

Zinc Nickel (*Zn Ni 12 – 15%*) Alloy Process: Features for High Performance and Economic Process Control

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The use of zinc nickel alloy finishes with 12-15% Nickel electroplated from alkaline electrolytes has gained importance in several industry areas. Driven by the European ELV legislation, attractive hexavalent chrome free black and silver finishes have been developed which meet the most demanding requirements of the automotive specifications in terms of corrosion prevention, friction properties de-embrittlement features and temperature resistance.

As particularly, the automotive industry is substituting various finishes with high alloy zinc nickel thus the electroplating industry has been challenged to ensure consistency and improved economics of the process.

This article presents recent developments in process control and maintenance to help maintain quality with respect to nickel content, deposit thickness and plating efficiency in highly automated processes.

Electrolyte and rinse water regeneration technologies combined with adapted zinc nickel electrolytes help maintain the plating efficiency above 60% by removing organic and inorganic impurities. These adapted alkaline zinc nickel electrolytes often allow, in combination with optimized pre treatment processes, direct plating on hardened steels.

Further developments in X-ray fluorescence (XRF) methods enable the analysis of zinc and nickel in plating solutions. Consequently, zinc and nickel can be on-line monitored and controlled. By on-line control of temperature, current density, zinc and nickel concentration the process can be operated more consistently.

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Introduction:

High alloy zinc nickel finishes containing 12 – 15% nickel plated from alkaline electrolytes meet the highest performance requirements of the automotive and non automotive industries. Driven by the European ELV legislation, attractive hexavalent chrome free black and silver finishes have been developed, which meet the most demanding requirements of the automotive specifications in terms of corrosion prevention (Table 1), prevention of galvanic corrosion, friction control, temperature resistance and de-embrittlement requirements.

The most commonly specified zinc nickel finishes are composed of a high alloy zinc nickel (6-10 µm) layer protected by trivalent chrome based silver or black passivate and sealer layers. For application on fasteners, sealers often contain integrated lubricants for torque clamping force control, which can be varied to meet the individual OEM's friction control specifications.

Table 1: Corrosion protection results according to test standards.

	ASTM B117 [hr]		GMW 14872 [cycles]		VCS 1027,149 [cycles]	
	FWC	FRC	FWC	FRC	FWC	FRC
ZnNi + blue passivate	> 120	> 720	-	-	-	-
ZnNi + blue passivate + sealer	> 200	> 1008	> 20	> 80	> 2	> 9
ZnNi + black passivate + sealer	> 200	> 1008	> 20	> 80	2	> 9

The growing trend of the European automotive industry, especially French^{1,2} and German³⁻⁵ OEM's, to change to zinc nickel finishes is reflected in a number of specifications for interior and exterior applications. Very often zinc nickel finishes are used where alternative high performance finishes such as dip spin coatings cause problems with recess fill, friction control or post deformation corrosion performance. Parts which had been originally finished by dip spin coatings are assigned to zinc nickel, solving corrosion issues caused by handling damage as well as head and thread fill issues.

Recently, a black zinc nickel based finish has been approved by the US automotive industry as a cost attractive competitive finish to zinc nickel/cataphoretic painting⁶.

Besides meeting performance requirements, cost competitiveness is a key element for a coating to achieve the status of a main stream finish. The European

electroplating industry addressed the increasing demand for zinc nickel finishes by investments in additional production capacity. The implementation of efficient and automatic plating processes improves productivity, whereas cost savings have been achieved by electrolyte regeneration concurrent with waste reduction. High prices for nickel and zinc metals in 2007 reinforced the importance of economic process control (Fig. 1).

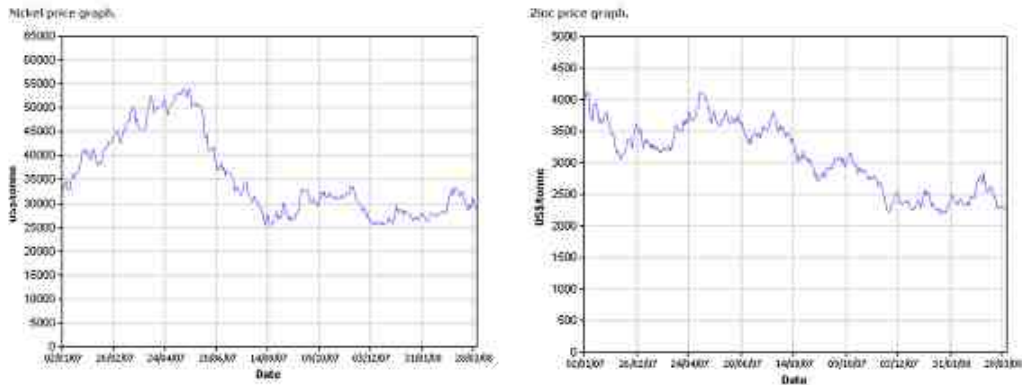


Fig. 1: Nickel and Zinc metal price graphs⁷.

