Troubleshooting Chrome Conversion Coatings on Aluminum

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Introduction

Chemical processing steps for chrome conversion coatings are well defined, and have been used in the metal finishing industry since first developed in 1946.

They are widely used for aluminum surface treatment when electrical conductivity is required or the fatigue impact of anodize is too great. The purpose of conversion coatings is predominantly to promote adhesion of the subsequently applied organic film. In addition, conversion coatings change the chemical nature of the surface, which can increase corrosion resistance.

While the chrome conversion coating process is generally reliable defects can arise unexpectedly. This presentation is intended to provide processors with an extensive troubleshooting tool when conversion coating failures are encountered.

Agenda

Coating Defects

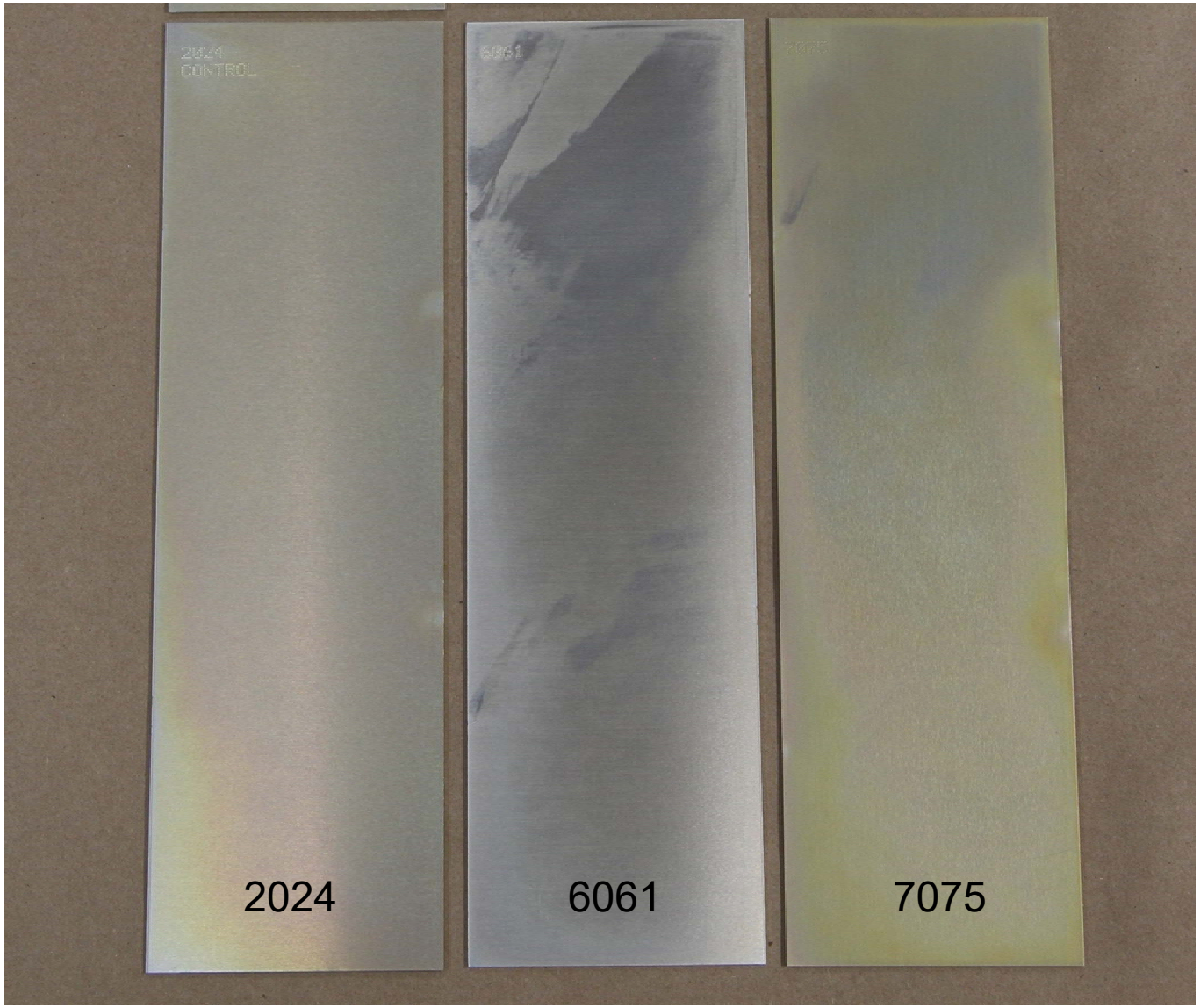
- Selective (Streaky/Blotchy)
- Loose (Powdery)
- Dull Brown
- Salt Spray Failures

