

The Do's & Don'ts of Trivalent Passivation Processes (Thick & Thin Film)

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This paper covers practical aspects in choice, make-up, care and disposal of trivalent passivation processes. Examples of typical products available today will be discussed, giving advice on choosing the correct passivate type based on application, equipment and plated coating. The paper also covers:

- Process Care: How to set up the chemistry and equipment.
- Control: What and how to control the additives.
- Maintenance: Making additions, control contamination, extend operating life and fix problems.
- Safe Disposal: How to waste treat rinse waters and spent solutions.

Alternatives to hexavalent passivates have existed since the late 1970s. These were based on the less toxic trivalent chromium compounds and were limited primarily to low performing, blue-bright type coatings. As these baths were relatively inexpensive to make up, maintenance / troubleshooting was not a big consideration and baths were frequently dumped.

Over the course of the last several years, there has been growing interest in hexavalent chrome free processes. This is due, in part, to the new ELV and WEEE legislation, which dictates that vehicles and electronic components sold in Europe can no longer contain hexavalent chrome.

In addition, specifiers are looking for enhanced performance properties that can only be achieved with trivalent conversion coatings. Passivate films now need to offer higher corrosion protection, thermal shock resistance, dye and topcoat absorbance characteristics, while being aesthetically appealing, and cost effective. As such, proper make up, maintenance and troubleshooting techniques have become paramount.

This paper will review both the common, and the lesser-known variables that can effect the performance of a trivalent based conversion coating, as well as troubleshooting strategies. The Topics to be discussed are:

- Effect of passivate time, temperature & concentration
- Solution agitation
- Solution pH
- Metallic contamination
- Plating thickness
- Predip solutions
- Water quality
- Drying temperature

Common variables: The three T's

The three most widely known variables in a metal finishing operation are known as the three T's. **T**ime, **T**emperature and **T**emperature. As is the case with most process solutions, these variables must all be tightly controlled within specific parameters to achieve the desired quality finish.

Time: Proper immersion time is one of the most important variables in a passivate process. When a zinc plated part is immersed in a passivate solution, the metal is dissolved, and a conversion coating is formed. The longer the solution is in contact with the plated part, the more of an opportunity it has for this to occur and in most cases a thicker passivate film results.

Trivalent passivates generally form coating films at a slower rate than their hexavalent counterparts. It is not unusual for a high build process to require an immersion time of 60 seconds or more. As such, the equipment, process cycle, etc need to be able to accommodate longer immersion times than had been the case in the past.

Too short an immersion time can result in low passivate thickness, thus poor corrosion protection. Too long an immersion time will result in excessive plate removal, also resulting in poor corrosion protection. Unlike hexavalent chromates, you cannot often determine film thickness through simple visual inspection. Therefore it essential that applicators monitor immersion time on an ongoing basis.

The conversion coating begins to form when the part first enters the process solution, and does not stop until the part enters the first rinse. Any time the passivate solution remains in contact with the plated metal, zinc continues to dissolve and the coating continues to form. When this occurs outside of the actual process tank, it does so without the benefit of heat, agitation and proper solution transfer at the part interface. As a result, a low quality conversion coating can result. In order to minimise this, dwell time, particularly between the passivate tank and the first rinse, should be kept as short as possible.

Temperature: In addition to longer immersion times, high build/high performance passivates often run at elevated temperatures. In the absence of strong mineral acids, these type systems often rely on heat to provide the “energy” for the conversion coating process to take place. It is not uncommon to see operating temperatures as high as 140-160 degrees F. When considering temperature as a possible trouble spot, it is important to measure the solution at the part interface, rather than away from the part. This temperature difference may be significant particularly when large parts first enter the passivate solution. In some instances, parts will be preheated in a rinse, prior to passivating. Most often PTFE, Teflon or quartz electric immersion heaters are recommended. Automatic thermostatic control and solution agitation is also advised to ensure optimum performance.

Concentration: Passivate concentration is another variable that differs greatly from older technology and must always be considered when troubleshooting. Where as hexavalent chromates typically run anywhere from 1-5% by volume, high performance trivalent passivates are routinely operated at 10% by volume or more. Much the same as temperature, these higher concentrations are required to give the solution the “energy” needed to produce the desired coating. Concentration can be easily measured tank side via a refractometer, and should be confirmed via wet analysis or instrumentally.

