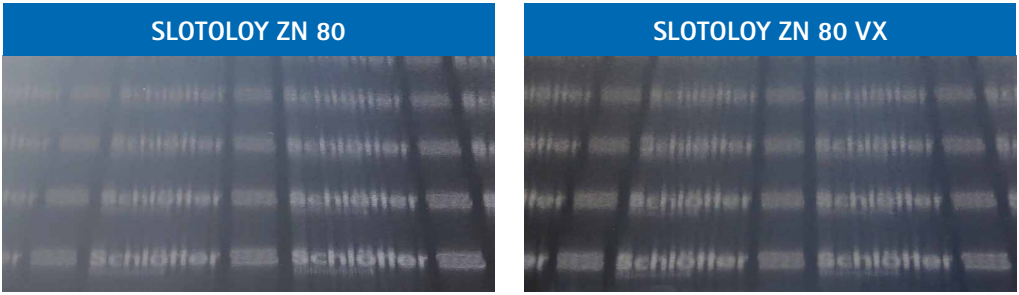


Image 5: Comparative Hull cell panels after an electrolyte load of 100 Ah/l.
Electrolyte load, significantly brighter deposition when SLOTOLOY ZN 80 VX is used.

4 Positive practical experience

First practical experience at customers confirmed and exceeded the results gathered in the Schlötter technology center. The results of the electrolyte analysis together with the practical deposition tests comparing an aged electrolyte with a load of up to 400 Ah/l with a newly made SLOTOLOY ZN 210 VX customers electrolyte are listed in the table below (image 6). The ampere hour dosing of the SLOTOLOY ZN VX electrolytes requires only three additives. Due to the lower aging of the electrolyte, the consumption quantities of the additives are very constant and help to operate the process economically.

The current efficiency is maintained constant in this process. This leads in the long run to stable and reliable deposition rates which in turn result in a very economical operation. Since nickel remains available for deposition and not bounded in the Tetracyanonickelate complex, a constant nickel co-deposition rate in the layer with significantly less nickel can be realized (image 7).

Load (Ah/l)	0	50	200	400
Zinc (g/l)	7,5	7,3	7,0	7,5
Nickel (g/l)	1,0	0,9	0,8	1,0
NaOH (g/l)	118	107	110	106
Cyanide (mg/l)	0	30	35	30
Complexer 1 (ml/l)	100	105	109	115
Complexer 2 (ml/l)	30	28	32	30
Brightener (ml/l)	0,2	0,2	0,3	0,2

Image 6: Constant analysis values for the electrolyte in practice SLOTOLOY ZN 210 VX

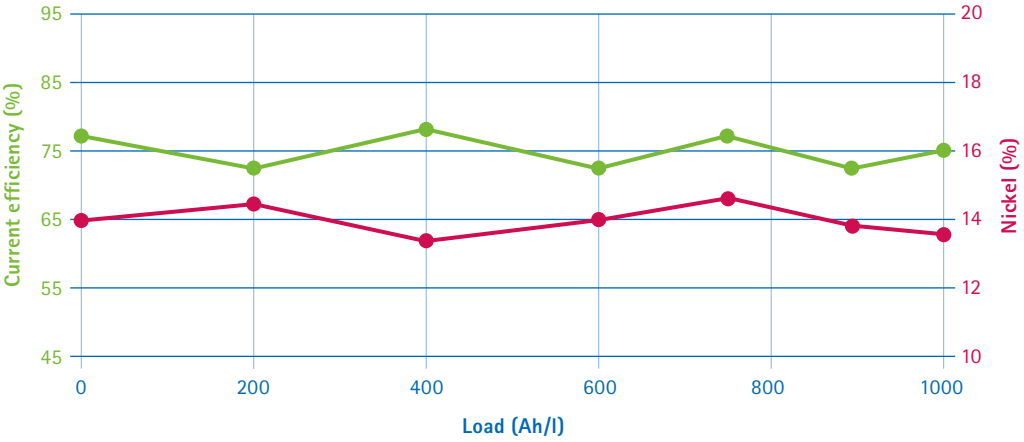


Image 7: Constantly high process safety with SLOTOLOY ZN 210 VX.

5 Easy conversion of existing Schlötter processes

A conversion of SLOTOLOY ZN 80 or SLOTOLOY ZN 210 electrolytes already in use to the new processes is possible and repeated resulted have already shown a positive effect. During operation, the cyanide content was reduced with the Special Anodes VX 1 and the optimized additive system. As a result, the nickel content in the electrolyte could be decreased (image 8) and the costs of expensive nickel caused by drag-out losses were avoided. Also the productivity of the processes has been improved significantly by the conversion of the electrolytes in practice to the new technology.

6 Summary

Finally, all the basic innovative characteristics and the resulting advantages which guarantee a high productivity and constant plating quality are summarized in the table below (image 9). With the rack electrolyte SLOTOLOY ZN 80 VX and the barrel electrolyte SLOTOLOY ZN 210 VX two well-thought-out economic alkaline zinc-nickel electrolytes of the future are available for the job platers. The application of an elaborate membrane technology for zinc-nickel processes compared with the new processes of the SLOTOLOY Zn "generation" VX results in no advantage, on the contrary the membrane technologies are economically more cost intensive.

