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The Use of Alkaline Cyanide-Free Zinc Plating Under Paint and Powder Coatings

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The scope of this paper and presentation is to address the properties and benefits of the alkaline cyanide-free zinc deposit as a base coating for paint and powder coating applications. The deposition structure and process characteristics for alkaline cyanide-free zinc plating will be evaluated and compared to acid chloride zinc plating, zinc phosphating and iron phosphating. Salt spray testing and production costs for an alkaline cyanide-free zinc deposit will be compared to other commonly used base coatings.

INTRODUCTION

Zinc plating is utilized by many different industries for many different reasons. It is a very versatile deposit primarily used for its functional properties but with recent advancements in technology, it is beginning to replace more expensive finishes as a decorative coating. However, the functional properties are still what make zinc one of the most widely used finishes around the world. It is a soft, ductile deposit offering excellent corrosion-resistance. Zinc protects the substrate by sacrificing itself and thus corrodes before the base metal. The corrosion resistance of zinc is a function of the plating thickness. Additional corrosion resistance can be given to the zinc deposit by adding a chromate conversion coating. There are many different types of chromate conversion coatings offering different colors and different levels of corrosion resistance.

Three main types of zinc plating are being done today: cyanide zinc, acid chloride zinc, and alkaline cyanide-free zinc. With the never-ending environmental pressures that are being placed on industry, there is a worldwide push to move away from cyanide zinc and into alkaline cyanide-free zinc plating. Alkaline cyanide-free zinc deposits have very unique characteristics that lend themselves well as a base coating for paint and powder applications.

ALKALINE CYANIDE-FREE ZINC PLATING OVERVIEW

Work on the first alkaline cyanide-free zinc plating systems began in the early 1960s when waste treatment requirements became stringent. This was the beginning of the push to eliminate cyanide zinc plating. Many processes were introduced into the market but did not prove to be viable plating processes. In the last forty some years, technology has come a long way and alkaline cyanide-free zinc plating has become a very large part of the zinc plating market. There are still some problems with alkaline cyanide-free zinc plating, such as the inability to effectively plate heat-treated fasteners and high-carbon steels. Alkaline cyanide-free processes can plate these types of parts but additional steps in the pretreatment or cleaning stages of processing need to be taken.

The composition of an alkaline cyanide-free zinc plating bath is very simple. It consists simply of zinc ions and caustic soda.

Zinc Metal	0.75-3.5 oz/gal (5.6-26.25 g/l)
Caustic Soda	10.0-20.0 oz/gal (75-150 g/l)

*Proprietary brightening agents are also added to control the characteristics of the zinc deposit structure. The deposit structure will be discussed later in the paper.

Preparation of steel parts for alkaline cyanide-free zinc plating requires a simple three-stage cleaning cycle prior to entering the plating bath. The first stage is a hot caustic soda soak tank, followed by a caustic electrocleaner. The final pre-plate process is a hydrochlori or sulfuric pickle. It is important to note that any work entering the alkaline cyanide-free plating tank must be completely free of all oils. Parts that are not properly cleaned can cause blistering of the zinc plate. This, in turn, will adversely affect the paint and powder coatings. See Diagram 1 for the process cycle typically used for alkaline cyanide-free zinc plating.

DIAGRAM 1

HOT ALKALINE SOAK CLEANER 150°-185°F
ELECTROCLEANER 150°-185°F
RINSE #1
RINSE #2
RINSE #3
HYDROCHLORIC ACID PICKLE 20%-40% BY VOLUME
RINSE #1
RINSE #2
RINSE #3
ALKALINE CYANIDE-FREE ZINC PLATING TANK ZINC METAL 0.75-3.5 OPG CAUSTIC SODA 10-20 OPG
RINSE #1
RINSE #2
RINSE #3
CHROMATE
RINSE #1
RINSE#2
HOT WATER RINSE
DRY

NOTE: All rinses are counter-flowing from Rinse #3 to #2 to #1.

ALKALINE CYANIDE-FREE DEPOSIT CHARACTERISTICS

One of the greatest strengths of alkaline cyanide-free plating is the ability to plate in deep, low-current density recesses without overplating the outside, high-current density edges. This is very evident with acid chloride zinc since this process will deposit 0.8 to 1.0+ mil in the high current density area of a part to hit a 0.2 mil spec in the lows.

