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# METAL

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## ZINC PLATING

### How to Achieve Successful Yellow Chromate Adhesion Over Acid Chloride Zinc Plating

by Rick Holland

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The lack of chromate adhesion over a bright acid chloride zinc deposit, a.k.a. chromate slough-off or rub-off, is a problem that has probably plagued every acid chloride zinc plater at one time or another. At best, this problem can mysteriously appear during the middle of a run and quickly disappear within hours. At worst, slough-off of the yellow chromate becomes an ongoing problem appearing on most or all processed work for days, weeks, and even months.

The yellow chromate film is most susceptible to adhesion problems, although problems also exist with clear, blue, olive drab, and black chromates. This paper will address the major factors contributing to slough-off, as well as the troubleshooting actions that can keep yellow chromate firmly adhered to a bright acid-chloride zinc deposit.

#### PROBLEMS WITHIN THE WORKING YELLOW CHROMATE SOLUTION

Since there is a myriad of things that can go wrong within the working yellow chromate solution itself, this should be the first area of focus to either verify the problem or eliminate it as a suspect.

The focus should be on the "Big 4": (1) concentration, (2) dip time, (3) temperature, and (4) chromate solution condition. All four factors have some effect on chromate film formation and adhesion.

#### High Chromate Concentration and Dip Time

As expected, an overly thick chromate film will be inherently prone to adhesion problems. Since dip time and chromate concentration directly affect the film buildup, off-line testing should be performed by hand dipping parts in a pail with adjustments made accordingly.

If the chromate concentration is too high, the immersion or dip time should be reduced or the solution should be diluted.

#### Temperature

A cold solution will lay down a chromate film that does not adequately bite into the zinc deposit and sets up poorly after the final warm water rinse. Optimum chromate film adhesion is achieved at temperatures of 70 to 95°F.

#### Chromate Condition

The overall condition of the chromate should also be checked. This includes: foam formation from drag-in of proprietary brighteners and wetters; buildup of zinc and iron; and miscellaneous contamination from downstream processes. With old, aged, or contaminated chromate solutions, it is best to dump and make up a new solution.

## SPECIALTY CHROMATE FORMULATIONS AND ADDITIVES

The use of modified conventional yellow chromate products or specifically formulated yellow chromates for bright acid chloride zinc is an option well worth investigating. Here are a few ideas.

### Chloride-Based Yellow Chromates

Proprietary yellow chromates containing various chloride salts were developed specifically to adhere to the bright, high leveling, tight grain refinement of the acid chloride zinc deposit. These chloride chromates contain all of the conventional chromium compounds and inorganic acids; however, they were formulated with moderate to high concentrations of chloride salts. These salts provide a better “bite” into the highly polished structure of the acid chloride zinc deposit.

### Boric Acid and Ammonium Bifluoride

Two nonproprietary additives that can be added directly to the working yellow chromate solution are boric acid and ammonium bifluoride. These additives can be added at 0.5 to 1.0 oz/gal to enhance the “bite” of the chromate.

## PROBLEMS WITHIN THE ACID

### CHLORIDE ZINC PLATING SOLUTION

Brightener overload, bath contamination, and low carrier/wetter content have a detrimental effect on chromate adhesion. These troubleshooting techniques can be used to correct problems within the plating bath:

#### Proprietary Carrier/Wetter Content

All state-of-the-art proprietary carriers and wetters used today in bright acid-chloride zinc plating are highly concentrated with solubilizing wetting agents (surfactants). One of the many functions these wetting agents perform is microemulsification of the proprietary brightening agent in the brightener. If the carrier/wetter content is low, co-deposition of the brightener and film-forming organics will occur on the surface of the plated work, causing poor chromate adhesion. In this case, the carrier/wetter content should be increased to meet the supplier’s optimum operating specification.

#### Potassium Permanganate

Unlike carbon treatment,  $\text{KMnO}_4$  is a commonly performed treatment for zinc platers and is generally accepted within the industry as routine. Treatments can be done in-tank using 1 to 2 pounds of dissolved potassium permanganate per 1,000 gallons of plating solution, using maximum agitation and continuous filtration. The solution will clear within 8 hours of treatment, with well-maintained filters. Potassium

permanganate has two functions. First, it breaks down the main proprietary brightening agent during bath overloads; second, it is a strong oxidizer for precipitating soluble ferrous iron to insoluble ferric iron. During treatment, the precipitated iron will collect and pull out some stray oils, wetting agents (surfactants), and miscellaneous charged organics.

