Development of a Novel Hexavalent-Chromium-Free Aluminum Sacrificial Paint

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SUR/FIN 2022
Where Finishing Connects

Hexavalent Chromium is a known carcinogen, repro-toxin, and mutagen. Its elimination is of high importance to the aerospace industry which has struggled to find high performing alternatives. Legacy aluminum sacrificial paints have traditionally utilized hexavalent chromium to prevent corrosion and oxidation of steels. Due to the high performance nature of these coatings, work to approve alternate coatings has been difficult. To date, most attempts have failed.

The process of developing a novel hexavalent-chromium-free aluminum sacrificial paint will be summarized. The history, failures, and key factors will be summarized. This presentation is intended to be tandem with the Rolls-Royce presentation on the testing results of this novel coating system.

- How It All Began.
  - Sacrificial Al-Ceramics Enable Gas Turbine Development.
- The Poison Pill.
  - Hexavalent Chromium (Cr^{+6}) Poses Problems.
- Stumbling Away from Cr^{+6}.
  - Steps and Missteps Toward A Safe Alternative.
- An Answer at Last?
  - A More Suitable Cr-Free Coating System.
- Lessons Learned.

For Want of a Nail . . .

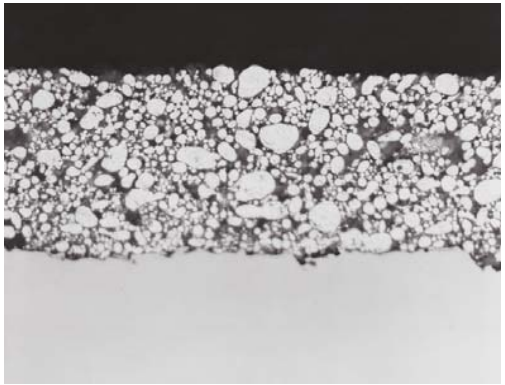
- In the 1950's, development of viable flight gas turbine engines was hindered by the lack of coatings to protect steels from salt corrosion and heat.
- Apart from aluminum-flake filled stoving enamels, there were few coatings that would remain well-bonded to steels at the temperatures being seen in these innovative designs.

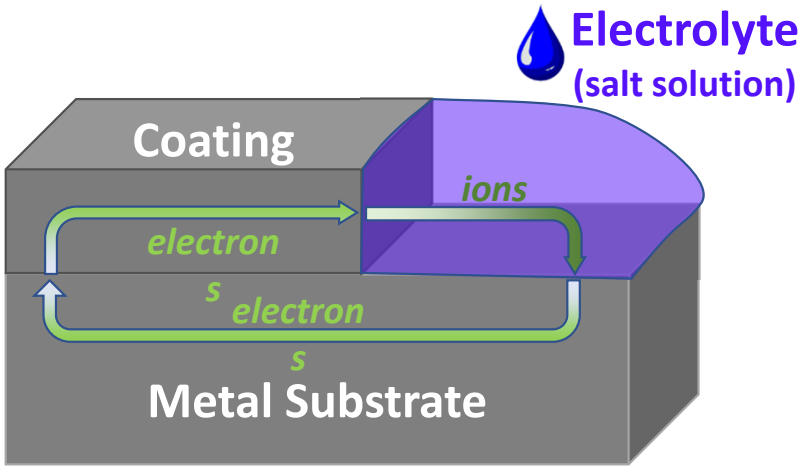
Do Not Despise Small Beginnings . . .

- In 1963, Teleflex Inc. (North Wales, PA) was granted a patent for a glassy, heat-curable, aqueous binder that combined phosphoric acid with 5-6 wt. % chromic acid (50, to 60,000 ppm Cr^{+6}).
  - US 3,248,251 – Charlotte Allen.
- By 1965, Pratt, Allison (now Rolls-Royce), and GE were protecting steel shafts and compressor cases in their turbines with a coating of aluminum powder dispersed in this binder.
- The Al-filled slurry sprayed like a paint, yet when baked at 600^{o}F it limited oxidation and salt corrosion of steels up to 1000^{o}F.

An Unexpected Capability

- Soon it was discovered that the aluminum-chromate/phosphate coating would become electrically conductive when it was baked for 90 minutes at 1050ºF or lightly blasted with fine grit or beads. When conductive, the coating was galvanically sacrificial.



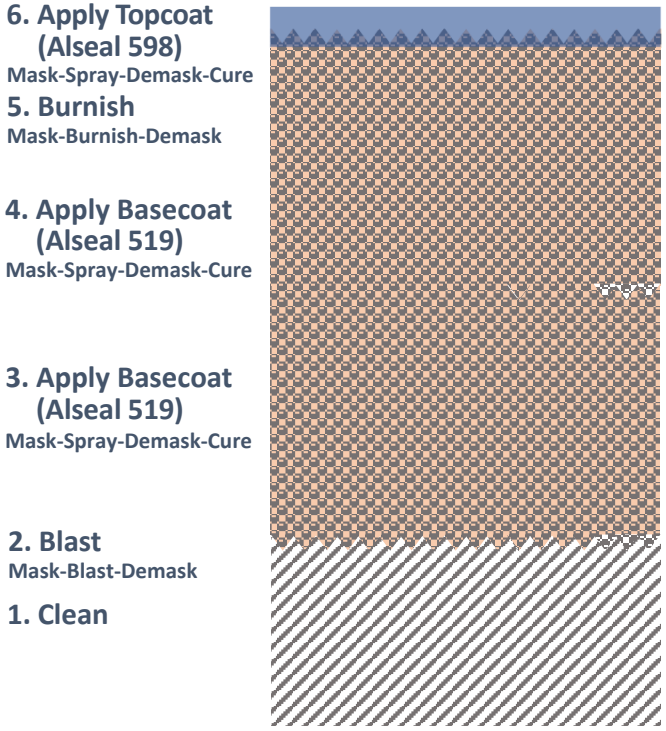


Building Upon A Good Thing

- In 1970, Teleflex introduced a chromate/phosphate sealer for burnished (sacrificial) SermeTel™ W creating a sealed coating system, SermeTel™ 725, with longer life in high salt environments.
- In 1975, Teleflex's Sermatech Division introduced Process 5375, mechanically polished smooth SermeTel W that increased flight turbine efficiency and reduced fuel consumption by as much as 2%.
- SermeTel 5380DP, a smoother, sealed and more corrosion resistant coating, that did not need polishing supplanted Process 5375 in 1980.
- In 1980, Coatings For Industry patented Alseal 500 which cured at temperatures low enough to allow its use on aluminum & HSLA steel.