Productivity

Ideally, productivity maximization starts with the conceptual design of a new plating line, preventing bottle necks in the process flow during production. In the past, the efficiency and plating rates of alkaline zinc nickel process limited the output of the plating lines. Meanwhile, the plating efficiency of alkaline zinc nickel processes has been increased from 35 – 45% to 55 - 65% by improved process chemistry. Process control and application technology resulting in higher plating rates and shorter plating cycle times have also been achieved by

- Optimized process additives
- Improve process control
 - Controlled additions of additives
 - Control of the zinc, nickel and hydroxide concentrations
 - Control of inorganic and organic contamination
- Adoption of the hardware, e.g. barrel design and danglers

Process control:

Alkaline zinc nickel processes are composed of a complex chemistry package to enable consistent plating performance. The process solutions contain strong

complexants to keep the nickel in solution and several additives to control the deposit characteristics like appearance, throwing power, thickness distribution and alloy content. Older types of zinc nickel processes operated with 5 – 9 additives to control the performance of the zinc nickel electrolytes, whereas newer processes can be operated using only 3-5 additives for continuous maintenance. Overdosing some additives can lead to reduced plating rates and therefore tight control of the addition rates is mandatory to achieve high efficiency. By adjusting the composition of additives, the optimum working window of the process has been increased resulting in more consistent plating rates.

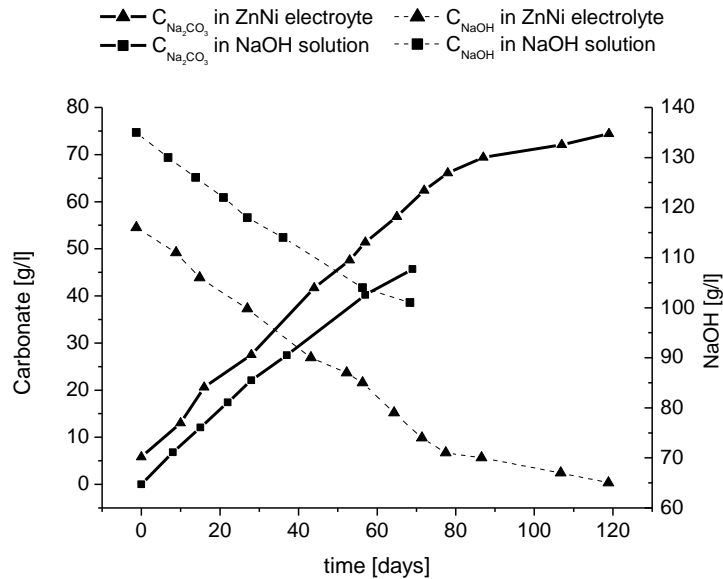


Fig 2: Carbonate Build up in alkaline zinc nickel Electrolyte and NaOH solution as well as Related NaOH decrease by Carbon dioxide dissolution in alkaline media.

Besides the organic degradation products, inorganic contaminants like carbonate affect the efficiency of zinc nickel plating processes. Carbonate accumulation in alkaline electrolytes is caused by dissolution of carbon dioxide from the air and by oxidation of organic additives at the anodes. The rate of carbonate build up is also affected by the agitation of the electrolyte. About 80% of zinc nickel plating installations in Europe are equipped with de-carbonation units, which remove carbonate continuously by “freezing out” sodium carbonate. De-carbonation units are commercially available and maintain the sodium carbonate levels in the range between 45 - 65 g/l. At these levels the carbonate does not significantly affect the plating performance of the alkaline zinc nickel processes.

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Electrolyte Purification and Rinse Water Recycling

In 2002 a new technology was developed to maintain high productivity of zinc nickel electrolytes⁸. The technology removes organic and inorganic accumulation from electrolytes and additionally recycles the rinse water.