Process Break Down of Potential Causes

- Pre-cleaning
- De-oxidizing
- Chrome Conversion Coating
- Rinses
- Drying & Racking
- Testing
- Part Condition

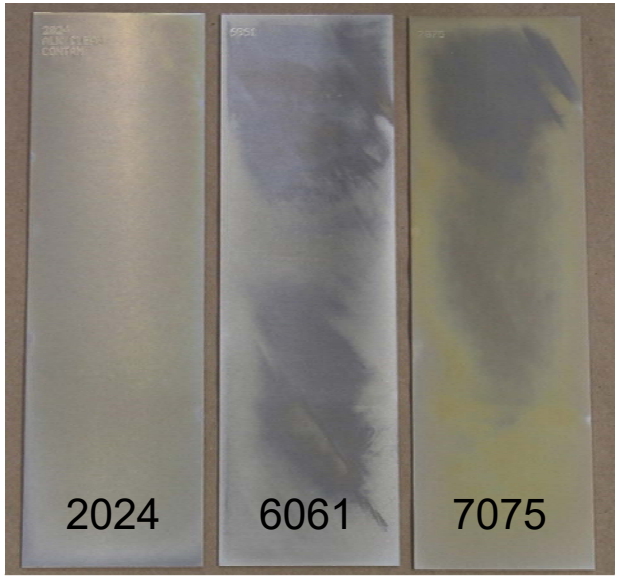
Coating Control Conditions

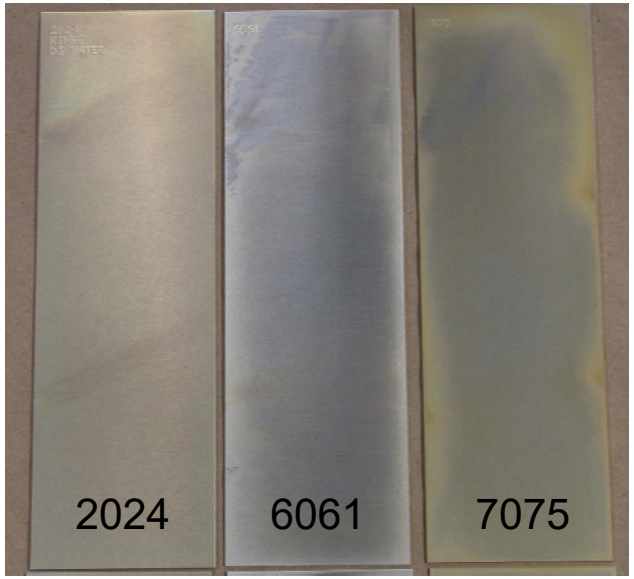
- Solvent Wipe
- Alkaline Clean
  10 min
- Deoxidize
  5 min
- Chrome Conversion Coat
  1 min

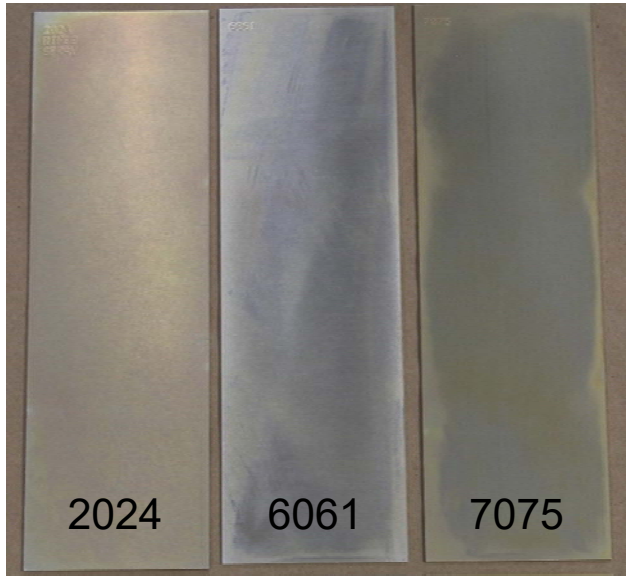


Coating Defect
Selective (Streaky/Blotchy)

