Cyanide Replacement In Zinc Plating: A Case History

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Before 1970 practically all bright zinc plating was cyanide based. Since that time, the development of non-cyanide alkaline and acid processes offers new options to the zinc plating industry. Today, the majority of zinc platers use cyanide free solutions. This elimination of cyanide is possibly the most successful achievement in the ongoing search of environmentally acceptable alternative technologies. In this paper the development of alternatives to cyanide zinc, from their inception to the present, is traced. The history of the evolution of alternative processes clarifies the general strategies required for the successful development of environmentally friendly technologies.

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Introduction

Zinc plating is possibly the most successful example of the replacement of cyanide in a major industrial plating process. How the alternative technologies were found and developed offers an excellent opportunity to determine the critical strategies required for a new ecologically friendly technology to be successful in replacing a well established process that may be ecologically tainted.

Until 1970 practically all bright zinc was plated from so called "full cyanide solutions", containing about 100 g/L of sodium cyanide. The only cyanide free processes available were acid plating solutions, based on zinc sulfate or chloride. These were used mainly for industrial plating where brightness was not required. This has changed completely during the last thirty years. Today we estimate that over 70% of bright zinc deposits produced in the United States are from solutions free of cyanide. Of the remaining 30% that use cyanide, at least 4% use formulations where cyanide concentrations are minimal[1].

While environmental requirements provided a permanent incentive for cyanide elimination, the route to find alternatives was anything but easy or smooth. The classic zinc plating solutions containing high amounts of cyanide are extremely robust, with good throwing and covering power, generating deposits with uniform thickness and appearance. The zinc coating is inherently smooth and fine grained and can be brightened with simple additives. The adhesion is good and the surface preparation requirements are undemanding.

At the same time, the classic cyanide zinc plating process presented problems that are inherent in the deposition mechanism. Due to the relative inefficiency of the cathodic process (typically 50 to 70%) large amounts of hydrogen are produced at the cathode, causing the embrittlement of steel parts, This requires that the parts be baked after plating. The low cathodic efficiency also interferes with the coverage on high carbon steels and cast iron parts. Alternative cyanide-free electrolytes offered the possibility of overcome these intrinsic problems of cyanide plating.

By 1970 zinc plating technology was in crisis, attempting to cope with new demands from users and regulators. Three forces were simultaneously impacting the plating industry:

1) New environmental regulations
2) Reduction of costs
3) Enhanced quality requirements

Today we take for granted that the environment, quality, and cost must be dealt with simultaneously to achieve success in any industrial innovation. In the early '70's" industry was not ready for the new "tri-dimensional " way of creating technology. Thought processes were essentially linear and a major change in the way of thinking was needed before a friendlier, cheaper, and better zinc plating could be developed. As chemical suppliers we were ready only to improve brighteners and we had to learn from scratch how to formulate completely new plating solutions.

A number of bright zinc plating processes were proposed initially. On the acid side, solutions based on fluoborates, sulfates, complex chlorides, and organic acids were proposed. On the alkaline side, formulations based on zincate, pyrophosphate, and amines were recommended. Each of these approaches offered potential advantages and disadvantages and much time was lost in discussing where to focus development efforts. Every group active in zinc plating research was concentrating on a single technology, trying to promote it as a perfect replacement for conventional cyanide plating. Several of these formulations were proven impractical and the approaches that survived the selection process are summarized on Table 1.

Table 1
Bright Zinc Plating Alternatives
(all solutions contain proprietary brighteners)

Full Cyanide Solution:	Zn	20 to 40 g/L
	NaCN	50 to 140 g/L
	NaOH	60 to 120 g/L
Low Cyanide Solution	Zn	5 to 15 g/L
	NaCN	5 to 15 g/L
	NaOH	70 to 100 g/L
Zincate Solution	Zn	5 to 15 g/L
	NaOH	70 to 150 g/L
Chloride Solution	Zn	20 to 35 g/L
	Chloride	120 to 150 g/L

Towards the end of the initial learning process it became evident that these alternatives were technologically viable and that instead of a single unique answer to cyanide replacement two approaches, one acidic and one alkaline, had to be pursued in parallel.

Alkaline systems.