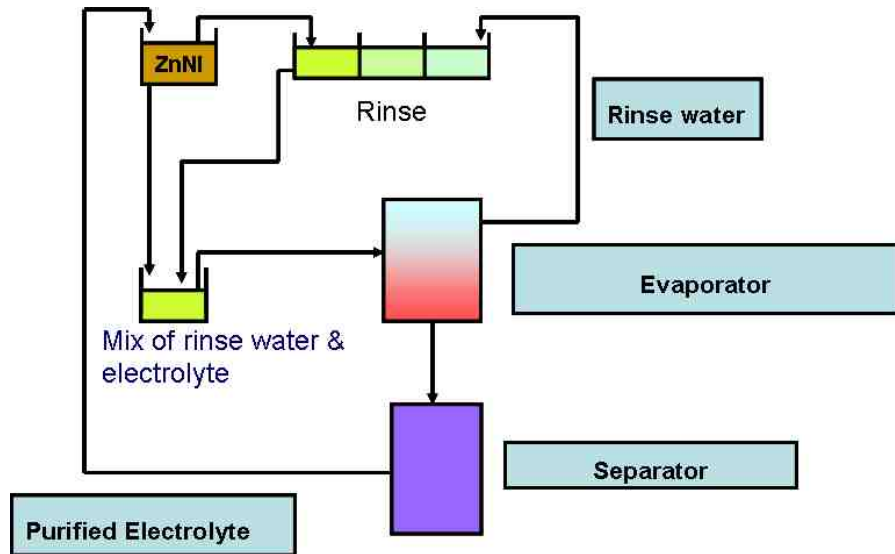


Fig. 3: Schema of the regeneration & purification technology

The principle (Fig 3 and 4) of the technology is evaporation of process solutions followed by separation into three phases. The rinse water from the counter flow rinse is collected in a tank and is mixed with zinc nickel electrolyte from the plating bath in a ratio between 2:1 and 3:1. This mixture is fed continuously to a vacuum evaporator and is concentrated by 1.3 – 1.5 times of the electrolyte concentration. The quality of evaporated water is sufficient to implement a close loop rinse water cycle (Table 2).

Table 2: Characteristics of the recycled water after evaporation.

pH range	9.6 – 10.6
Conductivity	0.18 – 0.20 mS/cm

The concentrate from the evaporator is pumped into the separator unit and is cooled to 15 – 18 °C. Within 18 to 20 h the concentrate separates into three phases as depicted in Fig 4.

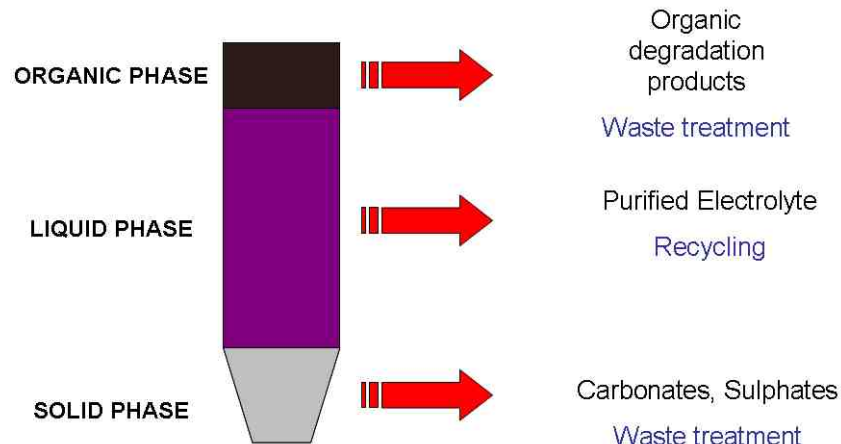


Fig 4: Schema of the separator and formed phases.

Organic Phase

The top phase contains organics, which are organic degradation products of the additives and excess of complexant. As the organic content is high, that phase is disposed by waste incineration.

Liquid Phase

The middle phase is concentrated zinc nickel electrolyte, which is purified from organic and inorganic contaminants. Zinc, nickel and hydroxide ions as well as organic additives like complexants are recycled to the process resulting in cost savings through regeneration.

Solid Phase

The bottom phase contains inorganic salts like sodium carbonate. These can be easily treated in standard waste treatment equipments or disposed by external waste disposal companies.

Table 3 lists the conditions of two barrel plating electrolytes, which operate in steady state condition for more than 18 months. The electrolyte **B** was continuously purified with the described technology whereas electrolyte **A** was not. The carbonate content of the electrolyte **A** is controlled by a de-carbonation unit mentioned above. Both electrolytes operate at similar zinc, nickel and hydroxide levels. Carbonate levels of the electrolytes are maintained below the critical limits.

The obvious difference in the condition of the two electrolytes are the COD levels (Chemical Oxygen Demand), which are related to the total organic content composed of organic additives and additive degradation products. The COD of the electrolyte **B** with purification unit is considerably lower than the COD of electrolyte **A** resulting in higher plating rates.

Table 3: Electrolyte conditions and plating rates.