Firmly Established Standard

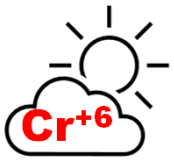
- By 1980s, chromate/phosphates specified by every major turbine engine OEM and many airframe OEMs.
  - PWA 110-21, GE F50TF62, Siemens 83342NU, GE P16-AG5, RPS 666, Allison PM 1314, MIL-C-81751B
  - Metallic-Ceramic Cathodic Coating (MCCC)
- Chromate/phosphate binder utilized in sealers and other functional coatings.
- Trade names:
  - SermeTel™ (Praxair), Alseal™ (Coatings For Industry), IPcote™ (Indestructible Paints), Ceral™ (CeralUSA/Morant)



Performance of Al-Chromate/Phosphates

	Al-Chromate / Phosphate
Sacrificial Corrosion Resistance 5% Salt Fog per ASTM B117 (2 mil/50 μm on steel, scribed)	no rust in 1000 hrs.
Max. Continuous Heat Resistance	1050°F (566°C)
Max. Peak Heat Resistance	1150°F (621°C)
Heat/Salt Corrosion Resistance Ten cycles; 6 hrs. @ 750°F/399°C/16 hrs., 5% salt fog (2 mil/50 μm on steel, scribed)	no rust in 10 cycles
Bend Test 90-degree bend around 1/4”mandrel (2 mil/50 μm coating on 0.04" steel panel)	no flaking
Hot Lubricating Oil 8 hrs. partly immersed, 400°F/204°C MIL-L-7808 oil	no effect
Hot Deionized Water (open) 24 hrs. partly immersed, 120°F/49°C	no effect

The Hidden Hazard



- The heat-curable ceramic binder Charlotte Allen had patented combined chromium trioxide (chromic acid) and phosphoric acid.
- While trivalent chromium (Cr^{+3}) was known to be a nutrient essential for human health, chromic acid (hexavalent chromium - Cr^{+6}) was known to pose health risks.
- That's why OSHA limited Permissible Exposure Limits (PEL) for workers to no more than 0.1 mg Cr^{+6}/m^3, requiring protection and monitoring when there was > 0.052 mg Cr^{+6}/m^3.

The “Simple” Fix: Remove Cr^{+6}

- Recognizing the risks posed by Cr^{+6}, around 1990, companies began developing Cr-free alternatives to the Allen binder.
- In 1993, Solar Turbines was granted the 1st patent for a Cr-free aluminum-phosphate coating composition. It was stabilized with vanadium pentoxide (V_2O_5), a toxin.
- By 2011, sixteen (16) US Patents had been granted for acid-phosphate binder chemistries containing no Cr^{+6} that could be used to make a heat-curable aluminum-ceramic.
- Every Cr-free acid-phosphate had/have limited shelf-life (no more than a few hours) and reacted with bare, blasted steel.

Cr^{+6} Hazard Revealed

- In 2000, Cr^{+6} in the water supply is indicted as cause of increasing cancer rates in Hinckley, CA. The fight to bring the company responsible for the contamination to justice is dramatized in the film "Erin Brockavitch" and the hazards of Cr^{+6} are no longer a secret.
- At the same time, airborne Cr^{+6} is linked to increased rates of lung cancer.
- A study published in 2004 estimates that exposure at 0.1 mg Cr^{+6}/m^3 permits an excess risk of lung cancer death that exceeds 1 in 10. In 2005, ~1 million US workers exposed to Cr^{+6}.

Back to Square One

- Blocked by patents on Cr-Free acid-phosphate binders, in 2001 Coatings For Industry, develops a heat-curable aluminum-filled inorganic silicate (water-glass) slurry that can be baked to form an aluminum-ceramic coating.
- The single component slurry has a one-year shelf-life. It is unreactive with steels and, when cured, it can be made electrically conductive and galvanically sacrificial by the same means now used for Al-chromate/phosphates.
- In 2003, CFI files for a patent on its innovative slurry.
- In 2010, Praxair is granted a patent on its own aluminum-silicate.
- The patent for CFI's Al-silicate finally issues in 2014.

Clamping Down on Cr^{+6}

- Acknowledging the risks of Cr^{+6}, in 2006, OSHA lowered the PEL for Cr^{+6} to 5 micrograms/m^3, a 20-fold reduction in the 8-hr. limit per employee. Employers must protect and monitor workers when exposure is a mere 2.5 micrograms of Cr^{+6} per cubic meter of air.
- And the European Chemicals Agency (ECHA), classifying chromium trioxide as a "substance of very high concern", proposes to restrict its use in the EU. ECHA's REACh regulations become law in 2017. Users must now be authorized (for a substantial fee) to import materials containing > 1000 ppm of Cr^{+6}, registered to use it and report how much they use. (Al-chromate/phosphates contain 30K – 55K ppm Cr^{+6}.)