Alkaline cyanide-free systems offered an important advantage: they used the same equipment as cyanide plating. The concept of plating zinc from an alkaline, cyanide-free zincate solution is not new. It was originated by the early observations that cyanide zinc solutions *plated efficiently only in the presence of large* concentrations of sodium hydroxide. A solution made up only with zinc cyanide and sodium cyanide will have a cathode efficiency of approximately 15%.

Early work by Thompson[2] and Hull and Wernlund[3] stressed the importance of the sodium hydroxide as a source of zincate ions. In conventional zinc cyanide solutions 75 to 90% of the zinc is in the form of zincate, according to the following equation:

$Na_2ZnO_2+4NaCN+2H_2O=4NaOH+Na_2Zn(CN)_4$

The cyanide provides a control medium for the appearance of the zinc deposit. In the absence of cyanide, the zincate solutions will deposit dark and spongy metal. Solutions containing high amounts of cyanide will produce white, fine grained zinc. Through the development of proprietary additives during the decade of the sixties, it became increasingly possible to obtain deposits with acceptable appearance. These materials were initially polyelectrolytes. In small concentration they were able to refine the grain structure.

The first studies of the alkaline systems using these types of additives gave very positive results. So much so that in a 1971 paper we were able to conclude that it was possible to formulate cyanide free electroplating solutions "that will show a performance comparable to that of conventional cyanide solutions used for decorative plating"[4]. By adjusting the metal and sodium hydroxide concentrations in the zincate plating solution, the current efficiency and thickness distribution curves were similar to those obtained in conventional cyanide solutions. This can be viewed in Figures 1 and 2, reproduced from the above mentioned article. In the same article production cost figures are quoted, indicating that the operating costs were lower than conventional cyanide plating.

Unfortunately, these statements, while valid, did not present the complete picture. It is true that zincate based plating operations have been in production for many years. However, the general view of the market is that alkaline zincate systems are not sufficiently robust for general use. This point is well illustrated by the opinions presented by Marty Borruso in the September 1998 issue *Plating and Surface Finishing*[5], that in these plating solutions "*concentrations varied widely*", *that* "*parts plated* are not bright and shiny" and that "latent blisters are a common problem".

These objections are based on experience gained over many years of industrial practice. From the start we have been investigating how to make the zincate process more robust. The earliest (and very successful) approach in this direction was the creation of the low cyanide solutions, where a reduction of up to 90% of the cyanide level was accomplished by using additives similar to the additives developed for the zincate process. The presence of low levels (5 to 10 g/L) of cyanide allows for a more robust process, alleviating the problems found in the zincate solutions. Low cyanide processes were more stable and deposited zinc over a wider range and with better adhesion than cyanide free alkaline solutions. Cost is one of the important advantages of these solutions. While cyanide is still present, the concentrations of the chemical components in the solution have been reduced. This allows important saving in replenishment and waste treatment costs.

At the same time, we have not given up the objective of improving the zincate systems by finding superior additives. The initial additives performed best in dilute solutions. As the concentration of zinc and sodium hydroxide increased, the current density range became too narrow. Newer additives have expanded the plating range allowing the use of more concentrated solutions, reducing the unpredictability of the solution composition. Also the blistering problem has improved through better additive technology. While there is no full explanation of the blistering, indications are that it could be related to stresses induced by the organic additives used as brighteners. Data presented by Keith Zone in SURFIN 1997 indicates that the stress/thickness patterns can vary with different brighteners (Figures 3 and 4). An other explanation could be the effect of hydrogen embrittlement. Still, zincate solutions appear to cause less embrittlement than cyanide solutions. [6]

Chloride Systems

Chloride zinc plating has a history that initially matched the progression of alkaline cyanide free plating. The first chloride solution was patented in the US in 1940 by Hubbell and Weisberg[7]. This solution used ammonium chloride as the conductive salt and it was useful in industrial plating. The first successful decorative chloride process was patented by Poor and Rynne[8] in 1967. This solution worked at essentially neutral pH values and used ammonium chloride and organic polyhydroxy acids as ligands for the metal.