	Electrolyte A	Electrolyte B
Zinc	9.5 – 10.5 g/l	8,5 – 9,5 g/l
Nickel	1,1 – 1,3 g/l	0,9 – 1,3 g/l
Sodium hydroxide	110 – 120 g/l	110 – 120 g/l
Sodium carbonate	65 – 75 g/l	60 – 65 g/l
COD	100 – 130 g/l	40 – 60 g/l
Current Efficiency	53 – 55 %	60 – 65 %
Deposition rate at 0.5 A/dm ²	0.09 – 0.12 µm/min	0.12 – 0.14 µm/min
Nickel content	13 – 14.5 %	12.5 – 13,5 %

The COD of electrolyte **B** is with 40 g/L about twice the COD of a new plating solution, whereas the COD of electrolyte **A** is about 5 times higher indicating higher concentrations of additive degradation products.

The accumulation of degradation products over time and the effect of electrolyte purification on the plating efficiency are depicted in Fig. 5.

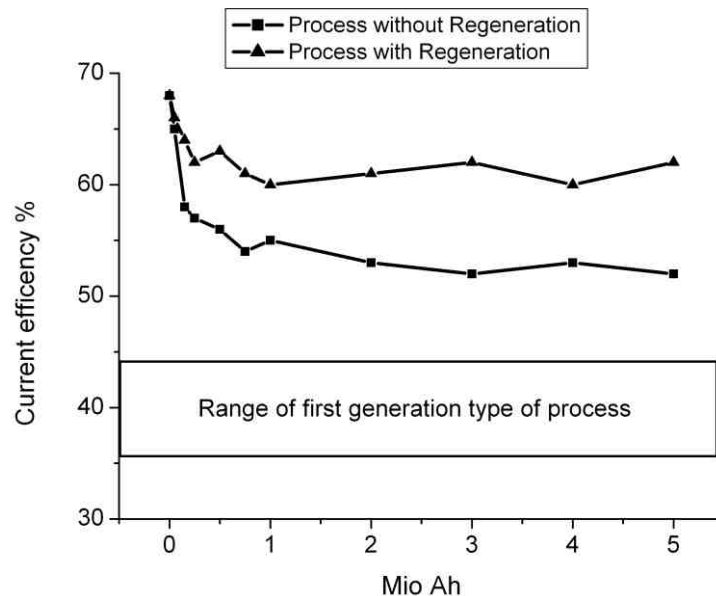


Fig 5: Effect of organic and inorganic contamination onto plating performance.

By continuous purification of the electrolyte the plating efficiency has been raised from 52 - 55% to above 60% and increased the productivity of the plating line. Furthermore cost savings have been achieved by waste reduction and lower metal consumption. The technology is installed at 4 applicators of zinc nickel finishes in Europe, the newest installation started early this year.

Control of zinc and nickel in alkaline zinc nickel processes

To ensure the high corrosion performance of zinc nickel deposits, control of nickel content in the deposits is mandatory. The nickel content and thickness of the deposits can be determined by XRF diffraction with low analytical efforts and costs. The investment in equipment is relative modest. Recent developments in XRF technology enables metal concentration analysis in process solutions (Table 4).

Table 4: Analytical results of conventional methods compared with XRF analytics. The XRF has been obtained by a mean of 10 measurements with a matrix calibrated method.

	Conventional method [g/l]	XRF [g/l]
Zinc Nickel Process		
Zinc	7.8 ±0.5 (titr.)	8.1±0.5
Nickel	0.98±0.1 (AAS)	1.05±0.1
Trivalent Passivate		
Chrome	4.8±0.5 (titr.)	5.1±0.5
Zinc	3.6±0.5 (titr.)	3.5±0.5
Iron	0.38±0.01 (UV-VIS)	0.4±0.05



Fig 6: XRF equipment and test cell for XRF analysis on liquids.

Several XRF equipment manufacturers are offering this equipment which analyse zinc and nickel online. These XRF machines take samples from the plating solution automatically and analyse the metal concentrations allowing automatic control of zinc and nickel in the plating solution in very narrow limits. These XRF machines can also be used to analyse other process solutions, e.g. chrome and metal contaminations in trivalent passivates (Tab. 4).

Summary:

Zinc nickel finishes are gaining market share in Europe as their performance meets the requirements of the end user. The electroplating industry responded early and developed and implemented technologies to meet OEM requirements in terms of productivity, quality and costs. The presented developments are only a selection of recent and ongoing projects that demonstrate the capabilities of the electroplating industry to successfully compete with other coating technologies. Several ongoing projects deal with further increases in productivity, ecological improvements and the prevention of hydrogen embrittlement.

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