The DoD's Preemptive Strike

- Anticipating OSHA's lowering of the PEL for Cr^{+6}, in 2005 the US DoD established The Propulsion Environmental Working Group (PEWG).
  - "Industry and government leaders striving to insert clean, safe, and cost-effective sustainment technology improvements in the propulsion community."
- PEWG's goal: "The Ultimate Green Engine"
  - Made with parts that lasted it's designed lifetime,
  - Contained no toxic materials,
  - Built, maintained, reworked without using or releasing any hazardous materials, with
  - Valuable components and/or materials recoverable at life's end.

Al-Ceramic Coatings Circa 2005

	Binder	%Cr^{+6}	ppm
• **Al-Ceramic Sacrificial Basecoat**			
SermeTel™ W/962 (Praxair)	chromate/phosphate	3.3 wt. %	30,000
Alseal™ 518/519 (Coatings For Industry)	chromate/phosphate	3.3 %	30,000
Ceral™ 114* (Morant GmbH, CeralUSA)	chromate/phosphate	(?) ~1.5 %	(?) 15,000
SermeTel CF 1725 (Praxair)	phosphate-borate	0 %	0
Alseal 5000 (now Alseal 5K)	sodium-lithium silicate	0 %	0
• **Ceramic Topcoat**			
SermeTel 570A/TCS-565 (Praxair)	chromate/phosphate	<5.0 wt. %	<50,000
Alseal 598	chromate/phosphate	5.1 %	51,000
VPW 350/Ceral 50*	chromate/phosphate	(?) <0.1 %	(?) 1,000
SermeTel CF 1726 (Praxair)	acid-phosphate	0 %	0
Alseal 5200 (now discontinued)	inorganic silicate	0 %	0

(* According to SDS contains "chromium oxide, CrO_3")

Moving (the) Target

- Using specs for Cr^{+6} slurries as a guide, PEWG seeks a Cr-free candidate(s) that match SermeTel W's performance.
- Finding no Cr-Free match in all tests, PEWG embraces a "low Cr^{+6}" Al-chromate/phosphate.

JTP Section	Test	SermeTel® W	Cr-Free aluminum-phosphate	Cr-Free aluminum-silicate
4.1	Electrical Conductivity	✓	✓	✓
4.2	Salt Fog Corrosion (Unburnished/No scribe)	✓	✓	×
4.2	Salt Fog Corrosion (Burnished/Scribe X/with and without topcoat)	✓	✓	✓
4.3	Cyclic Heat/Salt Spray Corrosion Test (Burnished/Scribe X)	✓	✓	✓
4.4	Abrasion Resistance		✓	×
4.4	Chipping Resistance	✓	✓	✓
4.4	Particle Erosion	✓	✓	×
4.5	Thermal Stability	✓	✓	✓
4.6	Elevated Temperature Material Compatibility	✓	✓	✓
4.7	Humidity Exposure	✓	×	✓
4.7	Pencil hardness after HE	✓	×	✓
4.8	Fluid Immersion (Hot H_2O)	✓	✓	×
4.8	Fluid Immersion (Hot Lube Oil)	✓	✓	×
4.8	Fluid Immersion (Anti/deicers)	✓	-	×
4.8	Fluid Immersion (Hydraulic fluid)	✓	✓	×
4.8	Fluid Immersion (Fuel)	✓	✓	×
4.9	Adhesion: 17-4PH	×	×	✓
4.9	Adhesion: 4340	×	×	✓
4.9	Adhesion: 4130	✓	×	✓
4.9	Adhesion: IN718	×	×	✓
4.9	Adhesion: A286	×	×	✓
4.10	Strip-Ability		✓	
4.11	Hydrogen Embrittlement	✓	✓	✓
4.12	Electrochemical	✓	✓	✓
4.13	Constant Amplitude Axial Fatigue (High Cycle Fatigue)	✓	✓	✓
4.14	Stress Corrosion Cracking	✓	✓	✓

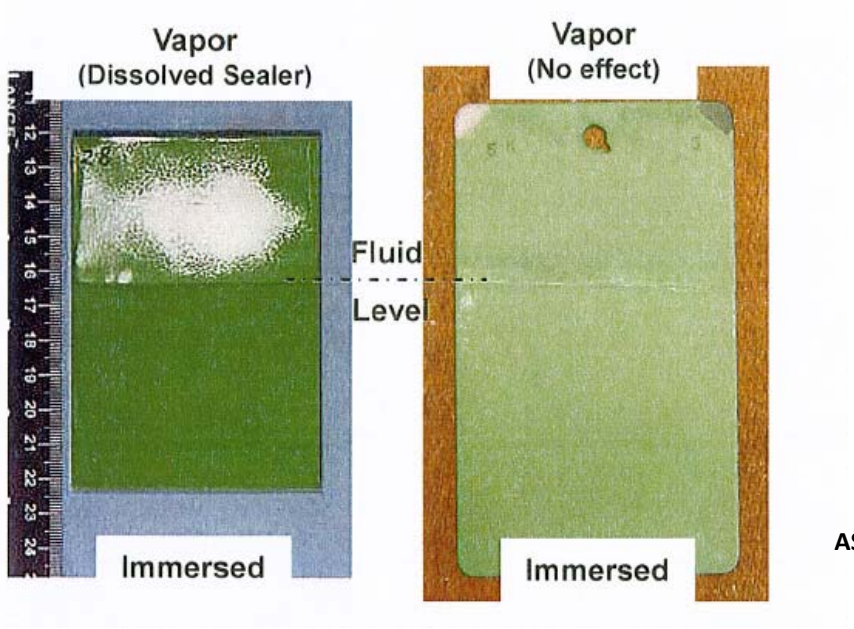
Alseal Cr-Free Slurries – Two Pathways

	Binder	pH	%Cr^{+6}	ppm
• **Al-Ceramic Sacrificial Basecoat**				
Alseal 5000 (5K)	sodium-lithium silicate	> 10	0 %	0
• **Ceramic Sealers**				
Alseal 5200	sodium-lithium silicate	> 10	0 %	0
Alseal 5KTC	Al^{+3}-acid-phosphate	~ 2.5	0 %	0

Synergy Between Cr-Free Pathways

- PEWG highlighted instability of silicate-based topcoats in water.
- Acid-phosphate (acidic) topcoat stabilized Al-silicate (basic) basecoat.