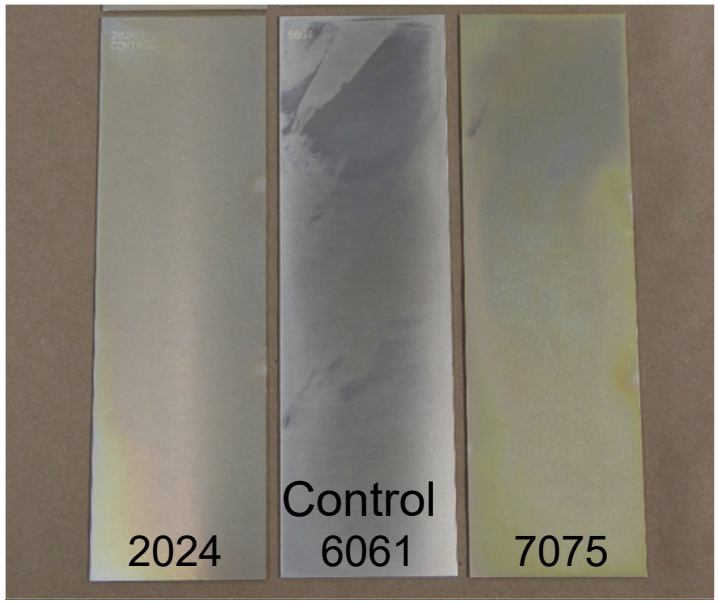
DI Water Rinse







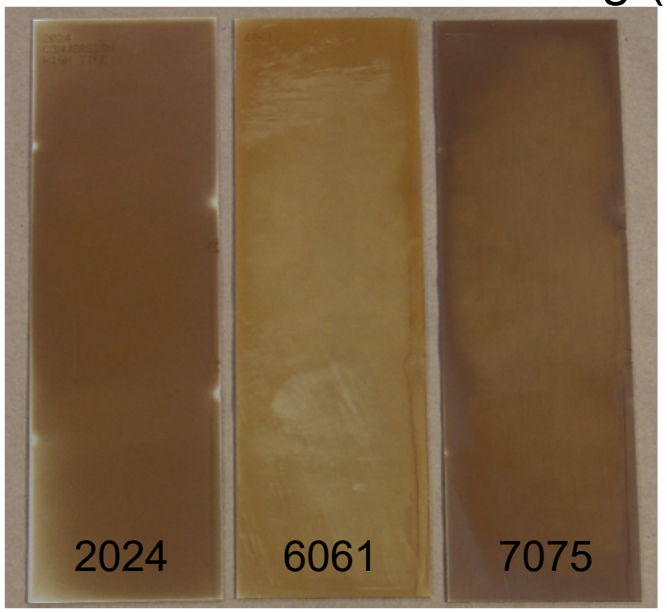
Alkaline Clean
Contamination



Aggressive
Spray Rinse

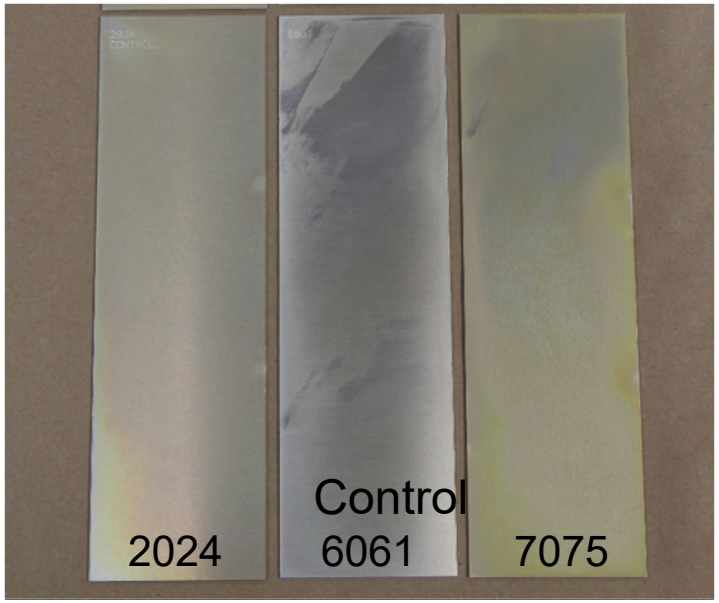
Coating Defects

Dull Brown/Loose Coating (Powdery)