While this solution provided excellent deposits over a wide variety of substrates, the presence of organic chelators interfered with precipitation of metals during the waste treatment. For this reason chelator-free solutions were developed on the weakly acid side (pH 5.5 to 6.0), always using ammonium chloride. This type of plating solution has been in use since the early seventies with very good results. The main objection to the industrial use of the ammoniated solutions is environmental. It is possible to precipitate zinc during waste treatment by simple adjustment of pH; still, other metals, like copper and nickel are hard to waste treat in the presence of ammonium ions. Also the effluent limitations for ammonia were an incentive to find an alternative formulation. Replacing the ammonium chloride with potassium chloride was the next step in the evolution of this technology and, by 1975, the fundamentals of the potassium chloride solution were fully established and reported [9]. This formulation, reported in Table II has been used (with no major alteration) up to the present.

Table II
Potassium Chloride Solution

Zinc metal	30 to 40 g/L
Total Chloride	120 to 160 g/L
Boric Acid	25 to 30 g/L
PH	5.0 to 5.5

Solutions using the ammonium or potassium formulations contain significant amounts of organic brighteners that are responsible for the excellent appearance of the zinc deposits plated in the chloride solutions.

It may be worthy to note how much sooner the chloride systems developed, compared with the alkaline zincate solutions. As mentioned before, only recently did the zincate solution reach the level of robustness required by industry. One explanation of the difference in the time required to fully development the two systems is the interest that the industry demonstrated in harnessing the unique improvements that the chloride solutions added to zinc plating. The enhanced brightness and the ability plate cast iron and high carbon steels made chloride solutions very attractive to zinc platers, prompting the chemical suppliers to focus on this technology. While the appeal to replace cyanide plating with zincate solutions is *mainly environmental, the appeal of chloride* solution is mainly the quality of the deposits. It is possible to conclude that when two processes are competing for the same segment of the finishing market, the one that offers better quality values will evolve first.

Future Developments

Cyanide free alkaline and chloride based solutions have reached a stage of maturity where the changes that can be expected in the near future will happen mostly as enhancements of present processes. Still, these novel plating technologies have opened a whole new area of innovation that has just started to yield its first commercial successes. It is possible now to deposit a number of zinc alloys with enhanced protective value from both zincate and chloride solutions. In the past, using cyanide-containing formulations it was not possible to co-deposit zinc with nickel, cobalt or iron. The industry is just learning how make use of the benefits of these new coatings.

The main purpose of replacing zinc coatings with zinc alloys is to improve the deposit's resistance to white and red corrosion. Presently both chloride and the zincate formulations are being used for producing zinc alloys. Initially only chloride solutions were used to deposit alloys containing nickel (about 12%) or cobalt (about 1%) using formulations similar to standard zinc plating. Recently the trend has changed to zincate based solutions, both for nickel and cobalt alloys. Alkaline processes form alloy coatings that are more uniform both in thickness and composition than the chloride based processes. If this trend persists, it may give further emphasis on the improvement of zincate technology. In any case, alloy plating has added a unexpected new level of activity to the zinc plating technology development, requiring improvements both in solution formulations and additive technologies.

Conclusions

Several technically and commercially successful alternatives to cyanide zinc plating were developed during the last thirty years. Based on the experience with zinc we may conclude that the development of alternative processes is an evolutionary process and to be successful in this activity several conditions must be fulfilled:

1) In selecting the initial approach, we should consider the full extent of the requirements of the industry, not limiting our thinking exclusively to the environmental concerns.
2) The research and development efforts should be focusing on several viable alternatives and evaluate them concurrently.
3) The expertise gained with the old technology will have little bearing on the application of the new processes.
4) Environmental friendliness by itself is no guarantee of success.

This last point can be observed in the case of the zinc cyanide alternatives, alkaline and acid. It was not sufficient to match the performance of the original cyanide plating process. To be successful, it was necessary to gain additional advantages. The cyanide free zincate processes bring significant cost advantages to the plating process, while the chloride process has enhanced the quality of the deposit. At the same time, both new processes provide a basis for the deposition of alloys, adding further value to zinc plating.