24 hrs. at 120F (49C) in open beaker of deionized water



Al-silicate with Alseal 5200 (silicate) sealer in PEWG test

Same Al-silicate with 5KTC acid-phosphate sealer in same test

ASME GT2013-94465, June 2013

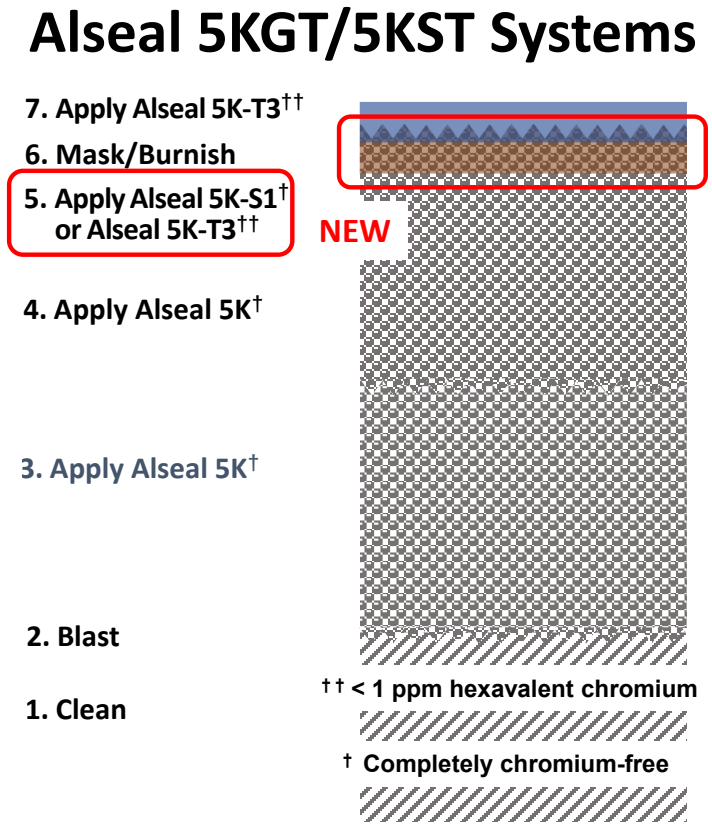
Another Backward Step!

- A Cr-Free coating that had passed lab tests FAILED in a power generation turbine operating with wet compression.
- The failure led the OEM to new Lab Test to screen Cr-Free systems.
  - 100 hr. partly immersed in DI water at 80°C in sealed container.

Cr-Free Al-silicate basecoat, burnished and sealed with Cr-Free acid-phosphate topcoat.
(4130 HSLA steel)

Using New Materials In a New Way

- Aluminum-Silicate Basecoat
- Heat-Cured Acid-Phosphate solution
  - Stabilizes basecoat in hot water and water vapor.
- Abrasive Burnish
  - Activates cathodic response of Aluminum-silicate.
- Smooth Acid-Phosphate Topcoat containing Trivalent Chromium
  - < 1 ppm hexavalent chromium



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Result: Stable, Sacrificial Cr-Free System

- Combining Innovative Cr-Free Slurries *and Novel Processing*
- Screening Test: ***1000*** hr. partly immersed in 80°C DI water.

Cr-Free Alseal 5KST coating system on 4130 steel.

Patents applied for

Performance of Cr-Free Al-Ceramic Systems

	Al-Chromate / Phosphate	5KST / 5KGT
Sacrificial Corrosion Resistance 5% Salt Fog per ASTM B117 (2 mil/50 μm on steel, scribed)	no rust in 1000 hrs.	**no rust in 1000 hrs.**
Max. Continuous Heat Resistance	1050°F (566°C)	**950°F (510°C)**
Max. Peak Heat Resistance	1150°F (621°C)	**1050°F (566°C)**
Heat/Salt Corrosion Resistance Ten cycles; 6 hrs. @ 750°F/399°C/16 hrs., 5% salt fog (2 mil/50 μm on steel, scribed)	no rust in 10 cycles	**no rust in 10 cycles**
Bend Test 90-degree bend around 1/4”mandrel (2 mil/50 μm coating on 0.04" steel panel)	no flaking	**no flaking**
Hot Lubricating Oil 8 hrs. partly immersed, 400°F/204°C MIL-L-7808 oil	no effect	**no effect**
Hot Deionized Water (open) 24 hrs. partly immersed, 120°F/49°C	no effect	**no effect**
Hot Deionized Water (sealed) 100 hrs. partly immersed, 176°F/80°C	no effect	**no effect**