With alkaline cyanide-free zinc plating, a typical high current density thickness of 0.5 mil would easily deposit 0.2 to 0.3 mil in the lows. The superb plate distribution properties of alkaline cyanide-free zinc plating and the covering power (ability to plate into deep recesses) makes this plating process ideal for post paint and powder applications.

The crystalline structure of the alkaline cyanide-free zinc deposit allows for better chromate and paint adhesion.

COMPARISON OF ALKALINE CYANIDE-FREE ZINC AND ACID CHLORIDE ZINC

There are a multitude of differences between alkaline cyanide-free zinc and acid chloride zinc plating solutions.

The most noticeable difference is the chemical makeup costs for the two. An alkaline system is far less costly than acid-based systems. Acquisition and maintenance of equipment are also more economically favorable for an alkaline cyanide-free zinc system. This is due primarily to the fact that an acid chloride solution will readily attack steel tanks and superstructures unless they are lined with a resistant material. The copper bussing can also be susceptible to

an attack, which has the potential to cause conductivity issues. Alkaline cyanide-free zinc systems are relatively inert when in contact with tanks or other steel components.

When comparing these two systems we must also consider maintenance of the bath itself. Acid chloride solutions have a tendency to accumulate precipitates of ferrous iron, which must be continuously filtered from the plating bath. It is also possible to build up high levels of soluble ferric iron that must be treated with an oxidizing agent to facilitate its filtration. Alkaline cyanide-free zinc solutions do not encounter these problems with iron but the zinc metal content must be monitored continuously to prevent it from falling outside of the limited operational range.

The efficiencies of these two systems can be described as good for alkaline cyanide-free zinc and excellent for chloride zinc. The alkaline cyanide-free zinc solution has an efficiency range of 40%-90% depending greatly on the zinc metal content. The conductivity of the hydroxide electrolyte is considerably less than that of the highly conductive chloride electrolytes. This explains the high cathode efficiency in acid chloride zinc solutions that can range from 95%-98%. This high efficiency can lead to shorter plating times and, in turn, increased productivity.

Some other characteristics of these two systems can be seen in Table 1 on the next page.

TABLE 1

	Alkaline Zinc	Acid Zinc
Plate Distribution	Excellent	Poor
Overall Brightness	Good to Excellent	Excellent
Covering Power	Excellent	Poor
Ductility	Excellent	Poor to Good
Chromate Receptivity	Excellent	Good
Operating Cost	Excellent	Good
Barrel Plating (Speed)	Good	Excellent
Rack Plating	Excellent	Good to Poor
Waste Treatment	Excellent	Good
Maintenance of Equipment	Excellent	Good
Ability to Plate Stampings	Good	Excellent
Ability to Plate Fasteners	Good	Excellent
Ability to Plate Chassis	Excellent	Poor

DEPOSIT STRUCTURE OF ALKALINE CYANIDE-FREE ZINC VERSUS ACID CHLORIDE ZINC

There are two basic deposit structures formed during zinc electroplating, laminar and columnar. Both the laminar and columnar zinc deposits have different effects on the appearance, physical properties of the chromate such as color, thickness and adhesion, and on formation and adhesion of topcoats.

The alkaline cyanide-free zinc deposit is columnar in structure with a vertical orientation to the substrate containing a multitude of micro peaks and valleys. This columnar structure increases the overall surface area, lending significantly more area for the paint to collect and adhere. Since the grain refinement of this deposit is porous, it is an ideal finish for paint adhesion.

With acid chloride zinc plating, the deposit is laminar in structure with a horizontal orientation to the substrate. This provides a tightly, overlaid electrodeposit with smooth grain refinement. The acid chloride zinc deposit is described as being nickel-chrome like in appearance with extremely deep brightness and having a smooth and level surface. This deposit tends to produce a more true clear, blue chromate finish (less yellowing than alkaline cyanide free) due to chromate film thickness and formation. There is also a greater tendency for chromate rub-off and problems with paint adhesion than with the alkaline cyanide-free deposit.

Although acceptable for paint adhesion, this deposit lacks the porosity of alkaline cyanide-free zinc. As Figure 1 demonstrates, the deposit is much smoother and more level as compared to Figure 2.