High Time
6 min

Low Time
10 sec

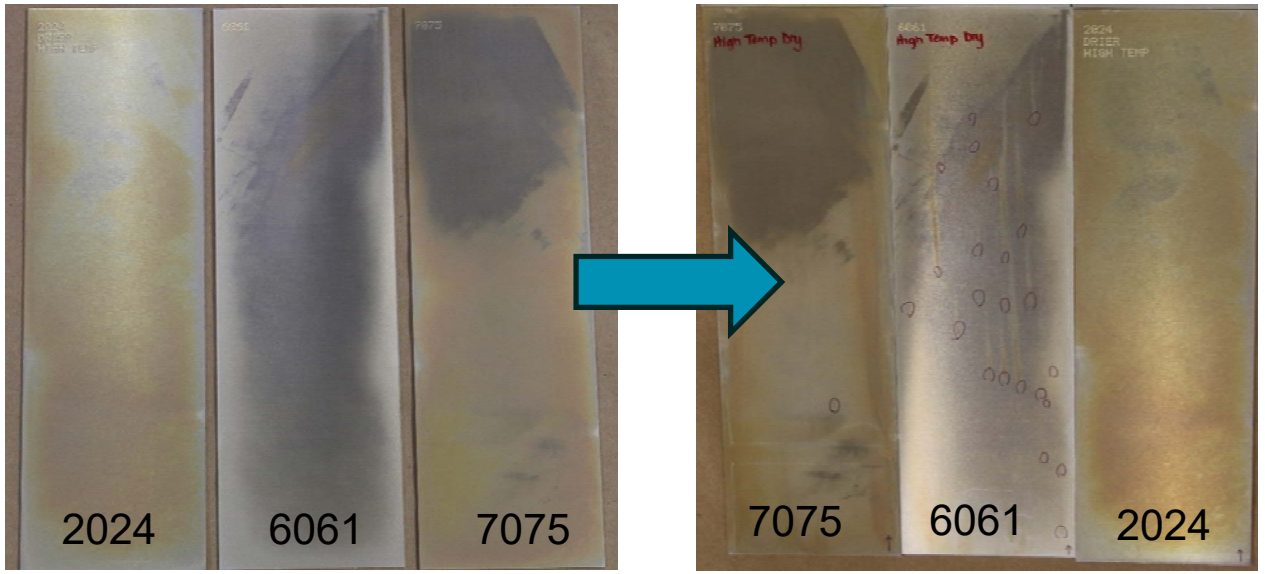


Coating Defects
Salt Spray Failures

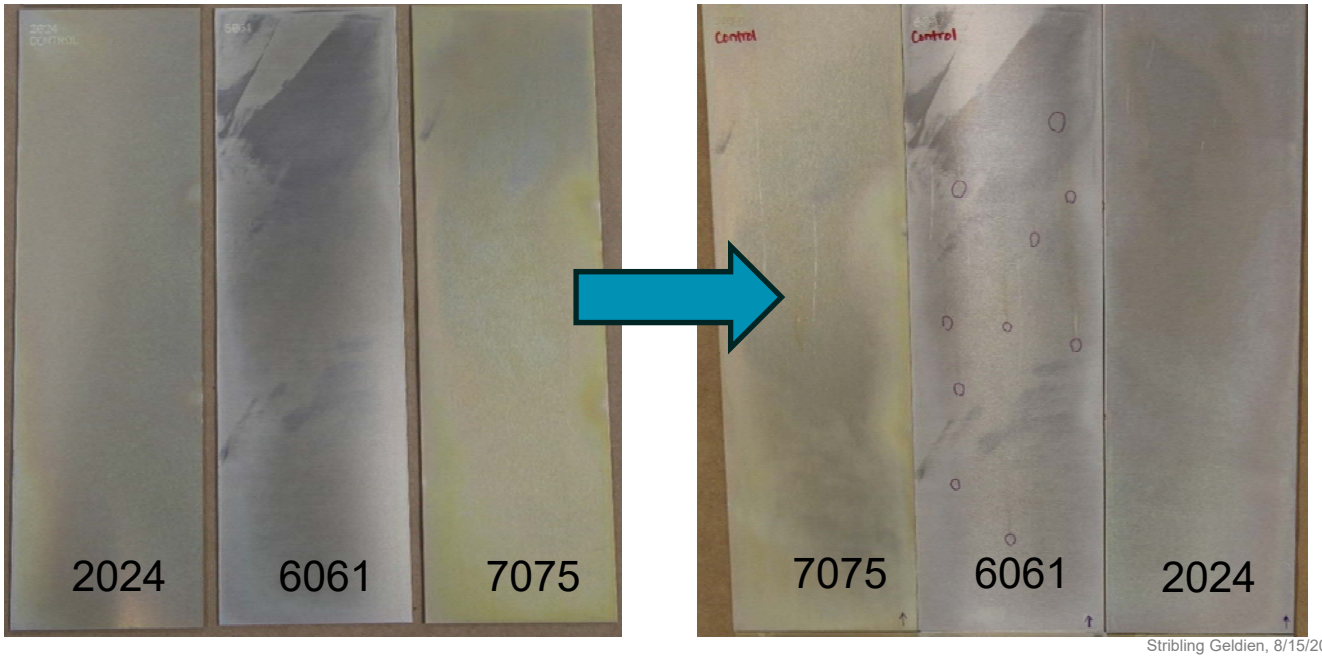
Before Exposure

After Exposure

High Drier Temp
180 F



Control



Precleaning

Conversion Coating Troubleshooting Matrix					
Cause	Condition (Defect)				
	Selective Coating	Loose Coating (Powdery)	Dull Brown Color	Salt Spray Failure	Comments
Solvent Cleaning					
Incomplete removal of inks	X				
Emulsion Degrease					
[Na_2SiO_3] too low (<100ppm)				X	
Excessively long immersion time				X	
Alkaline Cleaner					
Incomplete removal of grease/lube	X				
Concentration too low				X	
Alkaline Etch					
Immersion time					
Too long				X	
Too short	X*				*(scale not fully removed)

Emulsion Degrease

- If the emulsion degreaser is operated at a pH (10.0-11.5), then a corrosion inhibitor is needed (Example Na2SiO3). If the concentration drops below 100 ppm then micro-pitting could result.
- In extreme cases, all the corrosion inhibitor constituents can be lost if exposed to freezing temperatures during shipment. Parts will come out with a thin coating of black smut.
- Excessively long emulsion degrease immersion times should be avoided.

Alkaline Etch

- Early report test results showed that aluminum products that have been etched, either alkaline or acid, exhibit a higher rate of Salt Spray failure. This is thought to be the result of exposing the insoluble alloying elements in the aluminum by etching, thus providing more potential sites for corrosion.
- However, process optimization (reduced immersion time) has made the use of alkaline etch-cleaners commonplace for surface finishing pre-treatment prior to conversion coating.

De-oxidizing

Conversion Coating Troubleshooting Matrix

Cause	Condition (Defect)				
