

PLATING and
SURFACE FINISHING

**Ammonium Chloride Makes
Good Sense For
Chloride Zinc Platers**

Ammonium Chloride Makes Good Sense For Chloride Zinc Platers

By William E. Rosenberg Jr., CEF and Fred H. Holland, CEF

The presence of small amounts of ammonium chloride in chloride zinc plating baths can significantly reduce the cost and increase the quality of plated parts without causing serious waste treatment problems.

Acid chloride baths have undoubtedly had a tremendous impact on the zinc plating industry. Not only do these baths offer safe alternatives to cyanide zinc technology, but they also produce extremely bright, ductile deposits—even on hardened steel or cast iron. Quality deposits can be obtained from any one of the three most widely used chloride zinc baths: potassium chloride, ammonium chloride and mixed chloride (ammonium chloride/potassium chloride). Of these three, the mixed chloride bath presents several significant advantages over the other two. These advantages relate to solution cost, bath maintenance, consistency of quality and waste treatment.

Cost Advantage

It is evident from the chemical makeup of the chloride zinc baths (Table 1) that the mixed chloride bath offers considerable savings over the potassium chloride bath. Mixed chloride baths operate with 15 to 22 g/L (2 to 3 oz/gal) of dissolved zinc, whereas potassium chloride baths require almost twice this amount. The zinc ion concentration in potassium chloride baths must be maintained at high levels to obtain the best possible high current density burn-free range.* These high levels of zinc mean more zinc is dragged out, which, in turn, increases chemical replacement costs.

In baths containing ammonium chloride, excellent, bright, high current density burn-free deposits are obtained at much lower zinc concentrations than in potassium chloride baths. Since the cost of addition agents is a significant portion of the total cost of operating a chloride zinc bath, it is also worth noting that the brightener additives for ammonium chloride-containing baths are generally less expensive than those for potassium chloride baths and less are required.

While the full-ammonium chloride bath shares many of the advantages of the mixed chloride bath, the higher cost of ammonium chloride over potassium chloride makes the full-ammonium chloride bath more expensive to maintain.

*High current density burn is defined as rough, dull electrodeposits in high current density areas.

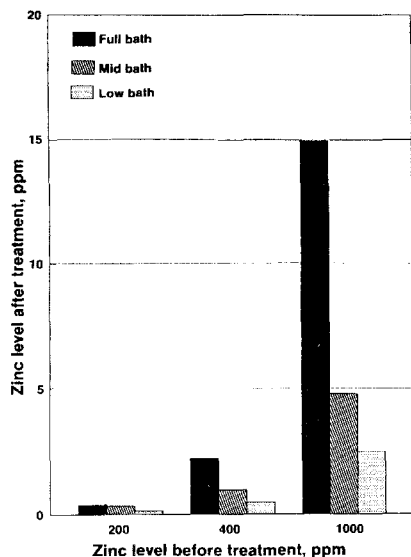
Easier Bath Maintenance

With respect to bath maintenance, plating solutions containing ammonium chloride have several advantages over potassium chloride baths. First of all, potassium chloride baths require boric acid to buffer the solution, whereas baths containing ammonium chloride do not. It is important to note that boric acid can crystallize out onto the anodes during cold weather shut-downs, causing serious current distribution problems. This can result in poor coverage in low-current-density areas, and can even cause high-current-density burning. In addition to providing a cost savings, removing boric acid from the system simplifies bath maintenance by reducing the number of necessary analytical procedures.

Furthermore, it is easier and less costly to maintain an adequate zinc level in a high-dragout barrel bath containing ammonium chloride than a

Table 1
Chemical Composition of Chloride Zinc Baths

Component	Type Bath		
	Potassium chloride zinc bath	Mixed ammonium chloride/potassium chloride zinc bath	Ammonium chloride zinc bath
Zinc	26 to 41 g/L (3.5 to 5.5 oz/gal)	15 to 23 g/L (2.5 oz/gal)	15 to 23 g/L (2.5 oz/gal)
Total chloride	120 to 150 g/L (16 to 20 oz/gal)	120 to 150 g/L (16 to 20 oz/gal)	120 to 150 g/L (16 to 20 oz/gal)
Ammonium chloride	None	15 to 45 g/L (2.0 to 4.5 oz/gal)	180 to 225 g/L (24 to 30 oz/gal)
Boric acid	23 to 34 g/L (2.0 to 4.5 oz/gal)	None	None



Precipitation of zinc at pH nine from the wastewater of baths containing ammonium chloride.

similar potassium chloride bath. In a high-dragout mixed chloride bath, the anodes are able to provide all the zinc ions necessary, and the only chemical additions required are potassium chloride and ammonium chloride at a 5:1 to 10:1 ratio to maintain the chloride ion concentration. With barrel potassium chloride baths it is often necessary to make additions of zinc chloride.