FIGURE 1 (BRIGHT ACID CHLORIDE)

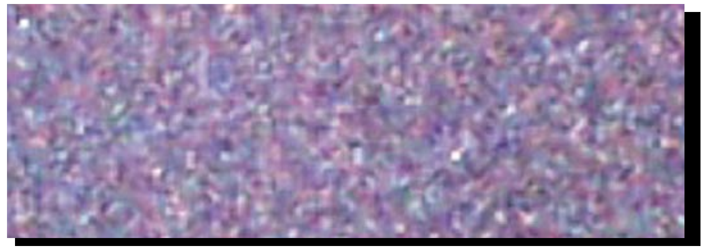

FIGURE 2 (BRIGHT ALKALINE CYANIDE-FREE)

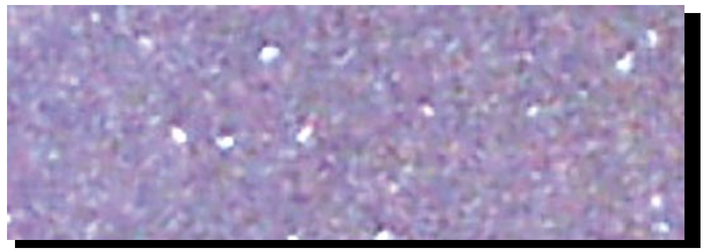

FIGURE 3 (SATIN ZINC)

The requirements for almost all zinc plating worldwide is for a bright deposit that is functionally capable of meeting or exceeding the corrosion requirements. This holds true for both alkaline cyanide-free zinc as well as for acid chloride zinc.

Although it is known throughout the metal finishing industry that alkaline cyanide-free zinc does not produce the luster of acid chloride zinc, it can achieve comparable brightness and crystalline grain refinement with the use of state-of-the-art brightener additives and optimum controls on bath chemistry.

Since an extremely bright deposit with good grain refinement is not desirable for paint and powder coating applications, the use of customized proprietary alkaline cyanide-free zinc plating additives can reduce brightness and provide a semi-bright, matte-satin finish. This satin finish further increases the porosity and surface area of the deposit, thus enhancing the bonding ability of the paint and powder coatings.

The alkaline cyanide-free "satin" finish offers all of the benefits of its bright counterpart, such as superb plate distribution, an inexpensive electrolyte, economical waste treatment, and excellent ductility, with the added benefit of improved paint adhesion. The comparison of "satin" zinc in Figure 3 clearly shows the desirable porosity of the deposit.

PERFORMANCE BENEFITS OF ZINC

Zinc phosphate, iron phosphate and manganese phosphate are commonly used pre-coatings for paint and powder. They provide an excellent porous base for enhanced adhesion and insulate the metal substrate from corrosion. Prior to painting, the corrosion resistance of phosphates (with and without chrome/non-chrome seals) is minimal and provides only 2 to 4 hours to red rust of the base metal. On the other hand, zinc (with and without chromate conversion coatings) extends the corrosion resistance to 150+ hours before paint and powder application.

A unique property of electrodeposited zinc is its ability to selectively corrode prior to oxidation of the steel, even when the steel substrate is directly exposed to the environment. Since zinc is known as a sacrificial metal, it forms a galvanic bridge across small scratches, fractures and voids of the zinc deposit, protecting the steel until the galvanic bridge is broken.

The extended corrosion protection of the zinc deposit and the sacrificial properties of this metal are extremely important if there are flaws or imperfections in the paint coating. Whereas phosphates will fail quickly, the zinc deposit will offer significant corrosion resistance. The corrosion resistance comparison for zinc and phosphates can be found in Table 2 below.

TABLE 2

Salt Spray Corrosion Resistance of Zinc with Chromate Conversion Coatings

Chromate Conversion Coatings	Salt Spray Results*
Trivalent Blue Chromate	10 to 18 hours to first white rust
High Performance Trivalent Blue Chromate	120 hours to first white rust
Hexavalent Blue Chromate	24 hours to first white rust
Hexavalent Yellow Chromate	96 to 175 hours to first white rust
Sealed Zinc or Iron Phosphate	2 to 4 hours to first red rust

*Salt spray testing was performed using the ASTM B-117 Standards. First white rust is defined as the first sign of zinc corrosion. First red rust is defined as complete corrosion of the zinc layer and first sign of base steel corrosion.