	Selective Coating	Loose Coating (Powdery)	Dull Brown Color	Salt Spray Failure	Comments
Deoxidizer					
Concentration too low					
Mixed acid deoxidizer	X				
Non-Cr deoxidizer (not recommended)				X	
pH is too high				X	
Immersion time					
low	X*			X**	*(smut not fully removed) **(6061 needs longer times)
high				X	(especially for high [Al], aged solutions)
Ion contamination					
Chloride concentration					(more pronounced for non-Cr deoxidizers)
low (<12ppm)				X	(for low [Al], new solutions)
high (>350 ppm)				X	
High [Al] (>11000ppm)				X	(with long immersion times)
High [Cu] (>50ppm)				X	
High [Zn]				X	
High [Fe]				X	
Low Sulfate(<1000ppm)	X				
Too many adds				X	(dump when adds equal tank volume)
Use of sulfuric based deoxidizers				X	(nitric based recommended)
High mineral content in Make-up water				X	
Green color				X	(for Cr-based deoxidizers)
Stray current				X	
Etch rate (too high)				X	
Long dwell time from Deox to rinse	X				

De-oxidizing

Selective Coatings

- Very clean deoxidizer rinses can passivate the deoxidized surface and also cause selective coatings due to a lack of ions in the water. Processors that use deionized water rinses may add an ionizing salt such as sodium sulfate to the final deoxidizer rinse in the concentration range of 15-50 ppm to improve coating uniformity.
- Sulfuric acid deoxidizers can result in drag-out to the conversion coating tank and “poison” that solution. Therefore sulfuric acid based deoxidizers require very clean rinses to avoid drag out of sulfate ions into the chrome conversion coating solution, and are at risk to produce selective coatings.
- Nitric based deoxidizers producing selective coatings have been remedied by adding ~1000 ppm sulfate to the deoxidizer solution.
- Long transfer times between the deoxidizer and deoxidizer rinse can result in selective coatings.