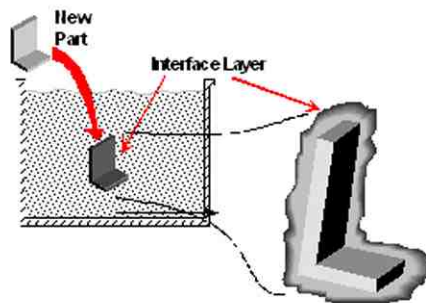
It is often asked if one of these three variables can be used to offset another. For instance, can running a higher concentration compensate for too short an immersion

time? In almost all cases, the answer is a resounding no. There is a delicate balance between time temperature and concentration that results in a proper conversion coating forming at a controlled rate. Running a process solution outside of the manufacturers recommendations will almost always produce an inferior coating.

In addition to these "primary" variables that can effect a conversion coating process, there are other operating parameters that are lesser known, but equally important to consider.

Agitation: Proper solution movement is essential to produce a quality conversion coating. This can be done with air, solution (via a pump) or part movement. Regardless of the method, it is important to have proper solution exchange at the part interface.

What Happens During Passivation



During the passivate process, there are many chemical changes that take place. Zinc is readily oxidized in the presence of acids and trivalent chromium, resulting in a significant pH rise at the zinc/passivate solution interface.

This causes the precipitation of chromium III hydroxide, on the surface; hence the conversion coating is formed.

Without proper agitation, the solution rapidly becomes depleted, and the conversion coating is not adequately produced. The usual method of agitation is to use a low-pressure blower forcing air into the solution. The air is pumped through perforated pipes lying near the bottom of the tank, creating a rolling motion. Compressors must not be used, since these invariably contaminate the solution with dirt and oil. Even using a blower, it is advisable to have an air filter in the inlet line. Components plated in bulk usually receive sufficient agitation during the passivating process and usually do not require air.

pH: pH is an important aspect of process control that is often overlooked. High build trivalent passivates operate within a fairly narrow pH window, and often require

adjustment, both upon new make up and during normal operation. Running the pH above the recommended operating range can impede the formation of the conversion coating, resulting in too thin of a film. Too low a pH level results in rapid forming and stripping of the passivate film, again producing low thickness and inadequate salt spray protection.

The pH can be controlled with either a meter or papers. Non-leachable type papers are recommended with a range of 0 – 2.5. Under normal operating conditions, the pH of the passivate will rise with time. Either product or dilute nitric acid is added to reduce pH. A drop in pH of a passivate solution is unusual, normally caused by large amounts of drag-in. Add dilute caustic soda to increase pH. A ¼% to ½% by vol. nitric acid pre-dip is recommended to activate the zinc plate prior to chromating.

Metallic contamination: Metallic contamination levels can have a significant effect on passivate film performance. Metals can be introduced through the normal processing of parts (for instance zinc or iron), can come from some outside source (for instance copper metal used in fixturing) or can even be part of the proprietary formulation (i.e. cobalt). Regardless of the source, all of these metals can have a detrimental effect on the passivate performance.

Zinc and iron are the two most common metal contaminants found in trivalent passivates. Of the two, iron contamination is the most problematic.

Today's technology tends to be more tolerant to zinc dissolution than earlier versions. It is not uncommon to see passivate solutions running well with zinc levels above 5000 ppm. Iron, on the other hand, can have a significant impact on corrosion performance, even at levels as low as 300 ppm.

Due to the acidic nature of the chemistry, the solution continues to react with parts accidentally dropped into the bath. This results in build-up of iron in the bath, which ultimately reduces the bath life and increases the operating expenditure. To avoid this, parts that have fallen off racks or out of baskets and barrels should be removed as soon as possible.

Cobalt is an often-overlooked source of metallic contamination, as it is introduced as part of the proprietary formulation. When added in the proper amount, cobalt metal acts as a catalyst, significantly increasing passivate film thickness and corrosion protection. Should the ratio of cobalt to chrome get too high, the film formation is retarded and the corrosion protection compromised.

Evidence of an excess of metallic contamination can be difficult to detect, but may be seen as discoloration, or "cloudiness" of the passivate film. Filtration of some passivates is recommended, as this will help remove metallic contamination. The

solution concentration can also be raised to give temporary relief from the problem. There are also proprietary addition agents available to precipitate, or inhibit the dissolution of metals.

In some cases, filtration of the passivate can help prolong solution life by removing metallic impurities. This is usually achieved by filtering the solution through a 20 - 50 micron disc or cartridge filter. Filter pumps lined with polypropylene are recommended. One solution turnover per hour is recommended.

