



DoD Metal Finishing Workshop – Chromate Alternatives for Metal Treatment and Sealing

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Alternatives to Hexavalent Chromates: An Evolution of Trivalent Passivate Technologies

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Introduction

- For over ten (10) years, the substitution of chromate processes on zinc and zinc alloys has been the main focus of chemical suppliers' R&D departments.
- Passivates based upon trivalent chromium seem to be the accepted replacement.
- These passivates have developed through several generations to provide comparable alternatives to predecessor chromate films.
- Future generations will be completely free of chromium compounds.



Introduction

- **ELV** (End-of-Life Vehicle), **RoHS** (The Restriction of Hazardous Substances in Electrical and Electronic Equipment) and **WEEE** (Waste Electrical and Electronic) Directives mandate the elimination of hexavalent chromium by July 1, 2006 (RoHS, WEEE) and July 1, 2007 (ELV).



Introduction

- While OEM specifications evolve to exclude hexavalent chromium, they also evolve to include increased requirements in terms of deposit quality.
- Initial field results indicated certain restrictions – mainly consistency of corrosion protection afforded by trivalent passivates.
- Self-healing properties of coatings produced from typical “thick film” trivalent passivates are inferior to those of hexavalent chromates.



The Replacement of CrVI

- The use of hexavalent chromates presented a number of advantages, namely excellent corrosion resistance, self-healing properties, relatively low cost and a wide range of identifiable colors (clear, yellow, black, olive drab).
- Despite all of these advantages, there is one major drawback to the use of CrVI - it's toxicity.



The Replacement of CrVI

- The mechanism of film formation is markedly different in CrVI and CrIII.
- CrVI oxidizing action is provided by ions such as chromate and dichromate.
- CrIII oxidizing action is provided by nitrates.
- The resultant trivalent film is much thinner.



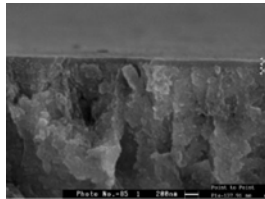
CrIII Passivates

- To improve performance, these thin CrIII films needed to be enhanced. The first step to achieving this goal was to increase active ingredients, temperature, time, etc.



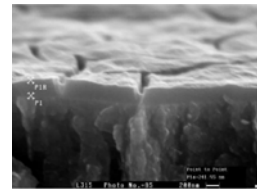
1st & 2nd Generation Passivates

- 2nd Generation adds “more of same” (chromium, temperature, fluoride) to 1st to increase NSST performance.
- Thickness: ~ 100 nm
- Temperature: Ambient
- Appearance: Clear/Blue
- Corrosion protection: 24-48 HRS to WR in 5% NSST
- Need topcoat (silicate, polymer, wax, etc.) to meet automotive requirements
- Thermal shock resistance exceeds that provided by chromate films.

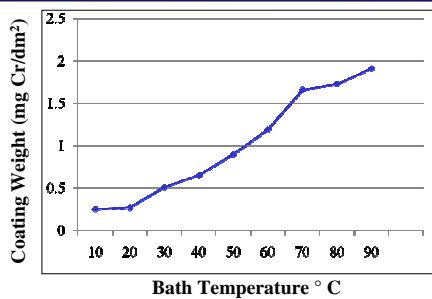


3rd Generation – “Thick Film” Passivates

- Thickness: 200-250 nm
- Temperature: 60°C
- Base: Organic Acid
- CrIII: 10 g/L
- Corrosion Protection: 250 HRS to WR in 5% NSST
- Appearance: Iridescent Green/Yellow
- Inconsistent NSST Results
- Potential for Waste Treatment Difficulties

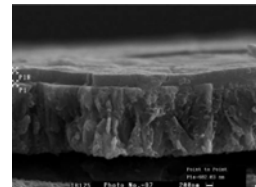


3rd Generation Passivates

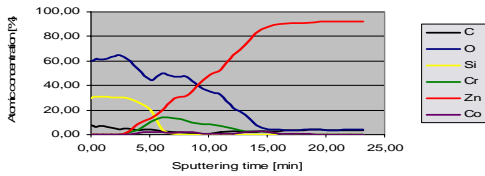


4th Generation Passivate

- Thickness: 400 – 500 nm
- Temperature: Ambient
- Base: Nano-Particle
- Appearance: Clear/Iridescent
- Corrosion Protection: 250 HRS + to WR in 5% NSST
- Self-Healing
- Totally Inorganic – No WT or Stability Issues
- Excellent Heat Resistance
- Consistent results



