Zinc-Nickel (Zn / 12-15% Ni) 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 industrial areas. Driven by European ELV legislation, attractive hexavalent chromium-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, hydrogen embrittlement susceptibility and temperature resistance. In particular, the automotive industry is substituting various finishes with high alloy zinc-nickel and the electroplating industry has been challenged to ensure consistency and improved economics of the process. This article discusses 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 modified zinc-nickel electrolytes help maintain the plating efficiency above 60% by removing organic and inorganic impurities. These alkaline zinc-nickel electrolytes often allow, in combination with optimized pretreatment 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 monitored and controlled on the plating line. By on-line control of temperature, current density, zinc and nickel concentration, the process can be operated more consistently.

Keywords: *Zinc-nickel plating, alkaline zinc-nickel plating, process control, ELV, hexavalent chromium replacements, electrolyte regeneration*

Introduction

High alloy zinc-nickel finishes, containing 12 to 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 chromium-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), wear, temperature and hydrogen embrittlement resistance.

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

The growing trend in the European automotive industry, especially French[1,2] and German[3-5] OEMs, 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 with dip spin coatings have been re-specified with 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 U.S. automotive industry as a cost attractive competitive finish to zinc-nickel/cataphoretic painting.[6]

Besides meeting performance requirements, cost competitiveness is a key element for a coating to achieve the status of a mainstream finish. The European electroplating industry has 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 have reinforced the importance of economic process control (Fig. 1).

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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

Notes: ASTM B117: Standard Practice for Operating Salt Spray (Fog) Apparatus
GMW 14872: GM Cyclic Corrosion Laboratory Test (Replaces GM9540P).
VCS 1027,149: Volvo Cyclic Corrosion Test
FWC: First white corrosion; **FRC:** First red corrosion.

Productivity

Ideally, productivity maximization starts with the conceptual design of a new plating line, preventing bottlenecks in the process flow during production. In the past, the efficiency and plating rates of alkaline zinc-nickel processes 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
- Improved process control
    - o Controlled additions of additives
    - o Control of the zinc, nickel and hydroxide concentrations
    - o Control of inorganic and organic contamination
- Adoption of improved 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 as well as several additives to control the deposit characteristics such as appearance, throwing power, thickness distribution and alloy content. Older types of zinc-nickel processes were operated with up to nine additives to control the performance of the zinc-nickel electrolytes, whereas newer processes can be operated using only three to five additives for continuous maintenance.

Overdosing some additives can lead to reduced plating rates. 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.