Plating thickness: Generally speaking, a minimum thickness of 6 microns of zinc is required for a quality conversion coating. High build passivates can remove as much as 1-2 microns of zinc plate. Low plating thickness will result in poor performance to FRR or, in extreme cases, complete removal of the plating. This is particularly true in the low current density areas where thicknesses tend to be the lowest.

Acid predip: Non uniform or poor initiation, prior to passivation, can be another factor that can influence coating performance. In order to provide a bright, active surface, an acid predip is often used immediately before the conversion process. It is important, when utilising this step, that the predip chemistry is properly controlled, and that the specific acid being used is compatible with the passivate solution.

Water condition: Condition of water rinses both before and after the passivate is an important, but often overlooked variable. Process tanks contain many ingredients that, if introduced into the passivate solution would be harmful. Zinc metal, chlorides or hydroxides from the plating tank, as well as mineral acids from the predip will significantly reduce the life of a passivate solution. Hard water salts also can act as metallic contaminants, shortening the life of the passivate solution. As such, hard water should be softened, or replaced with DI, demineralized or RO water prior to being used in passivate solutions.

Post passivate rinse quality is equally important. High build passivates often have a high solid content and surface tension, resulting in rinse water getting quickly contaminated. As the concentration in the rinse increases, the solution begins to take on more and more of the properties of a passivate. The result is a low quality conversion coating being formed over the existing coating, which diminishes the overall performance considerably. When troubleshooting any passivate process, be sure the rinse water flow rates, agitation and immersion times are all sufficient to provide adequate rinsing.

Drying temperature: When hexavalent passivates are subjected to high heat, they generally perform poorly in salt spray testing. This is because, on heating, hexavalent systems dehydrate and crack exposing the underlying plating. Therefore white rusting takes place extremely quickly. Tests show that hexavalent passivates on zinc, zinc-

iron and zinc-cobalt lose as much as 90% of their original corrosion protection after exposure to high temperatures.

Resistance to heat is the major advantage of some, but not all trivalent passivates. Factors that can influence heat resistance include: level of hydration, presence of a topcoat, as well as the specific form that the chrome complex is in. Testing shows that the corrosion performance of certain high performance systems do not deteriorate significantly after being subjected to temperatures of up to 150°C. However longer time and higher temperatures can adversely affect performance.

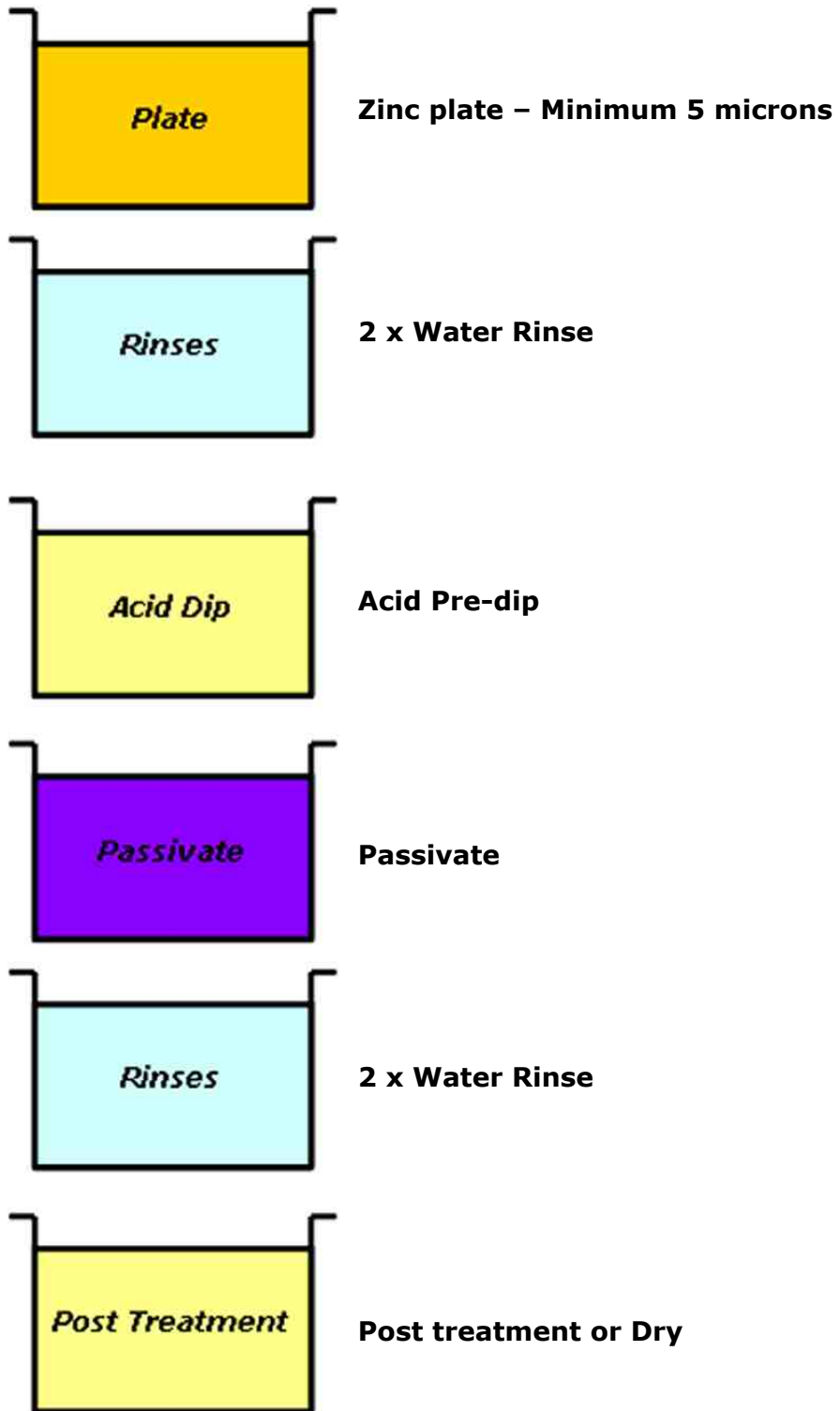
Disposal: Even with the most rigorous process control, eventually a passivate solution reaches the end of its useful life and must be discarded. The absence of hexavalent chromium makes this a much simpler task, as the trivalent chromium is readily precipitated as a hydroxide.