Zinc plated steel, especially "satin" zinc is an excellent secondary base for chromate conversion coatings where the steel is plated with "satin" zinc, the zinc is chromated and the chromate film is then painted. Like "satin" zinc alone, blue and yellow chromate conversion coatings form an extremely good base for paint and powder receptivity. The added corrosion protection and good adhesion property makes chromated satin zinc a perfect undercoating for paint applications.

PLATING COSTS ASSOCIATED WITH ALKALINE CYANIDE-FREE ZINC VS. OTHER ZINC PLATING PROCESSES

Compared to other types of metal finishing, zinc is one of the least expensive finishes that can be plated. Zinc electroplating makes up a large part of the electroplating industry, not only because of its deposit characteristics but also because of its cost compared to other types of electroplated deposits. The cost of zinc metal is very low compared to other metals such as nickel, copper, silver, gold and tin. This low cost and exceptional corrosion resistance properties make zinc electrodeposits a very attractive finish. When considering the cost and corrosion resistant properties of zinc, there is not a better option.

Of the three types of zinc plating, alkaline cyanide-free is the least inexpensive, and the electrolyte is very simple to make up and operate.

Typical Alkaline Cyanide-Free Zinc Make-Up Cost:

Zinc Metal	
Caustic Soda	Approx cost of electrolyte = $0.35-$0.50/gallon
Proprietary additives	Approx cost of additives= $0.35-$0.50/gallon
	Total Cost = $0.70-$1.00/gallon

Typical Acid Chloride Zinc Make-Up Cost:

Zinc Chloride	
Potassium Chloride	
Ammonium Chloride or Boric Acid	Approx cost of electrolyte = $0.60-$1.00/gallon
Proprietary Additives	Approx cost of additives= $0.40-$0.60/gallon
	Total Cost = $1.00-1.60/gallon

Typical Cyanide Zinc Make-Up Cost:

Zinc Cyanide
Sodium Cyanide
Caustic Soda

*With the heavy worldwide push to eliminate cyanide zinc and the associated high cost of wastewater disposal, this paper will exclude the cost associated with cyanide zinc plating.

Along with the make up cost being lower for alkaline cyanide-free zinc plating, the day-to-day operation costs are also lower. The zinc metal concentration is typically half that of acid chloride zinc plating reducing drag out and replenishment costs. Proprietary maintenance additions are also typically lower for alkaline cyanide-free zinc plating per amp/hour than for acid chloride zinc. Overall, acid chloride zinc is more expensive to make up and operate than alkaline cyanide-free zinc.

CONCLUSION

The low cost and exceptional corrosion resistance properties of zinc make zinc electrodeposits a very attractive finish for paint and powder coating. Of the three types of zinc plating available, the alkaline cyanide-free zinc deposit — especially the satin finish — provides an ideal base for these applications. Not only is it the most economical, but the columnar structure and porous grain refinement of this deposit provides optimum surface conditions for enhanced adhesion of the paint and powder. The superb plate distribution properties of alkaline cyanide-free zinc allows it to plate deep into low-current density recesses without overplating the outside. In addition, the electrolyte is very simple to make up and operate on a day-to-day basis. Overall, the performance and financial benefits of alkaline cyanide-free satin zinc make it an ideal base coating deposit for paint and powder coat applications.

Every Benefit You Could Want In One Process

Columbia's Excel® Non-Cyanide Zinc combines every possible plating benefit into one "Total Package" process:

- ✓ Extremely bright deposits that are comparable to acid zinc plating.
- ✓ Excellent deposit ductility, eliminating blisters even at 1 mil thickness.
- ✓ Superior plate distribution on the most tough-to-plate part configurations.
- ✓ Economical and easy to use.
- ✓ Widest possible current density bright range for rack and barrel plating.

Add these benefits to Columbia's extensive technical support, and you get a total package that is unmatched in the industry.

Let us show you what the Excel "Total Package" process can do for your plating operation. You have nothing to lose and everything to gain.

We are the Zinc Plating Experts.

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