# High Performance Alkaline Cyanide-free Zinc Plating Carbon-rich Deposit

Nabil Zaki, AESF Fellow, Sur-Tec International, Zwingenberg, Germany & Ray Lindemann, CST-SurTec, Middleburg Heights, OH

A new alkaline zinc plating process with unique properties has been developed. The process uses an additive designed to modify the deposit structure and its surface energy. These modifications resulted in a substantial increase in corrosion resistance approximating performance in zinc alloy plating. Another property attributed to the new zinc process is its ability to plate directly on cast iron, thereby improving plate distribution and overall corrosion resistance when compared with conventional acid zinc processes. The paper explains the process chemistry, deposit structure, and reviews its economic advantage as well as applications supported by case studies.

## For more information, contact:

Nabil Zaki, AESF Fellow SurTec International 9 Skyline Drive West Orange, NJ 07052 973-325-2427 nzakemail@aol.com

#### Introduction:

Since the early 1980's the evolution of alkaline cyanide free zinc plating processes took on a particular importance in an effort to rid the industry of toxic cyanide and meet increasingly tighter pollution prevention requirements. Presently, acid and alkaline zincate type plating processes account for the bulk of all zinc plating processes while cyanide based electrolytes are continually being phased out. Existing acid chloride based and alkaline cyanide free zincate types have advantages and limitations. A recently introduced process based on the alkaline zincate electrolyte, bridges advantages of both systems and adds new improved properties.

## Advantages and limitations of current processes:

Advantages of the acid chloride based electrolytes include a brighter deposit mostly suitable for decorative applications, high bath efficiency with fast plating rates, and ability to plate a wide range of steels and cast iron. Disadvantages of this system include a tendency to develop brittle deposits at a thickness higher than 6 – 8 microns. Due to its high efficiency, the acid type electrolyte typically produces uneven deposits that vary with current densities. This leads to underplate or even total lack of coverage in recessed areas and internal surfaces. Rust and corrosion products inside tubing and deep recessed areas are common problems associated with this process. Overplate and brittle deposits result at high current densities, such as at heads of fasteners and protrusions in general.

Advantages of the alkaline zincate bath include better deposit thickness distribution across parts configurations, and better throw inside deep recesses, blind holes and internal surfaces of tubing. This property, along with the alkaline nature of the electrolyte, results in improved corrosion protection of part as well as process equipment. The deposit is ductile, but plates at 30 - 40 % lower efficiency and at a lower rate than its acid counterpart. The system is inadequate for plating high carbon steels and cast iron due to low hydrogen overvoltage and deposition of hydrogen in preference to zinc at the cathode.

## A new alkaline cyanide free zinc process:

A new additive (brightener) system was developed to overcome many of the shortcomings of the alkaline zincate type process. The electrolyte, mode of operation

and process control are identical to those used in conventional alkaline zincate systems. The additive, based on a novel reaction product of modified cationic amines, creates a range of new properties and advantages:

## 1 – Modified crystal structure

The zinc layer deposited from the new system was found to contain from 0.8 – 1.0 % carbon by weight in the form of organic carbon. This is resulting from a controlled codeposition of the additive with the zinc. This co-deposition affects the zinc deposit crystal orientation. Fig (1-A) shows X-Ray diffractions of a conventional alkaline zincate system with a single peak, typical of oriented crystal deposits. Fig. (1-B) shows multiple peaks indicating an un-oriented crystal formation associated with the carbon-rich zinc system. This is similar to crystal orientation found in alkaline zinc alloys.



## **Conventional Alk. Zinc Crystal Orientation**

Fig (1-A)







When tightly packed oriented crystals are subjected to internal stress due to inclusions of organics, impurities, etc., crystals move in an upward direction to release stress, leading to dislocation from the bulk. Deposits with un-oriented crystals are generally more stable, with much reduced potential for delayed blistering.

## 2 – Improved corrosion resistance

Another property realized by the new deposit is its increased reactivity to passivating solutions, resulting in substantially increased corrosion resistance. Fig (2) shows the chromium content in the passivation layer of three types of electrolytes , acid, conventional alkaline zincate and carbon-rich zincate, as a function of time. Trivalent chrome solution was used for passivation. As can be seen, the passivation layer obtained on the carbon-rich zinc applied under the same conditions is much higher.