Occasionally, trivalent passivate solutions may contain organic acids, which can complex certain metals. In those cases, iron (in the form of ferric sulfate) is added, to facilitate metal precipitation. A typical waste treatment cycle may look like this:

1. Dilute the working solution 1:1 or more with water.
2. Add 0.5% ferric sulfate (liq. 50% grade).
3. Allow the iron time to react at low pH (1.0-2.0) with the passivate. Mechanical mixing or air agitation for 30 minutes will help.
4. Neutralize to pH 8.0-9.0 with liquid caustic soda, using a properly calibrated pH meter.
5. Add sufficient polyelectrolyte flocculating agent with gentle mixing.
6. Allow to flocculate and precipitate.

Prior to using any recommendations for waste treatment, the user is required to know the appropriate local/state/federal regulations for on-site or off-site treatment, which may require permits. If there is any conflict these regulations take precedent.

Typical process cycle



Troubleshooting guide

Silver passivate film (lacking in blue colour)	
Possible cause	Remedy
High pH	Reduce pH with nitric acid
Low solution temperature	Increase temperature
Immersion time too short	Increase immersion time
Solution too weak	Analyze solution concentration
Drying temperature too high	Reduce drying temperature
Solution exhausted	Prepare new solution

Passivate film 'yellowing' particularly around holes	
Possible cause	Remedy
Low pH	Increase pH with 10% Caustic solution
Too high solution temperature	Reduce temperature
Immersion time too long	Reduce immersion time
Solution too strong	Dilute solution concentration
Transfer time too long	Reduce transfer time
Rinse after passivation contaminated	Renew rinses
Passivate solution contaminated with foreign metals	<ul style="list-style-type: none"> i. Filter solution ii. Discard a proportion of Solution iii. Prepare a new solution

White haze in passivate film, possibly with white powder on surface after drying	
Possible cause	Remedy
Low pH	Increase pH with 10% Caustic
Too high solution temperature	Reduce temperature
Immersion time too long	Reduce immersion time
Solution too strong	Dilute solution concentration
Transfer time too long	Reduce transfer time
Contaminated rinses	Renew rinse water
Passivate solution contaminated with foreign metals	<ul style="list-style-type: none"> i. Filter solution ii. Discard a proportion of Solution iii. Prepare a new solution
Water quality very poor	Check salt concentration (i.e. Ca, Mg, Fe) of water used to prepare passivation solution

Patchy passivate film	
Possible cause	Remedy
No acid pre-dip	Install appropriate acid predip
Solution too strong	Dilute solution concentration
Immersion time too short	Increase immersion time
High pH	Reduce pH with dilute nitric acid