Salt Spray Failure

- Iron-based deoxidizers are attributable to poor salt spray performance. Theorized to be due to drag-out of deoxidizer into the conversion coating solution resulting in an excess of ferrous ion (Fe+2). The ferrous ion contamination contributes to early depletion of Cr(VI) by a simplified redox reaction which lowers the Cr(VI)/Cr(III) ratio, which is also known to be a problem associated with salt spray failure and can possibly result in a dull brown color on the part or panel surface.
- When Iron-based deoxidizers are combined with alkaline etch solutions the ferric sulfate in the deoxidizer and the copper residue on the aluminum surface react to convert to in soluble ferrous. The ferrous will settle in the tank, or be circulated as an insoluble particle and if enough of this material is present it can carry over to the rinse tank and then to the conversion coating tank affecting salt spray performance.
  - If sodium sulfide (from the alkaline etch solution) enters the iron based deoxidizer solution, it will compete with the ferric sulfate constituent of the iron based deoxidizer. The sodium sulfide is not as strong an oxidizing agent as ferric sulfate and will not convert as much insoluble copper to the soluble copper, thus allowing copper to remain on the surface of the aluminum and ultimately negatively affect salt spray performance of the conversion coating.
- Deoxidizer concentration is best to be targeted mid-range.
  - Too Low - in-complete smut removal (if preceded by an alkaline etch) and too high of a pH which is thought to have a detrimental salt spray failure effect.
  - Too High – An etch rate that is too high which could then negatively contribute to Intergranular attack.

De-oxidizing

Ion Contamination

- Iron based deoxidizers are more sensitive to chloride contamination when compared to nitric based deoxidizers. Studies have reported a maximum chloride concentration ranging from 25 ppm to 350 ppm.
  - New deoxidizer solutions having zero or very low levels of chloride (<12 ppm) can also result in salt spray failures. So, it is not recommended to use DI water for deoxidizer solution make-up.
- Long immersion times combined with high levels of Al >11,000 ppm as a solution ages is the reason why an established immersion time can work well for months or even years depending on and then suddenly Salt Spray failures occur.
- Copper, iron, and zinc can come from alloying elements in the aluminum parts or from degrading tankline support structure, auxiliary equipment or fallout from overhead rails during crane movement. No specific high levels are noted for iron and zinc, however reported maximum copper levels of less than 200 ppm for chrome deoxidizers are recommended.
  - High levels of tap water mineral content should be avoided.

Chrome Conversation Coating

Conversion Coating Troubleshooting Matrix					
Cause	Condition (Defect)				
	Selective Coating	Loose Coating (Powdery)	Dull Brown Color	Salt Spray Failure	Comments
Conversion Coating					
pH					
low		X			
high	X			X	
Agitation					
low	X				
high		X			(can also cause surface roughness)
Fluoride concentration					
low	X			X	
high	X*	X			*(when [Al] is low)
Solution concentration					
low				X	
high		X			
Cr(VI)/Cr(III) ratio is low (<1.0)	X		X	X*	*(better if 3:1)
Ion contamination					
High [Fe^{+2}]			X	X	
Chloride concentration					
below 12ppm				X	
above 43ppm (for new solutions)				X	
above 100ppm				X	
above 400ppm			X		
Aluminum concentration					
low	X				(when [F] is high)
high (>250ppm)				X	[Al] can be much higher (2.5g/L) for K3(FeCN)6 conversion coatings

Chrome Conversion Coating

Selective Coating

- New solutions have low aluminum concentration
  - high fluoride concentration
  - Using DI water for conversion coating solution make-up
- Aged solutions
  - Low Cr(VI)/Cr(III) ratio (<1.0)
  - Low fluoride concentration
  - High pH
- Poor solution agitation
- Low solution temperature

Loose Coating (Powdery)

- High agitation
- High Temperature
- High Immersion Time
- Heavy coating weight
  - The conversion solution reacts with the metal surface building a coating, but is self-limiting. If work is allowed to process beyond the period of surface coating formation the solution will continue to deposit creating a loose layer on top of the adhered coating.
  - If work is allowed to contact the solution for extended process times the acidic conversion solution may begin to attack the newly formed conversion coating.
- Failing paint adhesion can be an indication of loose coating.
- Powdery coatings can be caused by a solution that is too “aggressive” such as when the pH is low, the concentration is high and the fluoride concentration is high.