Composition – 4th Generation (TASDIP TR-175)

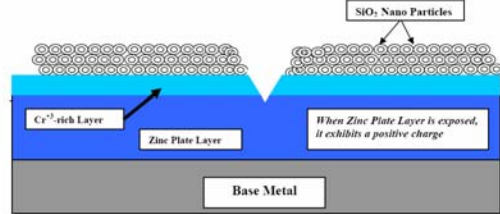


Element	Mass percentage in the film
C	9
O	45
Si	32
Cr	6
Zn	8



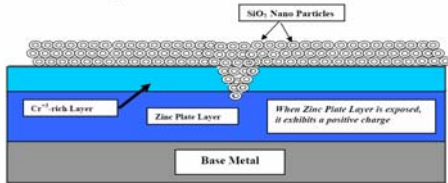
Graphic Explanation of Self-Healing Mechanism 4th Generation Passivate

Appearance Immediately After Passivate Film is Compromised:



Graphic Explanation of Self-Healing Mechanism 4th Generation Passivate

Appearance After Passivate Film "Heals":



Particles from the Special Protective Layer are negatively charged, and are attracted to the positively charged exposed Zinc. When they migrate to the scratch, they fill it in, thus automatically "healing" the defect.



Progression of CrIII Technology



1st & 2nd Gen.

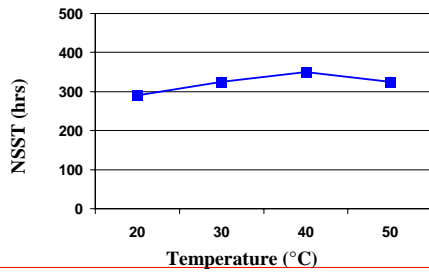
3rd Gen.

4th Gen. TR-175

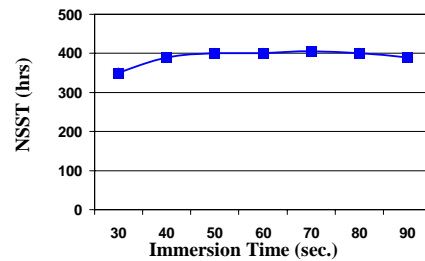
CrVI



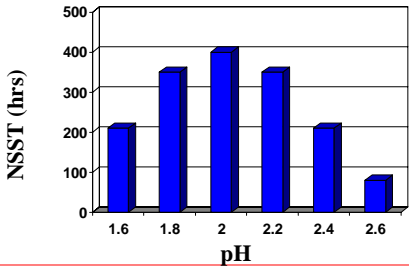
NSST Performance Vs. Temperature – 4th Generation Passivate (TASDIP TR-175)



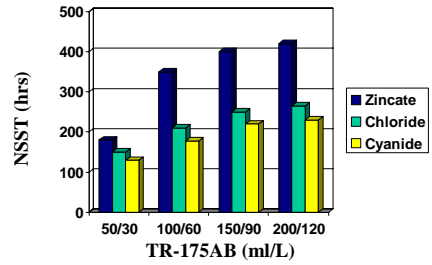
NSST Performance Vs. Time: 4th Generation Passivate (TASDIP TR-175)



NSST Performance Vs. pH: 4th Generation Passivate (TASDIP TR-175)

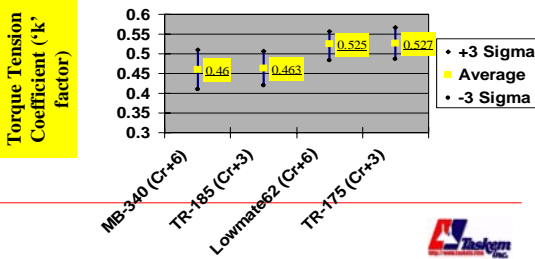


NSST Performance Vs. Zinc Electrolyte and Concentration - 4th Generation Passivate (TASDIP TR-175)



TR-175 Compared to Other Conversion Coatings

Aspect	Black		Yellow/Clear	
	Hexavalent Chromium	Trivalent Passivate	Hexavalent Chromium	Trivalent Passivate
Passivate	MB-340	TR-185	LOWMATE 62	TR-175
Post Treatment	RB-775	FT-190	N/A	N/A
Avg. + 3 Sigma	0.510	0.506	0.556	0.567
Ave.	0.460	0.463	0.525	0.527
Avg. -3 Sigma	0.410	0.420	0.483	0.487