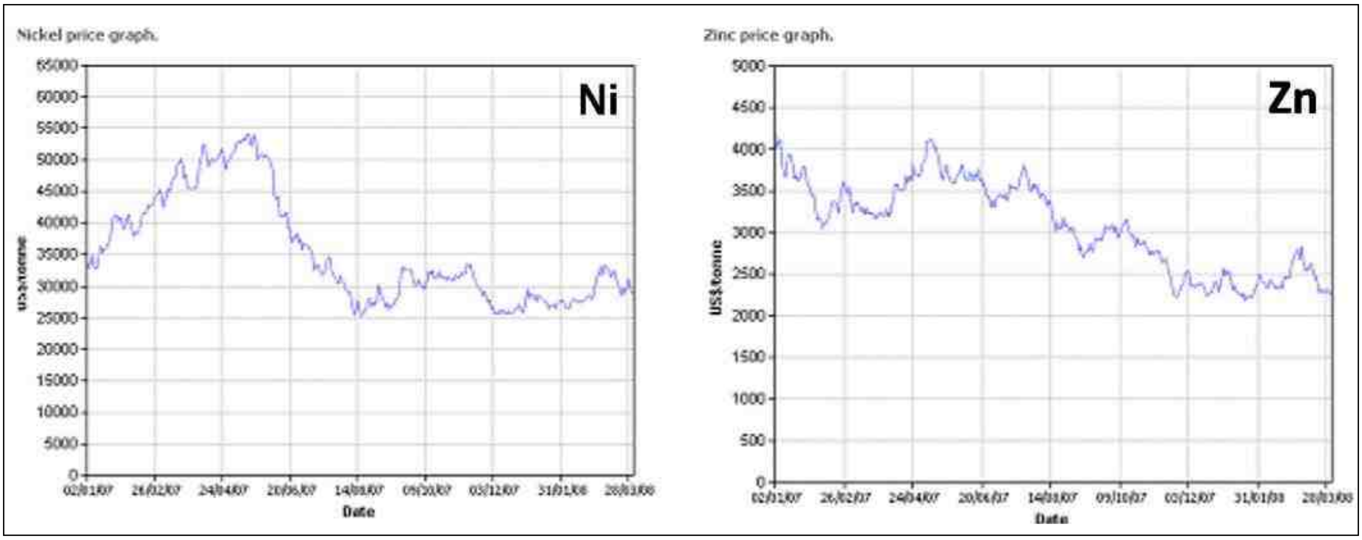

Figure 1—*Nickel and zinc metal price graphs.*[7]

Besides the organic degradation products, inorganic contaminants like carbonates 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 (Fig. 2). 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 process.

Electrolyte purification and rinse water recycling

In 2002, a new technology was developed to maintain the high productivity of zinc-nickel electrolytes.[8] The technology removes accumulated organic and inorganic breakdown products and contaminants from electrolytes and additionally recycles the rinse water.

The principle of the technology (Figs. 3 and 4) involves the evaporation of process solutions followed by separation into three phases. The rinse water from the counterflow 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 to 1.5 times the electrolyte concentration. The quality of evaporated water is sufficient to implement a closed-loop rinse water cycle (Table 2).

The concentrate from the evaporator is pumped into the separator unit and is cooled to 15 to 18°C (59 to 65°F). Within 18 to 20 hr, the concentrate separates into three phases, as depicted in Fig 4.

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 of 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 such as sodium carbonate. These can be easily treated in standard waste treatment equipment or disposed of 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. 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.

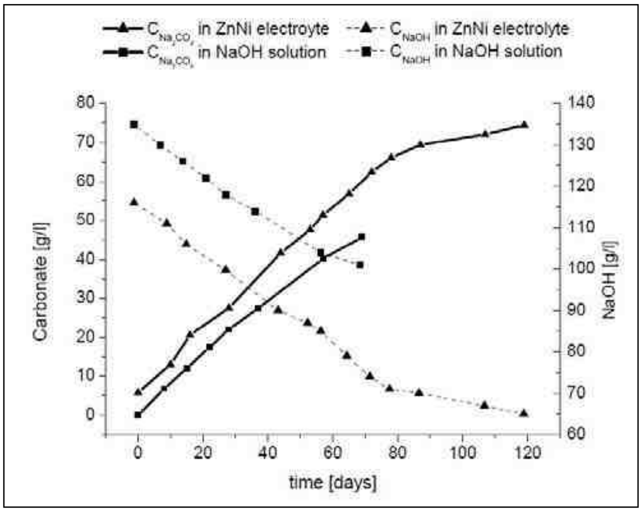

Figure 2—*Carbonate build-up in alkaline zinc-nickel electrolyte and NaOH solution and the related NaOH decrease by carbon dioxide dissolution in alkaline media.*

Table 2

Characteristics of the recycled water after evaporation

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

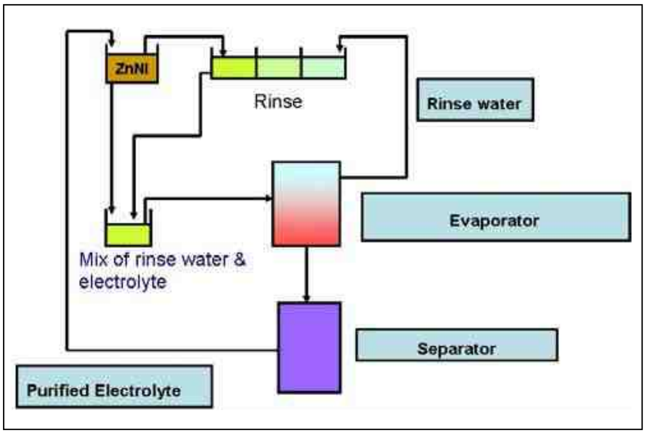

Figure 3—*Schematic diagram of the regeneration and purification technology.*

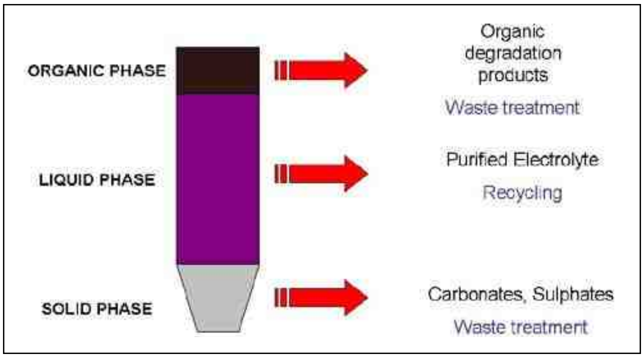

Figure 4 —*Schematic diagram of the separator and formed phases.*

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

The COD of Electrolyte ***B*** is at 40 g/L about twice the COD of a new plating solution, whereas the COD of Electrolyte ***A*** is about five 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.