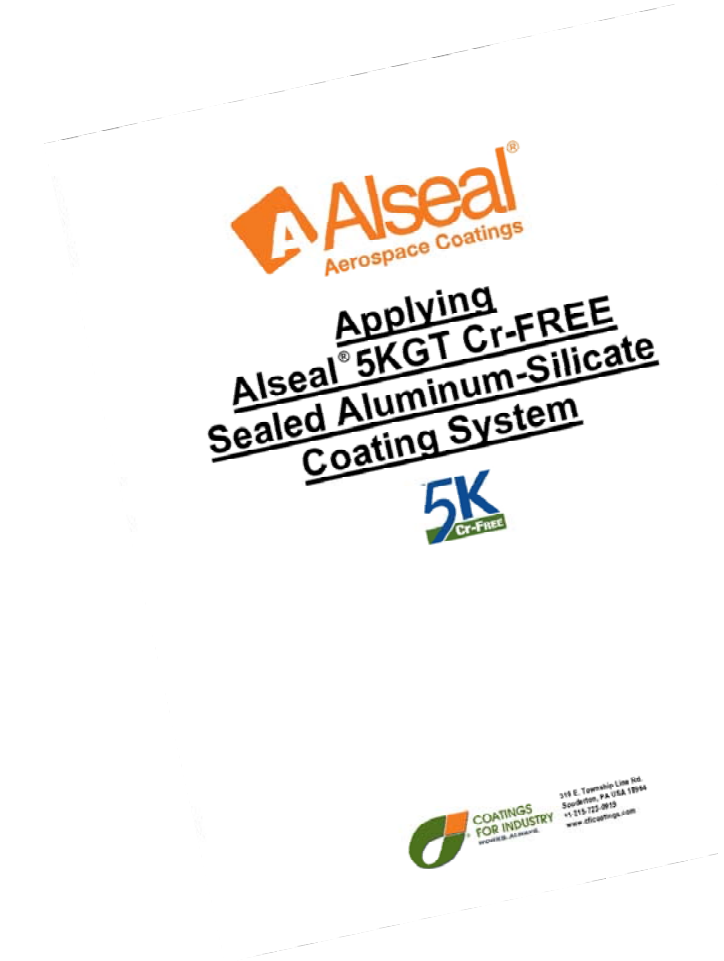
Innovative Cr-Free Slurries

	Binder	%Cr^{+6}	ppm
• **Al-Ceramic Sacrificial Basecoat**			
Alseal 5K	**sodium-lithium silicate**	**0 %**	**0**
• **Ceramic Sealers**			
Alseal 5K-S1	**Al^{+3}-acid-phosphate**	**0 %**	**0**
Alseal 5K-T3	**Al^{+3}/Cr^{+3}-acid-phosphate**	**< 0.0001 %**	**< 1**
	REACh Limits	**< 0.1 %**	**< 1000**

AND Innovative Processing:

Alseal 5KGT/5KST Coating *System*

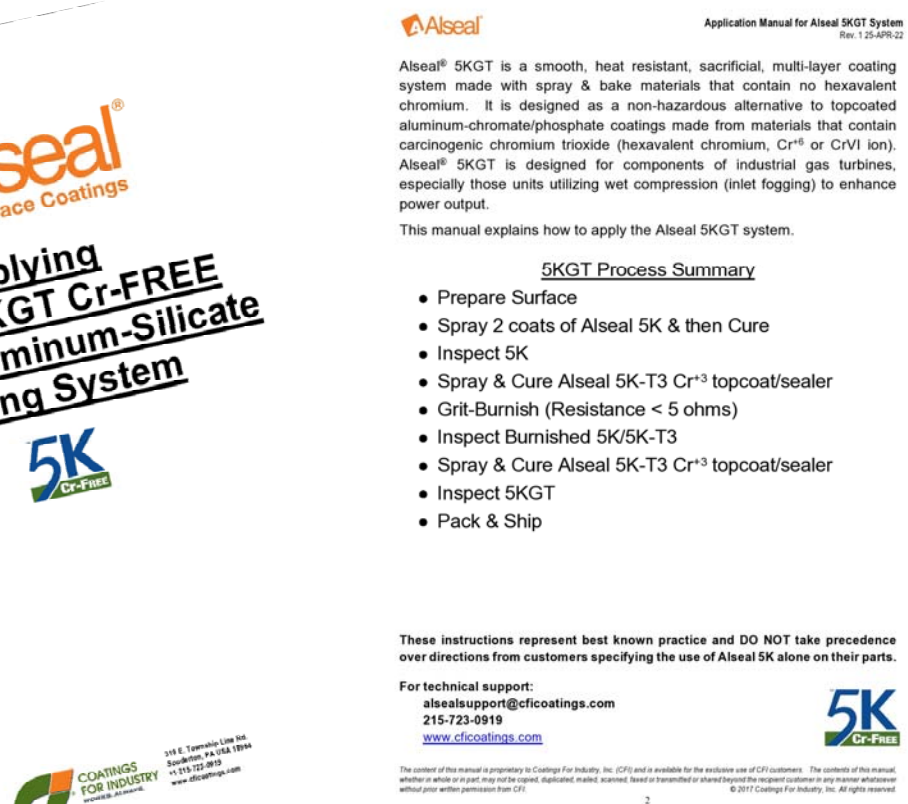
Processing: Alseal 5KGT/5KST Manuals


Alseal®
Aerospace Coatings

Applying Alseal® 5KGT Cr-FREE Sealed Aluminum-Silicate Coating System

5K Cr-Free

COATINGS FOR INDUSTRY


Alseal

Application Manual for Alseal 5KGT System
Rev. 1 25-APR-22

Alseal® 5KGT is a smooth, heat resistant, sacrificial, multi-layer coating system made with spray & bake materials that contain no hexavalent chromium. It is designed as a non-hazardous alternative to topcoated aluminum-chromate/phosphate coatings made from materials that contain carcinogenic chromium trioxide (hexavalent chromium, Cr^{+6} or CrVI ion). Alseal® 5KGT is designed for components of industrial gas turbines, especially those units utilizing wet compression (inlet fogging) to enhance power output.

This manual explains how to apply the Alseal 5KGT system.