#### Carbon Treatment

Although labor- and time-intensive, carbon treatment is an effective way to remove less-soluble organic contaminants such as dragged-in oils and overloads of brightener. This treatment requires transferring the entire bath to a separate mixing vessel where 1 to 2 pounds of activated carbon per 1,000 gallons of plating solution is mixed for 2 to 4 hours. The solution is then allowed to settle overnight and is decanted back to the plating tank through 5-micron filters.

#### pH

Lowering the pH of the plating bath by 0.5 to 1 point with hydrochloric acid has been found to increase receptivity of the yellow chromate film. As most zinc platers know, pH adjustments of the plating bath using moderate additions of hydrochloric acid will burn up some of the brightener. In the case of a bath that is overloaded with brightener, a convenient treatment to kill some of the brightener is a good slug of hydrochloric acid to bring the pH down to around 5.

## PROBLEMS IN THE POSTPLATE RINSES

The main purpose of postplate rinsing is simply to remove the acid chloride plating solution and all constituents from the plated work before entering the chromate dip tank. If the plating solution is not removed through rinsing or if inorganic/organic surface films set up prior to the chromate process, the yellow chromate will adhere poorly to the zinc deposit. If the chromate and plating solution have been eliminated as the cause of the problem, the following adjustments or modifications can be made to the postplate rinse cycle:

#### Poor Postplate Rinsing

The problem may be as simple as inadequate rinse water flow rate or the inability of the rinse waters to remove the acid chloride plating solution. The standard flow rate is 1 to 2 gpm of water through 3 counterflowing rinse tanks. A quick check to see if rinsing is adequate is to check the final counterflow rinse tank for pH and chloride content. The pH should be within 0.1 to 0.2 units of the fresh incoming water and chloride no higher than 0.5 oz/gal. If the final rinse is clean, install air agitation and warm the final rinse to 85°F to improve the scrubbing action of the water.

## Sour Dip

Formation of chloride residue on the surface of the work, organic staining from foam, or organic additives in the carrier/wetter/brightener will interfere with chromate receptivity. The use of mild acid "sour" dip can remove the surface film and allow the chromate to bite into the zinc. The most commonly used acids are: sulfuric, hydrochloric, and nitric acid at concentrations of 0.25 to 0.5% by volume. These sour dips are generally maintained for 8 hours at pH 1.5 to 2.0, then dumped and made fresh for the next 8-hr shift.

## Citric and Tartaric Acid

In some cases, the use of a sulfuric, hydrochloric, or nitric acid sour dip can actually set up or enhance staining caused by chloride residue or foam. An optional sour dip, although more expensive, is 0.5 to 1 oz/gal of citric or tartaric acid. Parts should be thoroughly rinsed so as not to contaminate the chromate with citric or tartaric acid. Replenishment of citric or tartaric acid is based on drag-out and the solution is dumped every 8 hours.

## Hard Water

The formation of calcium sulfate, calcium chloride, magnesium sulfate, magnesium chloride, and related hard water salts on the surface of the plated work is usually encountered at shops using untreated well, river, or lake water. These hard water salts are extremely difficult to rinse, very difficult to troubleshoot, and probably the most expensive to eliminate as the cause of the problem. All of the procedures mentioned above can improve adhesion caused by hard water conditions; however, if problems persist, the use of DI water in the rinses and the installation of a DI system may be needed. Unfortunately, not only is this a major expense but the problem could also be seasonal, due to changes in the incoming water. In any case, a thorough study should be done internally by shop management and by outside chemical suppliers to determine the water quality.

## CONCLUSION

Although chromate slough-off is a common problem, every plater can successfully keep yellow chromate firmly adhered to a bright acid-chloride zinc deposit. The key is to evaluate each step of the plating process, isolate potential factors contributing to the problem, and make modifications where necessary to assure good adhesion. First, the working yellow chromate solution must be checked for optimal chromate concentration, dip time, temperature, and condition. Second, the acid chloride zinc plating solution should be evaluated for proper proprietary carrier/wetter content, potassium permanganate treatment, carbon treatment, and pH. Lastly, the postplate rinses should be checked and the addition of a sour dip prior to chromating should be considered. These troubleshooting techniques will result in top-quality yellow chromated zinc parts.

## BIOGRAPHY

Rick Holland has 24 years in the development and technical support of zinc plating processes and has been the Technical Manager of Columbia Chemical Corp. since 1990.

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