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 were achieved by waste reduction and lower metal consumption. The technology has been installed at four applicators of zinc-nickel finishes in Europe. The newest installation was started early in 2008.

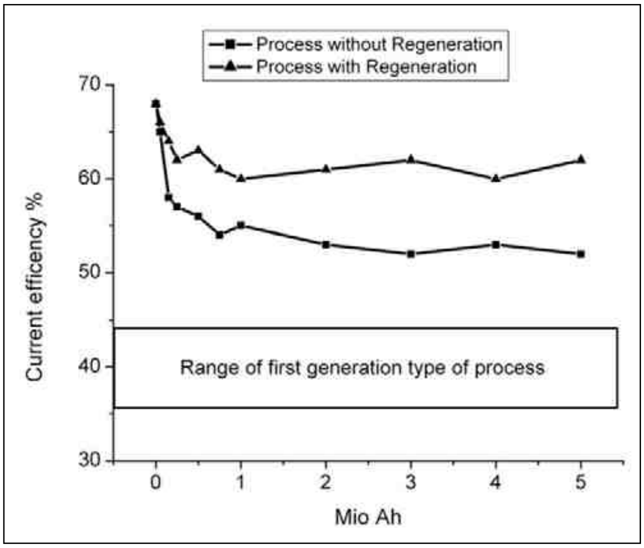

Figure 5—*Effect of organic and inorganic contamination on plating performance.*

Control of zinc and nickel in alkaline zinc nickel processes

To ensure the high corrosion performance of zinc-nickel deposits, close control of the nickel content in the deposits is mandatory. The nickel content and thickness of the deposits can be determined by x-ray diffraction and x-ray fluorescence (XRF) with low analytical effort and cost. The investment in equipment is relative modest. Recent developments in XRF technology now enable the measurement of metal concentration in the process solutions (Table 4).

Several XRF equipment manufacturers are offering spectrometers which analyze zinc and nickel on the plating line (Fig. 6). These XRF instruments take samples from the plating solution automatically and analyze the metal concentrations, allowing automatic control of zinc and nickel in the plating solution within very narrow limits. These units can also be used to analyze other process solutions, *e.g.*, chromium and metal contaminants in trivalent passivates (also shown in Table 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, developing and implementing technologies to meet OEM requirements in terms of productivity, quality and cost. The developments discussed here are only a selection of recent and ongoing projects that demonstrate the ability of the electroplating industry to compete successfully with other coating technologies. Several ongoing projects deal with further increases in productivity, ecological improvements and the prevention of hydrogen embrittlement.

[**] *Flat panels were plated at 1 A/dm^2 (9.29 A/ft^2) and the zinc/nickel deposit mass was determined by weight difference. The efficiency was calculated using Faraday's Law, coating weight and mean nickel content of the deposit.*

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 @ 0.5 A/dm^2	0.09 - 0.12 μm/min	0.12 - 0.14 μm/min
Nickel content	13.0 - 14.5%	12.5 - 13.5%

Table 4

Analytical results of conventional methods compared with XRF analysis. The XRF results were obtained by a mean of ten measurements using a matrix calibrated method

	Conventional method [g/L]	XRF [g/L]
Zinc-nickel process		
Zinc Nickel	7.8 ± 0.5 (titr.) 0.98 ± 0.1 (AAS)	8.1 ± 0.5 1.05 ± 0.1
Trivalent passivate		
Chromium Zinc Iron	4.8 ± 0.5 (titr.) 3.6 ± 0.5 (titr.) 0.38 ± 0.01 (UV-VIS)	5.1 ± 0.5 3.5 ± 0.5 0.4 ± 0.05

Figure 6—*XRF equipment and test cell for XRF analysis of liquids.*

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