# Control of Trivalent Passivates

**Q.** My corrosion protection is erratic due to variances in concentration. How do I better control the passivate solution to improve quality?

**A.** Control of trivalent passivates is an important focus due to the stringent quality requirements set by OEMs. At the core of every trivalent passivate, there are four parameters that are critical for control: concentration, pH, immersion time and temperature. Each of these parameters influences the passivate activity and overall performance.

Below is a chart that briefly outlines the effect that each of the variables has on passivate film thickness. As you can see, when we increase concentration, temperature, and/or time, the film thickness will increase. Similarly, if we decrease the pH, causing the passivate solution to become more acidic, this will increase the overall thickness. Conversely, as we swap each of the parameters to decrease concentration, temperature, time or increase pH, the overall passivate thickness will be lower.

**Effect of variables on chromium thickness (nm)**

| | CONCENTRATION (↑) | pH((↓) | TEMPERATURE (↑) | TIME (↑) |
|---|---|---|---|---|
| Thickness (nm) | (↑) | (↑) | (↑) | (↑) |

This information has important implications to the plating process operation as certain limitations may be present within the plating line and each variable can be seen as a lever that can be adjusted to impact or compensate for the other variables. For instance, if a low immersion time is required — to combat the reduced dip time which would cause lower thickness — we can counteract it by either increasing concentration or temperature, or by lowering the pH to increase the thickness.

After understanding the basic framework of a passivate film, maintaining the parameters with an upper and lower control limit is crucial. Specifically addressing your comment regarding erratic variances in concentration, controlling concentration is often done by calculating drag-out to determine the amount of passivate needed to maintain a set concentration. Understanding the drag-out in a trivalent passivate is key, as a majority of the usage in a trivalent passivate is due to the drag-out of solution. This can be done by calculating as follows:

- Determine the tank volume.
- Obtain a sample of newly made passivate or one at a known concentration.
- Process a determined amount of time/barrels through the solution and pull another sample.
- Calculate drag-out and addition rates.

**Example:**

Let's consider the tank volume at 250 gallons of working passivate solution on a barrel line. We obtain a sample, analyze the solution and conclude the passivate sample has a working concentration of 10.0% by volume. We then time 16 barrels worth of work being processed through the passivate (while not adding any passivate) and then we pull a sample. After we analyze the solution, we find that the concentration has dropped to 9.2% by volume. We can now conclude that over the course of 16 barrels, 0.8% by volume concentration was dragged-out or consumed through passivation. A 250-gallon working solution x 0.8% by volume = 2 gallons of passivate lost over the course of 16 barrels. This means that for every barrel, we would need to add approximately 0.125 gallons (473 mL) of passivate. In this example, assuming a barrel plater is pulling eight barrels per hour and running an eight-hour shift, we can conclude that they will pull 64 barrels per day. The amount of passivate would then be calculated by taking 64 barrels x 0.125 gallons = 8 gallons of passivate needed per day.

The passivate drag-out rate on this tank can be determined by calculating as follows:

Gallons Passivate added back / Tank Volume * 100 = % Drag-out of Passivate Per Determined Time Period

- 8 gallons / 250 gallons * 100 = 3.2% by volume Drag-out (per day) of passivate.

In this example, we see that 3.2% by volume of passivate concentration is lost per day. In some circumstances, platers can do an addition once per day to maintain within an upper/lower control limit. However, if certain OEM specifications dictate that concentrations must be maintained between 8.0-10.0% by volume to maintain a certain level of quality, then in this instance, waiting until the end of the day means the concentration

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would drop from 10.0% by volume to 6.8% by volume, which may result in corrosion resistance failures, appearance issues, and would ultimately affect the quality of finished products, resulting in rejected or returned parts and increasing the overall costs of production. This is precisely why calculating the drag-out rate and making the appropriate add-backs can allow you to help avoid such a scenario.

In terms of making the additions, relying on manual daily add-backs by operators is an option, but the usage of metering pumps on a barrel counter/touch-down switch has become increasingly popular in the industry today. These metered pumps can be set to pump the passivate over a certain amount of time, barrel touch-downs and even have the capability to pump passivate and adjust pH automatically with a pH controller setup. This allows the plater to adjust and control the feed rates of the passivates, ensuring they are of optimal concentration to pass the necessary quality requirements. Maintaining the concentration at the right balance based on true drag-out rate can result in cost savings, reducing unnecessary waste of product and less rejects.

To recap, when focusing on control of trivalent passivates to meet and exceed quality standards, it is important to consistently manage the parameters that impact passivate thickness (concentration, temperature, pH and dip time), but the critical step beyond that is to calculate your drag-out rate to be able to maintain accurate additions so you can keep the parameter ranges of the passivate in check.

It is commonly understood that not every part at a high-volume job shop is going to be the same or yield a consistent amount of drag-out every time. However, performing this test with regular frequency will allow the concentration to be maintained in a much tighter window, with only small adjustments needed on a less frequent basis.

Tapping into the technical knowledge and support of your chemistry supplier to help you get the drag-out rate calculated appropriately and set up the additions on your feeder pump can go a long way to establishing better control of your passivate solution and help make your quality manager a much happier person.

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