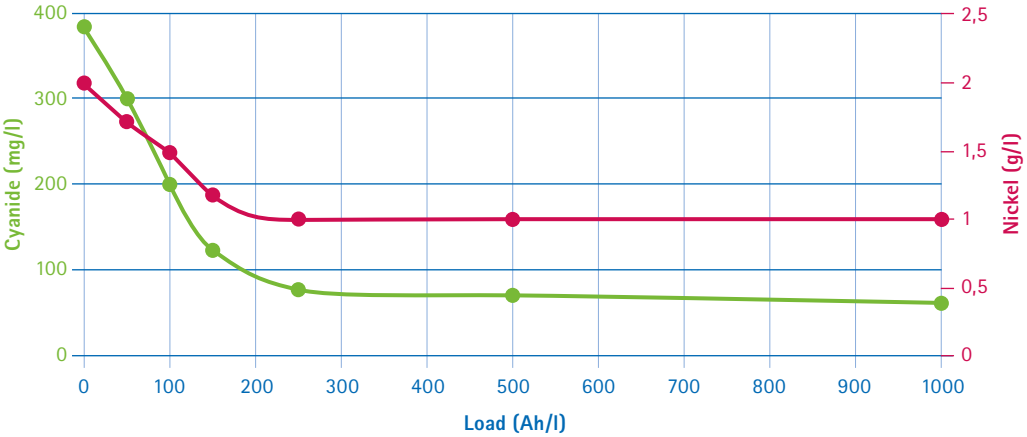
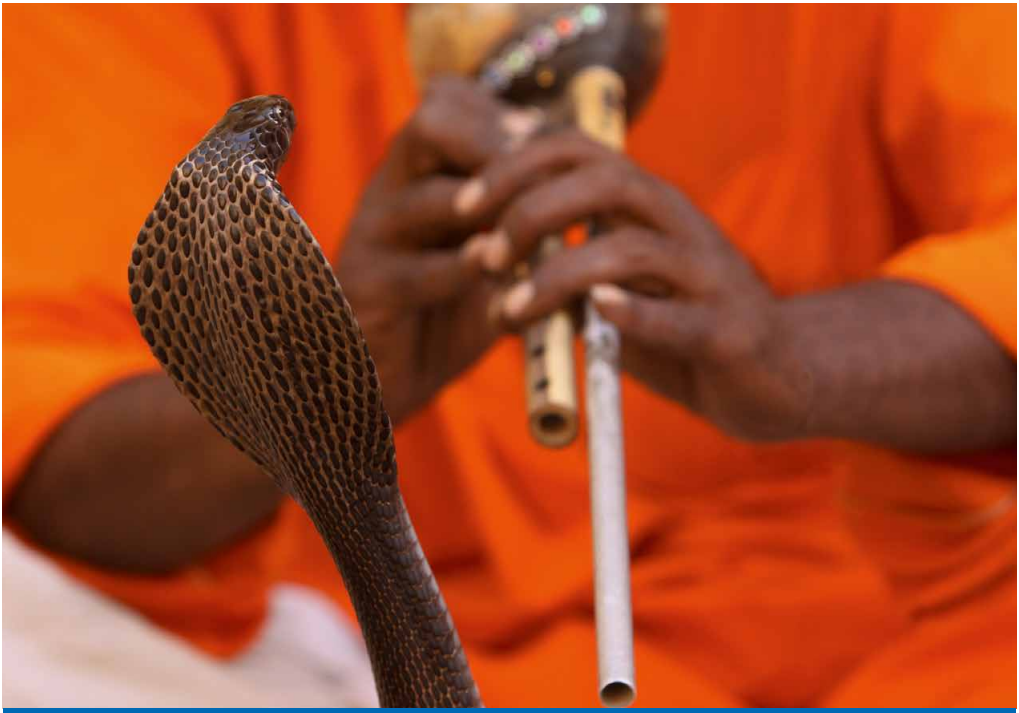


Image 8: Analysis progression of cyanide and nickel after conversion of the electrolyte in practice SLOTOLOY ZN 210 VX.

Our competent international service team will be happy to provide you detailed information and answers on your questions at any time.

Innovative charcteristics	state-of-the-art	SLOTOLOY ZN VX
Costs for chemicals · decomposition org. additives · nickel requirement	★★	★★★ less decomposition of organics; lower nickel concentration in the electrolyte
Current efficiency	★	★★ rack electrolyte: app. 5 – 7 % higher barrel electrolyte: 5 - 10% higher
Deposition rate	★★	★★★ app. 5 - 20 % higher (due to a higher current efficiency and a lower ageing of the electrolyte)
Costs for drag-out losses	★	★★ reduced, since less nickel necessary
Investment costs at conversion	○	★★★ no additional costs
Formation of cyanide	★	★★★ clear inhibition of the cyanide formation

Image 9: Summary, innovative characteristics



Always under control.

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