More Consistent, Higher-Quality Plated Parts

In addition to its superior burn-free range over the potassium chloride bath, the mixed chloride bath produces a more consistent day-in and day-out quality of plated parts. This is related to the solubility of the additives used in these baths.

Generally, addition agents have greater solubility at higher bath temperatures in the mixed chloride bath compared to the potassium chloride bath. The temperature at which the additives begin to lose their solubility is called the *cloud point* of the bath. Boric acid, higher zinc levels and more dense potassium chloride vs. ammonium chloride are major factors that influence cloud point.

A plating bath with a low cloud point can produce dull, grainy deposits that do not respond to brightener additions. In many cases the parts will not rinse properly, causing chromating problems such as staining, discoloration and even lack of adherence of heavy chromate films.

There is a tendency to overload a potassium chloride bath with emulsifiers (wetting agents) to compensate for low cloud point or lack of high current density burn-free range. As the bath becomes too rich in organic additives, rinsing problems and dullness can actually become worse. Since the mixed chloride bath exhibits high cloud point and superior high current density bright range, this type of brightener overloading (also called brightener spiral) can be avoided.

Frequent and even continuous carbon treatment is one method to increase the cloud point of a chloride bath. Also, the bath can be cut periodically (remove a portion of the bath, dilute with water and adjust the chemical composition). Both these methods are costly and time consuming, however, and are rarely required for mixed chloride baths.

Waste Treatment

Waste treatment for the mixed chloride bath is very manageable and is accomplished by using the standard method of precipitating the zinc by increasing the pH to nine and adding a small amount of flocculating agent. It should be noted that at very high concentrations, ammonium ions can interfere with the precipitation of zinc. This is not a problem with mixed chloride baths, which are low in ammonium chloride, but can present a problem with a full-ammonium chloride bath. Table 2 shows three baths containing different amounts of ammonium chloride. The bar graph illustrates the results of waste treatment tests on wastewater from these

baths. Zinc can readily be reduced to acceptable levels in rinsewater from a mixed chloride bath.

In the event that dissolved copper and/or nickel are introduced into the effluent prior to waste treatment, inexpensive sulfur-organic compounds are available that are capable of breaking the metallic complexes formed with ammonium ions, effectively removing these metals.

One of the biggest problems facing platers is the increasing expense of disposing of sludge from their waste treatment processes. Lower levels of zinc in baths containing ammonium chloride mean less zinc hydroxide sludge will be produced during waste treatment.

Summary and Suggestions

By adding a small amount of ammonium chloride to a potassium chloride zinc bath, a plater can experience significant cost savings, greater ease of bath maintenance and more consistent quality of plated parts.

In addition, full-ammonium chloride baths can be operated more economically by adding a mixture of potassium chloride and ammonium chloride to maintain the proper chloride level instead of adding the more expensive ammonium chloride alone. This will also eliminate problems with waste treatment caused by the complexing of zinc with high concentrations of ammonium ions. A comparison of the advantages and disadvantages of the chloride baths can be found in Table 3.

It should be noted that changes in brightener additives may be required

Table 2
Zinc Baths Containing
Three Different Amounts of Ammonium Chloride

Component	Bath Designation		
	Full bath	Mid bath	Low bath
Zinc	19 g/L (2.5 oz/gal)	19 g/L (2.5 oz/gal)	19 g/L (2.5 oz/gal)
Total chloride	135 g/L (18.0 oz/gal)	135 g/L (18.0 oz/gal)	135 g/L (18.0 oz/gal)
Ammonium chloride	176 g/L (23.4 oz/gal)	45 g/L (6.0 oz/gal)	15 g/L (2.0 oz/gal)

Table 3
Advantages and Disadvantages
Of the Three Chloride Zinc Baths

Factor	Type Bath		
	Potassium chloride	Mixed ammonium chloride/potassium chloride	Ammonium chloride
Cost of chemicals in bath	Higher cost	Lower cost	Higher cost
Amount of sludge generated	Higher amount	Lower amount	Lower amount
Need for boric acid	Needed	None needed	None needed
High current density burn-free range	Fair	Excellent	Excellent
Removal of zinc from effluent	Readily removed	Readily removed	Some difficulty at high concentrations
Cloud point	Fair	Excellent	Excellent
Overloading of additives	Common problem	Rarely occurs	Rarely occurs
Consistent quality of plated parts	Fair	Excellent	Excellent

to accommodate modifications in bath chemistry. It is important, therefore, that platers consult their suppliers before making changes in the operation of their baths. □



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