4th Generation Technology –

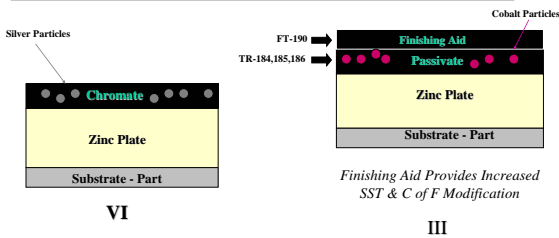
Zinc Alloys

- Excellent corrosion protection with Zn/Fe and high alloy Zn/Ni (300 + WR).
- Eliminates the need for topcoats/sealers common to alloy passivates.



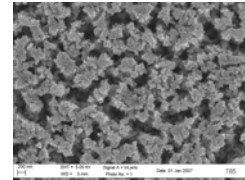
Black Passivates

Structure of CrVI Vs. CrIII Black



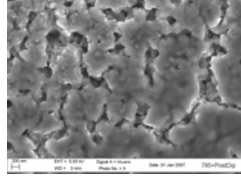
TASDIP TR-185 Passivate

- Thickness: 700 nm
- Temp.: 40°C
- Film: 0.6 mg Cr/dm²
- Corrosion protection: 72-96 HRS to WR in 5% NSST
- Appearance: Uniform Black
- Excellent Heat Resistance
- Consistent Results
- Exceptional Bath Stability
- Post Treatment - Yes



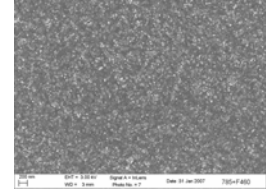
TASDIP TR-185/TASDIP FT-190

- Thickness: > 1µm
- Film: 1.2 mg Cr/dm²
- TASDIP FT-190 Base: Cr⁺³
- Temp.: 45°C
- Corrosion Protection: 192 HRS + to WR in 5% NSST
- Appearance: Uniform Black
- Excellent Heat Resistance
- Exceptional Bath Stability
- Consistent Results



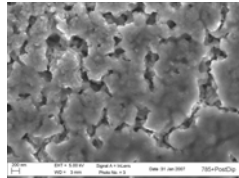
TASDIP TR-185/TASCOAT Finigard 460

- Thickness: 2.5 µm
- Film: 0.6 mg Cr/dm²
- 460 Base: Silicate/Polymer
- Temp.: Ambient
- Corrosion Protection: 168 HRS + to WR in 5% NSST
- Appearance: Uniform Black
- Excellent Heat Resistance
- Exceptional Stability
- Self-Healing
- Consistent Results



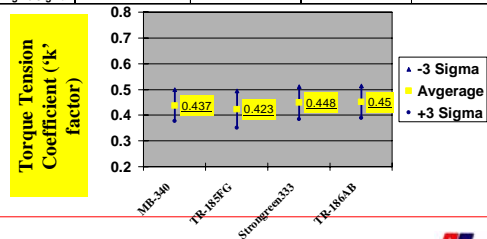
TASDIP TR-186AB/TASDIP FT-190B

- Thickness: >1.5 µm
- Film: 1.6 mg Cr/dm²
- FT-190B Base: Cr⁺³
- Temp.: 45°C
- Corrosion Protection: 240 HRS + to WR in 5% NSST
- Appearance: Uniform Green/Black
- Excellent Heat Resistance
- Exceptional Bath Life
- Exceptional Bath Stability



TR-186AB Compared to Other Conversion Coatings

Aspect	Black		Green	
	Hexavalent Chromium	Trivalent Passivate	Hexavalent Chromium	Trivalent Passivate
Type	MB-340	TR-185FG	Strongren 333	TR-186AB
Post Treatment	RB-775	FT-190	N/A	FT-190B
Avg. + 3 Sigma	0.499	0.474	0.511	0.512
Avg.	0.437	0.400	0.448	0.450
Avg. -3 Sigma	0.376	0.326	0.385	0.388



Future Generations...

- Goal is to continually improve performance.
- Achieved via wider operating windows, reduced costs, etc.
- CrIII free alternatives.



Conclusion

Thank You for Your Time and Attention!

Questions?