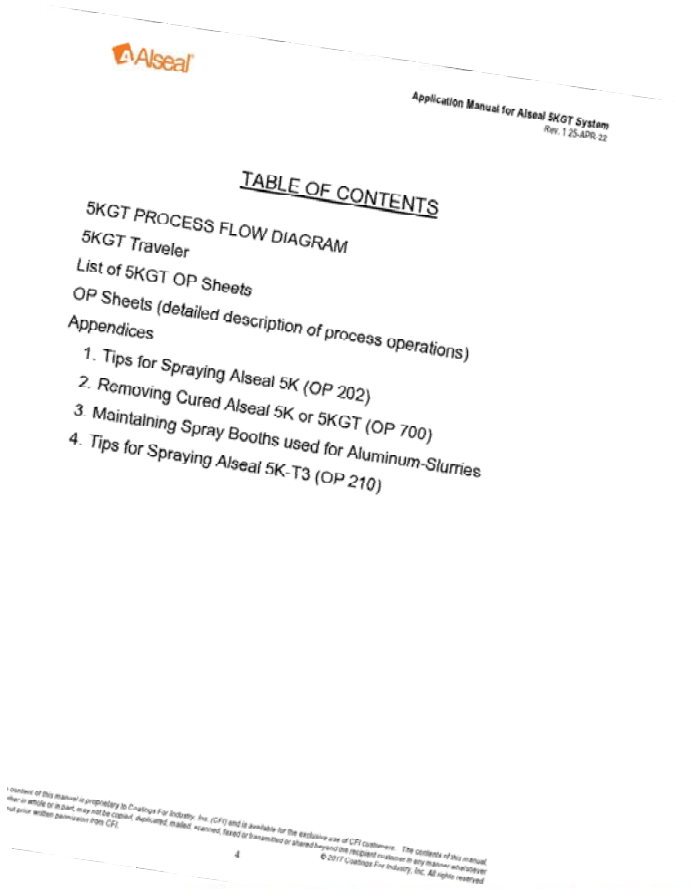
5KGT Process Summary

- Prepare Surface
- Spray 2 coats of Alseal 5K & then Cure
- Inspect 5K
- Spray & Cure Alseal 5K-T3 Cr^{+3} topcoat/sealer
- Grit-Burnish (Resistance < 5 ohms)
- Inspect Burnished 5K/5K-T3
- Spray & Cure Alseal 5K-T3 Cr^{+3} topcoat/sealer
- Inspect 5KGT
- Pack & Ship

These instructions represent best known practice and DO NOT take precedence over directions from customers specifying the use of Alseal 5K alone on their parts.

For technical support:
alsealsupport@cficoatings.com
215-723-0919
www.cficoatings.com