Fig (2)

Figures (3), (4) and (5) compare performance of new v.s. conventional systems in NSS

NSS – 500 hrs

Zinc Plated + Thick Layer Cr(3) Passivation



Fig (3) Acid Chloride Zinc

Fig (4) Alkaline NCN Zinc

Fig (5) C-Rich Alkaline NCN Zinc

## 3 – Direct plate on Cast Iron.

As mentioned earlier, some iron surfaces containing high levels of carbon and silicon are quite difficult to zinc plate out of alkaline electrolytes due to their low hydrogen overvoltage. Consequently, automotive parts made of cast iron, such as brake components and regulators are typically plated in acid chloride based zinc systems. Uneven plate distribution and corrosion in recessed areas are frequent problems associated with acid electrolytes on these components. When alkaline zinc alloys are specified, an acid type strike is used first as a base coating. This often leads to adhesion problems between the strike and the alkaline zinc layers.

The new carbon-rich zinc process, although based on the alkaline zincate electrolyte, overcomes the hydrogen overvoltage problem, and is capable of direct plating on a variety of cast iron surfaces. The deposit is more uniform and covers recessed areas while eliminating corrosion on bare surfaces. The same process can also be adapted for direct plating of zinc alloys on cast iron.

Fig (6) illustrates cast iron automotive components plated in the new carbon-rich zinc process and passivated with trivalent chrome. Close plate distribution is shown in Fig (7)





Fig (6)

## Fig (7)

C-Rich Zinc Alkaline Non-Cyanide Zinc •<u>Thickness distribution :</u> 1: 12.75 microns 2: 16.31 microns 3: 15.11 microns 4: 15.02 microns 5: 15.92 microns 6: 15.48 microns 7: 21.60 microns 8: 20.59 microns 9: 21.12 microns 10:16.85 microns 11: 20.03 microns 12:15.42 microns 13: 10.56 microns 14:16.36 microns Average Thickness : 16.58 Microns <u>Target Thickness :</u>

**15 Microns** 

Direct Plating on Cast Iron



The sum effect of on the corrosion resistance provided by the carbon-rich zinc process and thick layer trivalent chrome passivation on cast iron is illustrated in Fig (8). After 1000 hrs exposure to NSS testing, there was no red corrosion on the brake component.



**Fig** (8)

C-Rich Zinc Direct plate on cast iron + Cr(3) passivation Thick Layer - No Sealer -



## **Process Operating Parameters:**

The new process is based on conventional alkaline cyanide free zincate electrolyte, and simplified by the use of a single additive. An optional hard water conditioner is available as needed.

The basic bath composition is as follows:

| Zinc               | 10 – 15 g/l     |  |
|--------------------|-----------------|--|
| Sod.Hydroxide      | 100 – 150 g/l   |  |
| Or Pot. Hydroxide  | 150 – 210 g/l   |  |
| Additive           | 1.5 – 3 ml/l    |  |
| Temp               | 20 – 40 C       |  |
| Cathode CD         | 0.5 – 6 A/sq dm |  |
| Current Efficiency | 60 – 80 %       |  |

Effect of additive concentration on deposition rate and on carbon content in the deposit are shown in Fig (9) and (10) respectively. Fig (11) shows the effect of current density on carbon content. The system shows a fairly stable performance over a wide range of parameters. Optimum performance is obtained at 3 A/sq.dm and 2 - 2.5 ml/l additive. Carbon content under these conditions was 0.84 % by weight of deposit.



Fig (9)



| Fig | (1 | 0) |
|-----|----|----|
|-----|----|----|



Fig (11)

## **Typical Process Sequence:**

Adequate surface preparation is required as with all plating processes. This requirement is particularly critical when processing cast iron due to the high level of porosity of most cast components and inclusion of mold release and casting impurity. When parts of the cast component are machined, oil may be trapped in the pores and require proper degreasing. Typically, cast iron components are shot blast prior to further processing to reduce gross surface roughness and clean the surface to some extent. The cleanliness and the type of the shot blast media used in this step can have a profound effect on the plating quality, and must be carefully monitored.

Although there is no universal preplate cycle for cast iron, the following was found effective for the new plating process:

- 1 Alkaline degreasing (Optional)
- 2 Rinse
- 3 Anodic alkaline electrocleaning
- 4 Rinse
- 5 Acid activate
- 6 Rinse
- 7 Repeat steps 3 6
- 8 Caustic predip
- 9 Alkaline carbon-rich zinc plate
- 10 Rinse
- 11 Activate (As required)
- 12 Passivate
- 13- Rinse
- 14 Seal or Dry

#### Conclusion:

An alkaline cyanide free zinc process based on a new additive was developed resulting in a range of improved properties. The zinc deposit contains from 0.8 – 1.0% organic carbon and has a non-oriented crystal structure. Due to its higher surface reactivity, a heavier passivation film is obtained, resulting in increased corrosion resistance. The new process is capable of direct plating on cast iron such as automotive brake components, with improved coverage and better corrosion protection than with acid zinc plating processes.