References

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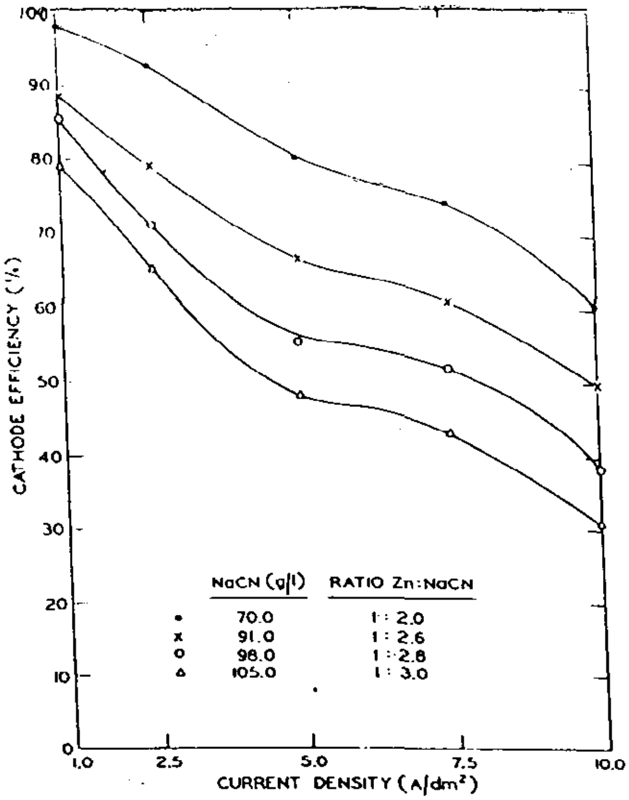

Figure 1. Cathode efficiency in full cyanide solutions (Zn 35 g/l, NaOH 75 g/l, Temp. 25° C)

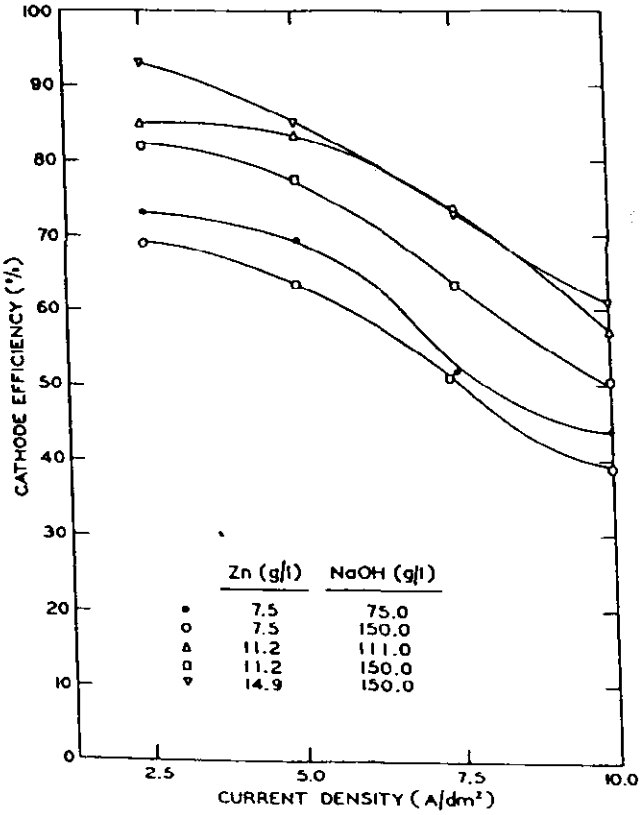

Figure 2. Cathode efficiency of zincate solutions (25°C)