5K Cr-Free


Alseal

Application Manual for Alseal 5KGT System
Rev. 1 25-APR-22

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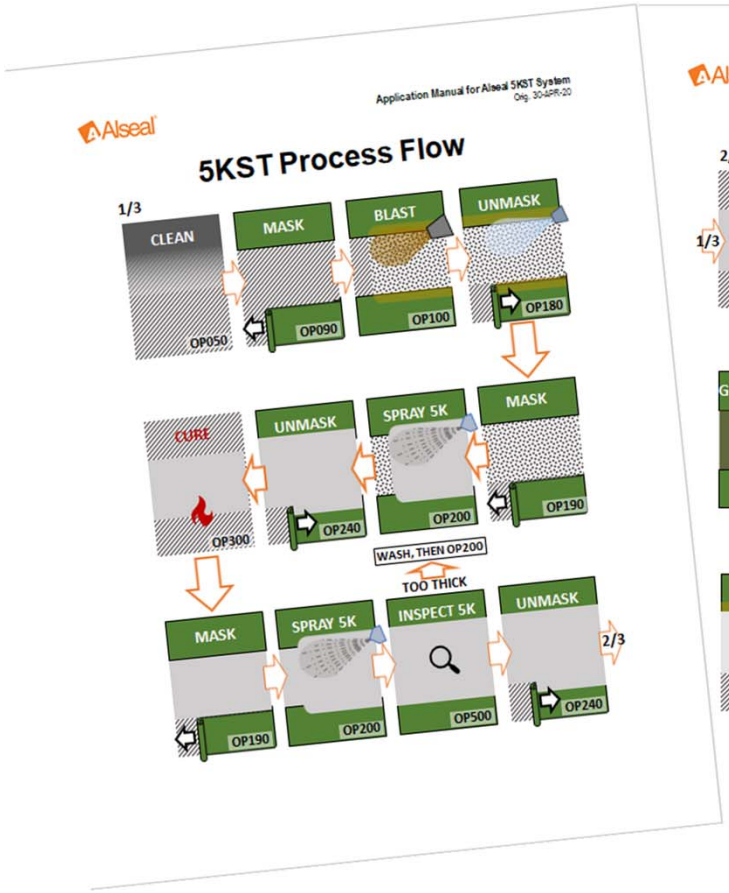
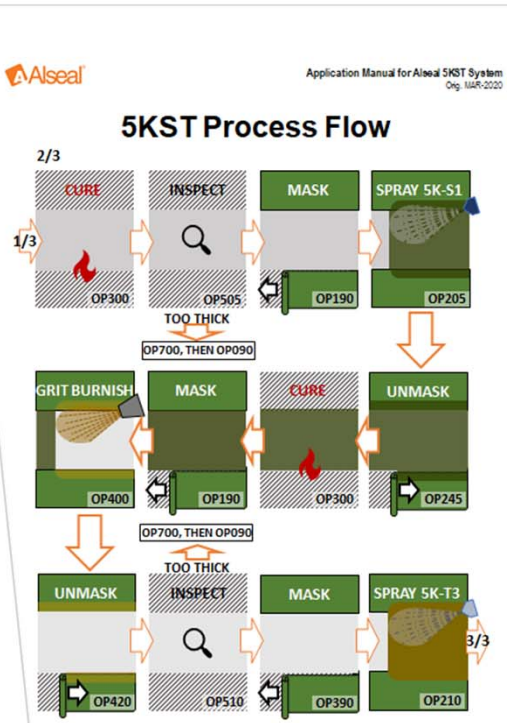
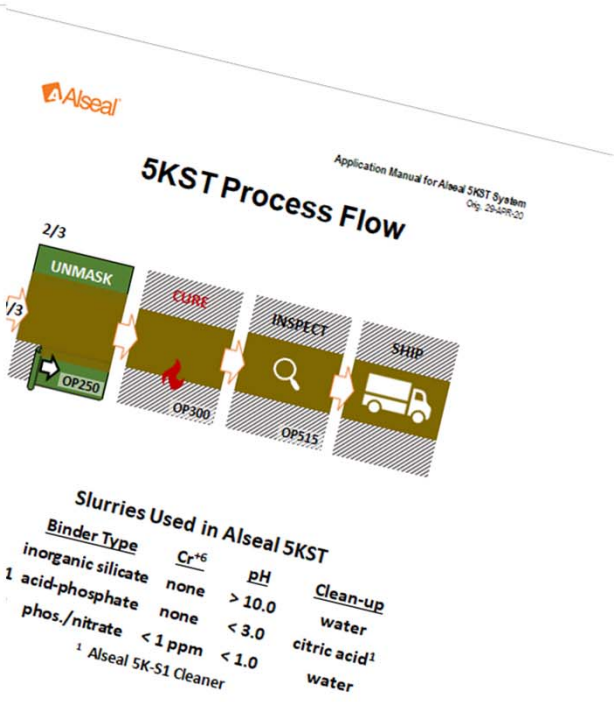
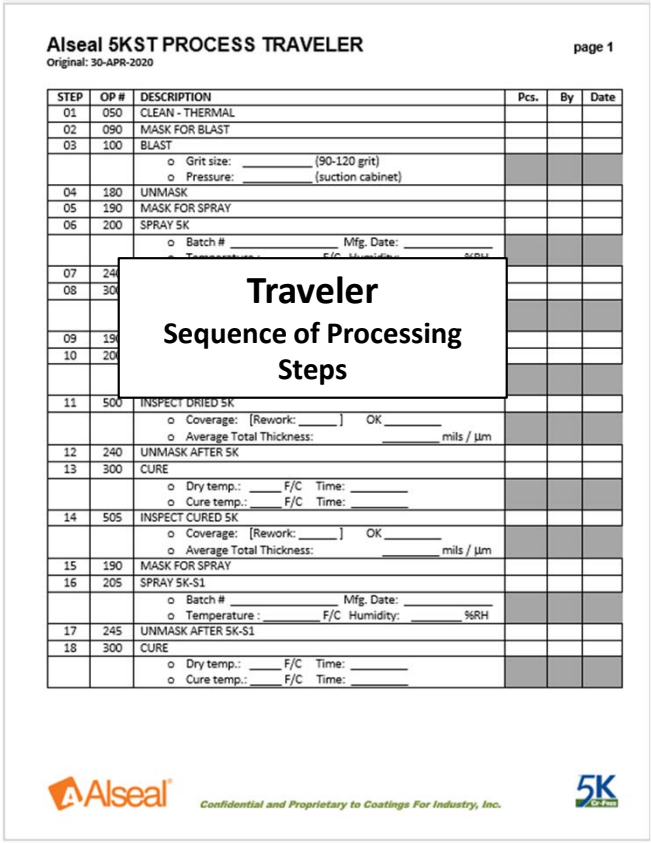
5KGT/5KST Flow Diagrams







5KGT/5KST Shop Documents with . . .