Chrome Conversation Coating

Conversion Coating Troubleshooting Matrix					
Cause	Condition (Defect)				
	Selective Coating	Loose Coating (Powdery)	Dull Brown Color	Salt Spray Failure	Comments
Combined [Cl] + [SO_4] is high (>400ppm)				X	
Sulfate concentration is high (>400ppm)				X	
Nitrate concentration is high (>200ppm)				X	
Copper concentration is high (>30ppm)				X	
Zinc concentration is high (>10ppm)				X	
Calcium concentration is high (>25ppm)				X	
Phosphate is high (>25ppm)				X	[PO4] can be much higher (2000ppm) for K3(FeCN)6 conversion coatings
Use of DI water for solution make-up	X				
New bath was not “seeded”				X	
Immersion Time					
Low	X			X	
High		X			
Temperature					
Low	X			X	
High		X			
Excessive transfer times		X			

Chrome Conversion Coating

Salt Spray Failure

- Aged solution is more reliable due to a build up of suspended insoluble salt particles.
  - If a chrome conversion coating solution must be completely discarded it is advantageous to retain a portion of the old solution as a “seed” of built up suspended particles of insoluble salt. K2NaAlF6, is theorized to draw newly etched Aluminum ions from solution which helps extend tank life. A commonly used amount of seed is 25-50% of the bath solution however if old solution is not an option due to contamination use of 2024 bare Aluminum sheet stock to artificially age new solution can be considered16,18.
- Chemical constituents of the conversion coating
  - Low Fluoride concentration
  - Low solution concentration
  - High pH
  - Low Cr(VI)/Cr(III) ratio (solution exhibits a green hue)
- Low coating weights from short immersion time, and low temperature
- Ionic contamination
  - Cation build-up can occur as a result of alloying elements
    - Copper over 30 ppm.
    - Iron contamination lowering the Cr(VI)/Cr(III)
    - Calcium, which should be kept at less than 25 ppm
    - Zinc over 10 ppm
  - Anionic contaminants
    - Chloride has a range of recommended maximum concentrations from a low of 25 ppm to a high of 350 ppm
    - Combination chloride and sulfate at 400 ppm or between 175 ppm to 800 ppm.
    - Phosphate has been noticed to be problematic depending on the conversion coating type.
      - Solutions with potassium ferricyanide: phosphate concentration of up to 2000 ppm.
      - Solutions without potassium ferricyanide: phosphate contamination level of up to 25 ppm.

Rinses

Conversion Coating Troubleshooting Matrix					
Cause	Condition (Defect)				
	Selective Coating	Loose Coating (Powdery)	Dull Brown Color	Salt Spray Failure	Comments
Rinses					
Alkaline Clean Rinse					
Transfer time too slow	X				
Long immersion time in first rinse				X	
TDS too high				X	
Contamination (that causes micro-pitting)				X	
Deoxidizer Rinse					
Less than 60ppm TDS (avoid DI)	X			X	
Contaminated final rinse		X		X	
Long immersion time				X	(especially if preceded by long deox time)
Conversion Coating Rinse					
Misaligned spray nozzles	X				
Clogged spray nozzles	X				
High ambient temperature	X				
Low pH in first rinse (<4.0)		X			
Excessive spray velocities	X			X	
TDS too high (>1000ppm)				X	
Temperature too high	X				

Loose Coating (Powdery)

- Rinses that follow the Deoxidizer process solutions that are highly contaminated can result in loose coatings to form. Consequently, the final rinse following the deoxidizer step should be controlled at less than 750 ppm.
- The first rinse that follows the Conversion Coat Process solution can cause loose coatings if it is too acidic. This is why the Boeing Process Specification25 requires that first rinse to have a pH above 4.0

Rinses

Selective Coatings

- Avoid long transfer times
  - Alkaline clean solution rinses are often heated and inadvertent drying of the rinse water can result in the part surface being lightly masked by residual cleaner going into the deoxidizer tank. The slightly masked part surface will unevenly deoxidize, and if part surfaces have been selectively deoxidized, they will then take on the conversion coat unevenly which will exhibit a streaked appearance.
- Deoxidizer rinses can be too clean resulting in passivation of the freshly deoxidized surface. Boeing process specifications note

  "Rinses that contain less than 60 ppm total dissolved solids (TDS) following nitric acid based deoxidizers, may inhibit localized color development of subsequent chemical conversion coatings."
- Conversion coating rinse conditions to watch for are:
  1. Spray rinses that have misaligned or clogged nozzles.
  2. Spray rinses where the water pressure is too high potentially damaging the still soft conversion coating.
  3. Ambient temperatures that are too high.
- Avoid aggressive spray rinsing
  - The fresh conversion coating having not yet been dried is subject to uneven or aggressive spray rinsing.
- Avoid High temperature rinses which can leach chromates

Salt Spray Failure

- Avoid long immersion times in the first alkaline clean rinse.
  - Micro-pitting of the part surface from the first alkaline clean rinse (which is still fairly high in pH) can selectively alkaline etch at the micro-structure level. Consequently long immersion times in a first rinse following an alkaline clean process solution should be avoided.
  - The final rinse following an alkaline clean process should be maintained at less than 750 ppm total dissolved solids
- Avoid deoxidizer rinse water that is too clean
- Avoid long deoxidizer immersion rinse time
- Spray rinses following conversion coating that have excessive velocities adversely impact the fresh conversion coating that has not yet had a chance to dry and harden.
- Final conversion coating rinses which are highly contaminated (Boeing Specs recommend TDS level <1000 ppm.