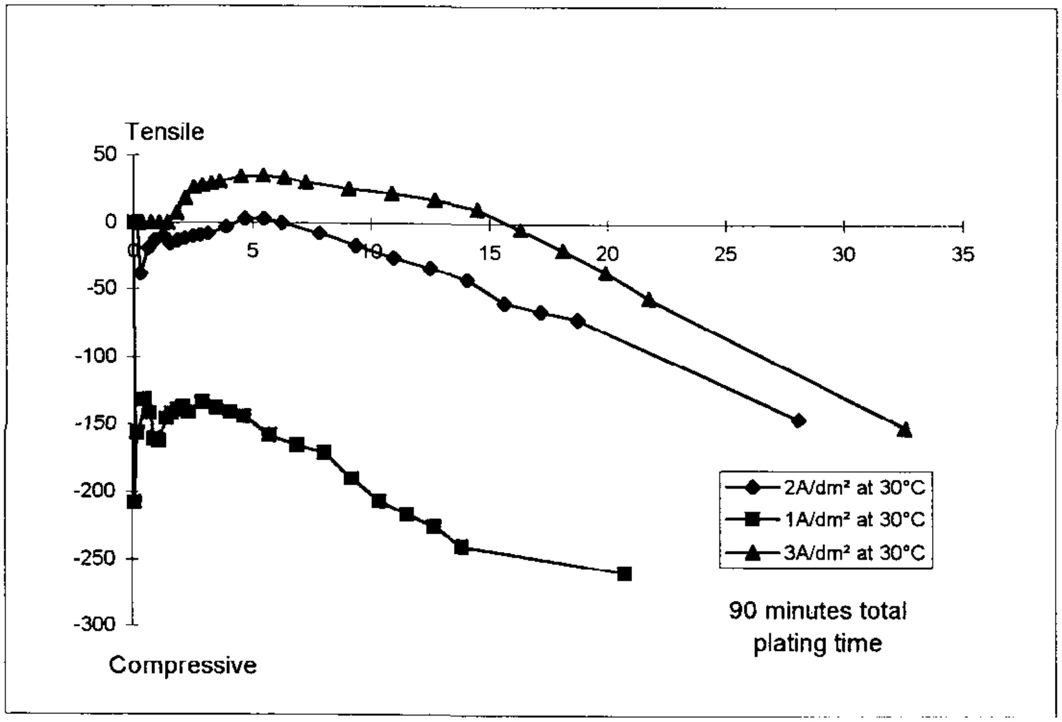

Figure 3. Relation stress/thickness using traditional additive system.

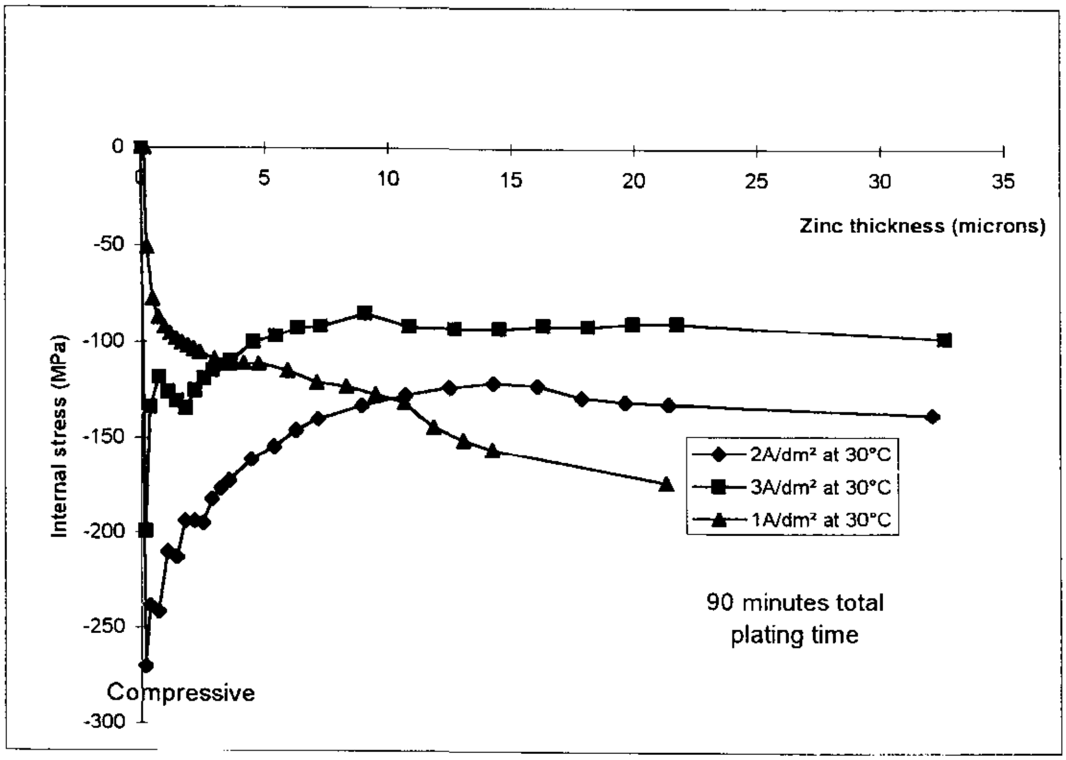

Figure 4. Relation stress/current density using advanced additive system.