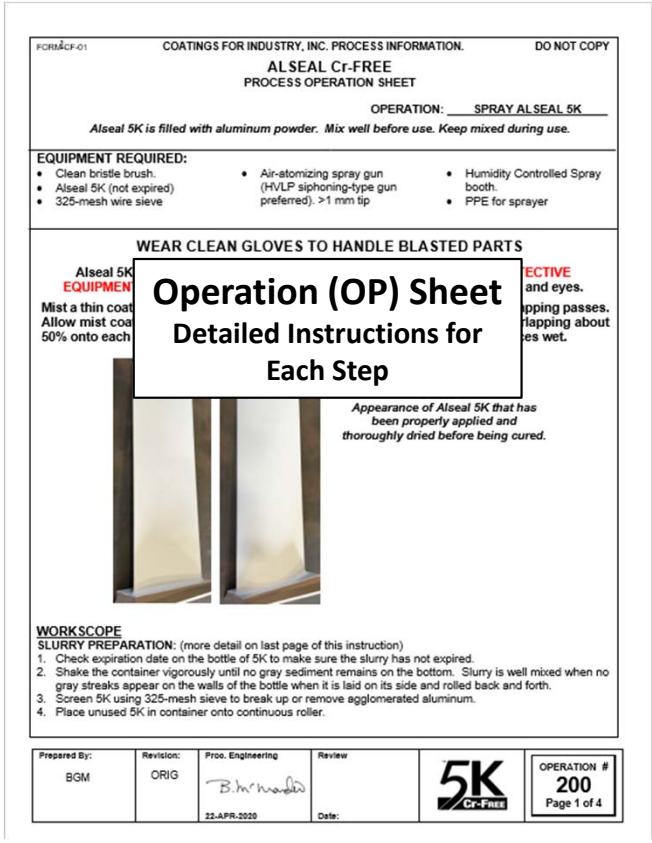


Alseal 5KST PROCESS TRAVELER
Original: 30-APR-2020 page 1

STEP	OP #	DESCRIPTION	Pcs.	By	Date
01	050	CLEAN - THERMAL			
02	090	MASK FOR BLAST			
03	100	BLAST			
		o Grit size: _____ (90-120 grit)			
		o Pressure: _____ (suction cabinet)			
04	180	UNMASK			
05	190	MASK FOR SPRAY			
06	200	SPRAY 5K			
		o Batch # _____ Mfg. Date: _____			
07	24				
08	30				
09	19				
10	20				
11	500	INSPECT DRIED 5K			
		o Coverage: [Rework: _____] OK _____			
		o Average Total Thickness: _____ mils / µm			
12	240	UNMASK AFTER 5K			
13	300	CURE			
		o Dry temp.: ____ F/C Time: _____			
		o Cure temp.: ____ F/C Time: _____			
14	505	INSPECT CURED 5K			
		o Coverage: [Rework: _____] OK _____			
		o Average Total Thickness: _____ mils / µm			
15	190	MASK FOR SPRAY			
16	205	SPRAY 5K-S1			
		o Batch # _____ Mfg. Date: _____			
		o Temperature : _____ F/C Humidity: _____ %RH			
17	245	UNMASK AFTER 5K-S1			
18	300	CURE			
		o Dry temp.: ____ F/C Time: _____			
		o Cure temp.: ____ F/C Time: _____			

Alseal Confidential and Proprietary to Coatings For Industry, Inc. 5K Cr-Free

Traveler
Sequence of Processing Steps



FORM CF-01 COATINGS FOR INDUSTRY, INC. PROCESS INFORMATION. DO NOT COPY

ALSEAL Cr-FREE
PROCESS OPERATION SHEET

OPERATION: SPRAY ALSEAL 5K

Alseal 5K is filled with aluminum powder. Mix well before use. Keep mixed during use.

EQUIPMENT REQUIRED:
- Clean bristle brush.
- Alseal 5K (not expired)
- 325-mesh wire sieve
- Air-atomizing spray gun (HVLP siphoning-type gun preferred). >1 mm tip
- Humidity Controlled Spray booth.
- PPE for sprayer

WEAR CLEAN GLOVES TO HANDLE BLASTED PARTS

Alseal 5K
EQUIPMEN
Mist a thin coat
Allow mist coa
50% onto each

ECTIVE
and eyes.
pping passes.
flapping about
es wet.

Operation (OP) Sheet
Detailed Instructions for Each Step

Appearance of Alseal 5K that has been properly applied and thoroughly dried before being cured.

WORKSCOPE
SLURRY PREPARATION: (more detail on last page of this instruction)
1. Check expiration date on the bottle of 5K to make sure the slurry has not expired.
2. Shake the container vigorously until no gray sediment remains on the bottom. Slurry is well mixed when no gray streaks appear on the walls of the bottle when it is laid on its side and rolled back and forth.
3. Screen 5K using 325-mesh sieve to break up or remove agglomerated aluminum.
4. Place unused 5K in container onto continuous roller.

Prepared By:	Revision:	Proc. Engineering	Review		OPERATION #
BGM	ORIG	B.M'Mahon 22-APR-2020	Date:	5K Cr-Free	200 Page 1 of 4

. . . Integrated Instructions

Alseal 5KST PROCESS TRAVELER page 1

Original: 30-APR-2020

STEP	OP #	DESCRIPTION	Pcs.	By	Date
01	050	CLEAN - THERMAL			
02	090	MASK FOR BLAST			
03	100	BLAST			
		o Grit size: _____ (90-120 grit) o Pressure: _____ (suction cabinet)			
04	180	UNMASK			
05	190	MASK FOR SPRAY			
06	200	SPRAY 5K			
		o Batch # _____ Mfg. Date: _____ o Temperature : _____ F/C Humidity: _____ %RH			
07	240	UNMASK AFTER 5K			
08	300	CURE			

Traveler

Lists Processing Steps in Order and Captures Critical Information for Quality Assurance.

OP Sheet

Provides Critical Information to Assure Each Operation is Done Correctly and Safely.

(Cross Referenced on Traveler)

- **Customize for specific parts, customers**

WORKSCOPE

SLURRY PREPARATION: (more detail on last page of this instruction)

1. Check expiration date on the bottle of 5K to make sure the slurry has not expired.
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Prepared By:	Revision:	Proc. Engineering	Review		
BGM	ORIG	22-APR-2020	Date:	5K Cr-Free	OPERATION # 200 Page 1 of 4

Alseal 5KGT / 5KST

Corrosion Resistant, Stable, Environmentally Safe
Aluminum-Ceramic Coating Systems

Unique Spray & Bake Process Utilizing
Unique Cr-Free Materials

Alseal®

SUR/FIN® 2022
Where Finishing Connects

Why So Long?

- Unavoidable tyranny of chemistry.
  - It's difficult (impossible?) to do all Cr^{+6} does with other elements.
  - Many chemical alternatives bring other (unacceptable) risks.
- Prior experiences and biases, bind and blind.
  - What is true of one technology is not necessarily true in another. AND, those differences are hidden, only to be revealed at inopportune times.
- It is exponentially more difficult to replace proven technology.
  - Inappropriate/Unrealistic targets can hinder innovation.
  - Factors that don't directly affect performance become "critical" too.

Adequate vs. Equivalent

- Challenge of meeting mature targets with new technology.
  - Cr^{+6} slurries have benefited from decades of development. No longer merely heat and corrosion resistant. Smooth, appealing appearance. Erosion resistance.
- Which targets of existing specifications are essential?
  - Specs written around capabilities of Cr^{+6} slurries, which may be more than needed in service.
- Accuracy and appropriateness of lab test(s)?
  - Difficult to accelerate degradation to accurately model life in the real world.

The Development of
Alseal 5KGT/5KST
Shows that Environmentally Safe Innovation . . .

- Can Take a LONG Time,
- Likely (Grossly) Underestimates the Task,
- Requires Much (Un)Learning, and
- Persistence, Persistence, Persistence.

Thank You

Alseal®

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Where Finishing Connects