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Examining Yellowing in A Blue Trivalent Passivate

by

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Zinc and Zinc alloy platers rely heavily upon trivalent passivates for maintaining a consistent and high-quality finish. The color of the passivate can be an important consideration for functional parts. Platers will occasionally struggle with the challenge of a blue passivate looking great upon initial makeup but yellowing in appearance after a period of two to four weeks.

There are a number of factors to be explored when it comes to this issue, but the most common cause of trivalent passivate yellowing is too much iron in the passivation tank. Typically, when the iron level climbs to over 100 ppm, one can start to see issues with yellowing - mainly due to iron being incorporated into the trivalent passivate film. This can also cause a loss of corrosion protection up to first white rust. The main culprit for iron levels in the passivation tank is parts on the bottom of the tank. To eliminate this common cause, plating shops must be sure to drag the bottom of the tank with magnets and routinely keep the tank clean. When running a barrel application, the barrels must be inspected to see where parts could be lost. Also, high iron levels can sometimes be caused by unplated surface areas, such as the inner diameter of tubes or drag-out from the nitric pre-dip tank. It is good practice to regularly clean the bottom of nitric pre-dip tank as well to eliminate this potential problem.

If it has already been determined that high iron levels in the passivation tank are not the problem, the yellowing problem could be related to thickness of the passivate. Passivate film thickness has a very distinct effect on the color of the film and what the human eye detects in terms of color.

Using technology such as x-ray fluorescence, the thickness of the passivate layer can be measured in nanometers and the color of the passivate film can be correlated to the film thickness. X-Ray Fluorescence (XRF) is a nondestructive method by which passivate thickness can be reliably measured. XRF relies upon powerful x-ray beams to excite the inner electrons of the various metals within the solid or liquid anolyte. This process creates fluorescent photons that are analyzed by a detector. Each metal on the periodic table has specific orbital energies (an ID tag of sorts), which allow the XRF instrument to identify which metal is being analyzed. Once the XRF instrument identifies the metal, it calculates the thickness value based on how many photons it intercepts. It's important to note that while the XRF instrument can measure thickness, it will not distinguish between oxidation states (*i.e.*, trivalent vs. hexavalent chromium). Regarding the color of the film and the thickness - in general, a passivate film measuring between 50-150 nanometers will yield a blue appearance. A film with higher than 150 nanometers will yield a yellow appearance. Film thicknesses of >200 nanometers will yield green and pink colors from the spectrum. Passivates with >200 nanometers are considered thick film passivates and, in most cases, yield an iridescent appearance.

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Another factor related to the thickness of the passivate layer is its correlation to corrosion protection. A general rule of thumb is that every nanometer of film thickness will yield approximately one hour of salt spray protection. For instance, a passivate film thickness of 100 nanometers will yield roughly 96-120 hours of salt spray protection as long as all other parameters are optimized.

After understanding how the thickness of the passivate can reflect a yellow appearance, it is necessary to explore the four important components that can impact passivate thickness:

1. **Dip Time:** Lower dip time means lower levels of passivate film thickness - higher dip time means higher levels of thickness. Therefore, if the dip time is higher (the part is in the solution longer) causing the resulting film to be thicker, the finish can easily turn yellow. An additional consideration with dip time when running rack lines is the timing of when the first parts hit the solution. If there are yellow variations found between the parts at the top and bottom of the racks, it may be necessary to examine the dip time factor and tighten the operating window.
2. **pH:** If the passivation has a lower pH, it will build film faster, while a higher pH will build film slower. Since each chemistry has its own pH range, maintain the pH according to the technical specifications provided by your chemical supplier.
3. **Concentration:** Higher concentration of the passivate will result in a higher film thickness and lower concentration will result in a thinner film. Again, it is important to pay attention to the recommended concentration provided by the specific chemistry supplier.
4. **Temperature:** If the passivation tank runs at a higher temperature range, it will increase the activity within the tank and build the film quicker, resulting in increased thickness and potentially more yellowing. On the other hand, a lower temperature range will plate slower and provide a thinner film.

Beyond high iron or color variance related to film thickness, a less common potential cause would be post-plate bake times. Long bake times and high bake temperatures can lead to dehydration which can cause yellow discoloration. This is also a factor with air drying when the temperature is elevated.

When comparing all these potential factors for yellowing of a blue trivalent passivate, the primary cause a plater can look to is high iron in the passivation bath and the #1 cause of that is typically parts in the bottom of the tank. Though each of the suggestions indicated are valid in addressing a high iron issue, adjustment of these factors can be more of a short-term solution than a permanent one. The most effective long-term approach, once the initial problem is identified and addressed, is to focus on prevention of iron build-up through the use of specialized iron control additives and passivate conditioners.



Chad Murphy is a longtime Technical Account Manager with Columbia Chemical. He provides technical service, analytical testing and troubleshooting expertise in the Michigan and Northern Indiana territories. He has an extensive background in the automotive plating industry and has previously worked for a global tier one supplier as a plating chemist and chemical and environmental manager. He is a member of NASF and is also active in the regional metal finishing associations.