Drying and Racking

Conversion Coating Troubleshooting Matrix

Cause	Condition (Defect)				
	Selective Coating	Loose Coating (Powdery)	Dull Brown Color	Salt Spray Failure	Comments
Dryer					
Temperature					
High (>130F)				X	
Low (< 90F)				X	
Dirty (FOD blows onto wet part)	X			X	
Racking					
Contact of parallel surfaces	X				
Entrapped solution draining down part	X				
Dirty Hooks	X				

Salt Spray Failure

- Drying conversion coating above 160F or for long dry times
  - A mud-cracking phenomenon of the conversion coat surface can happen which then gives a salt spray solution easy access to the unprotected aluminum surface.
- Drying conversion coatings below 90F
  - Perhaps, the newly formed amorphous gel coating does not properly coalesce.

Selective Coating

- Parts or panels are racked too close together can result in the flat part surfaces coming into contact with each other and thus creating poor process solution exposure and poor rinsing conditions.
- The cleanliness and design of racking can cause streaking such as when the hooks are not maintained and become dirty or if the rack entraps solution which can run down the parts when in flight between rinse tanks or when moved to the next process step.

Testing

Conversion Coating Troubleshooting Matrix					
Cause	Condition (Defect)				
	Selective Coating	Loose Coating (Powdery)	Dull Brown Color	Salt Spray Failure	Comments
Testing					
Panels					
Mylar residue not fully removed	X				
Unseen micro-pitting (storage issue)				X	
Ungloved hands				X	
Roll code not fully removed				X	
Cleaning with acetone				X	
Storage in desiccator				X	
Wet panels placed on brown Kraft paper				X	
Short age times (<48 hours)				X	
Operator variation				X	
Rust in salt spray chamber				X	
Rough handling during transport				X	
Spray impingement				X	
Condensate splatter during lid opening				X	

Selective Coatings

- Test Coupon protective Mylar film can be detrimental if
  1. Stored too long
  2. High humidity or High ambient temperature storage conditions
  3. A bad batch of Mylar film

Testing

Salt Spray Failure

- Test Coupons with segregated Copper or Silica rolled onto the surface at the mill that may not be removed by chemical methods.
- Test Coupons with corrosion are often times the result of
  - Age
  - Improper storage
  - Storing panels in brown Kraft paper. If the paper becomes wet it can leach sulfuric acid.

Part Condition

Conversion Coating Troubleshooting Matrix

Cause	Condition (Defect)				
	Selective Coating	Loose Coating (Powdery)	Dull Brown Color	Salt Spray Failure	Comments
Part Condition					
Work hardened (uneven Zn at surface)	X				
Inclusions				X	
Part geometry that is susceptible to coating fracture				X	(A600 best for tubing)
Heavy surface oxide	X				
Use of soap as media for Vibra Debur		X			

Selective Coatings

- 7075 aluminum alloys parts that are work hardened can have uneven Zinc in the surface layer which in turn will cause a blotchy appearance on the part surface.
- Heavy surface oxides where the selected deoxidizer is unable to remove the oxide uniformly

Part Condition

Loose Coating (Powdery)

- Vibra-Debur can involve use of a media that is comparable to a powdered detergent cleaner.
  - Conversion coatings do not all react the same when preceded by a Vibra-Debur process

Pitting

- Heavily machined parts are subject to micro-inclusions that cannot be seen readily without magnification. These micro-inclusions can be revealed during the tankline process as pitting at the inclusion site due to a galvanic corrosion.

Summary

This Chrome Conversion Coating process break down is intended to be used as a tool by engineering to quickly categorize issues by identifying defects and systematically reviewing the potential causes to implement corrections and stabilize the process avoiding lengthy investigation.

Since employing this technique at Boeing, being aware of the known defect types and related causes, Boeing has predominately avoided these types of defects in over a decade.

Questions?