NASF SURFACE TECHNOLOGY WHITE PAPERS
83 (1), 7-12 (October 2018)

Advances in Decorative PVD Chromium Coatings for Polymer Substrates

A Synopsis of a Presentation given at SUR/FIN 2018 (Cleveland, Ohio)*
by

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Editor's Note: The following is a synopsis of a presentation given at NASF SUR/FIN 2018, in Cleveland, Ohio on June 4, 2018 in Session 6, Advances in Surface Finishing Technology II - New Trends in Surface Finishing.

ABSTRACT

Much effort has been invested over the last ten years to produce an environmentally-safe alternative to decorative Cr^{+6} electroplating of polymer substrates. Cr^{+3} is one alternative but lacks the full wear and color attributes of Cr^{+6} that surface engineers and designers desire. This presentation will review a two-layer, selective coating process which incorporates a specially developed UV-cured paint base coating with a sub-micron thick PVD chromium top coating. We will illustrate the coating's testing protocols of automotive manufacturers and the necessities of controlling the stresses within the coating matrix.

Introduction

Physical vapor deposition (PVD) describes high-energy vacuum deposition methods used to deposit thin metal and ceramic films by the condensation of the vaporized desired film material (*e.g.*, aluminum, chromium) onto the substrate surfaces (*e.g.*, automotive plastic parts). These methods include thermal, sputter and cathodic arc deposition. The focus here is on sputter deposition.

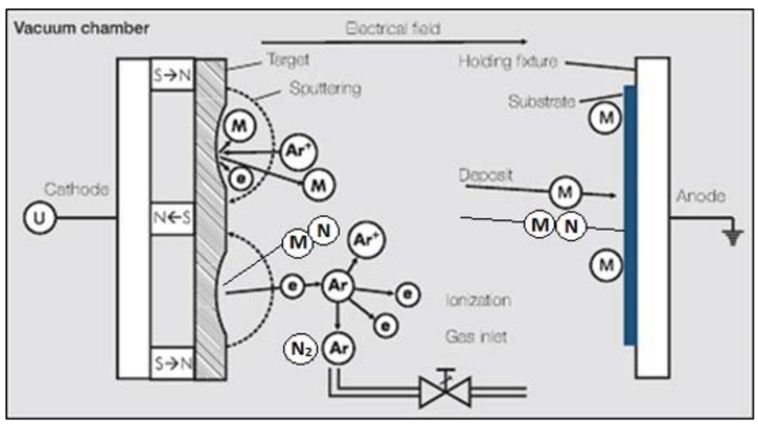

Figure 1 - Reactive sputter deposition.

As shown in Fig. 1, a high magnetic field near the target surface strips the outer valence electrons from argon (Ar) molecules, generating positively charged argon ions. The argon ions are accelerated towards and bombard the highly negatively biased target surface, "sputtering" out positively-charged metal ions. The metal ions travel across the vacuum space and condense on the substrate surface, giving up their energies and becoming a highly adherent thin film coating. The electrons generated in the process make the electrical return path to the positive anode(s). Reactive gases, such as nitrogen (N_2) react with the metal ion, becoming compounds, such as chromium nitride (CrN).

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*Compiled by Dr. James H. Lindsay, NASF Technical Editor

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PVD chromium development

PVD industry has been working on processes to gain an entrance into the decorative chromium market for decades, but the processes of the day suffered from cracking. Significant work was performed by John Thornton, *et al*. in the 1970s, applying sputtered chromium to ABS, with and without a paint base coating, and without a top coating.

Today, resins and as-molded surfaces have greatly improved and can be directly PVD coated. Applications requiring high levels of durability need paint base coatings for structural support of the PVD film and top coatings for abrasion resistance of soft PVD films. Protected applications (behind a lens) can be directly PVD coated and require no paint base or top coatings. For many years, reactive PVD coatings have been used over electroplated coatings on hardware and plumbing components. Patented PVD solutions have received OEM approvals.

Advantages of PVD processing

There are numerous advantages to PVD chromium processing. It is REACH-conforming and environmentally friendly, avoiding any use of hexavalent chromium and nickel plating chemistries. A broad spectrum of color shades and effects from bright to dark chromium and colors are possible. Corrosion resistance applies to automotive test requirements in combination with or without top coat. Because the PVD film is much thinner than electrodeposited chromium (and therefore lighter in weight), the deposit, coupled with the use of flexible substrates enables safety-relevant applications, *e.g.*, impact protection airbag emblems and others. Cost reduction can be realized as well.

For automotive applications, a large variety of substrate materials are amenable to PVD, and a wide variety of metal coatings, including many that cannot be readily electrodeposited (*e.g.*, aluminum, titanium, stainless steel), are available. Using laser etching and 3D-printed selective masking or light transparency properties (*i.e.*., coatings ~20 nm in thickness), internally lit day/night designs for interior instrumentation can be used. Because the thin PVD coatings are laser transparent, crash avoidance and lane monitoring systems are not blocked.

PVD chromium can be applied to a wide variety of applications, including automotive, motorcycle and RV trim components, steel wheels and wheel covers, appliance trim components, plumbing and sanitary components, commercial, and residential lighting trim components and electronic packaging.

Coating system advances

Figure 2 compares the layer arrangements from regular chromium plating, the traditional PVD triple stack base coat + PVD + top coat, and an advanced PVD chromium system which eliminates the top coat. Conventional chromium plating involves electrodeposited multilayers of copper, nickel and chromium, with the nickel consisting of single or multiple layers of varying composition and structure, depending on the level of corrosion service required.

Traditional PVD involves a metallized layer sandwich between a UV/thermal base coat on the substrate and a UV/thermal top coat. Here, chromium is one of several metals of choice depending on the finish color desired. The limitation here is that the top coat will darken the metal color, losing depth.

The latest PVD technology involves a two-layer proprietary PVD chromium over a base coat, with the top coat eliminated[†]. Here, the true deep chromium color is preserved, as with GM Specification 150. It can be applied to different plastics, metals and glass, and several UV-cured base coats have been tested and approved. There is minimal corrosion risk, with excellent adhesion, thermal stability and humidity resistance. In processing, strict attention is necessary to control stress throughout the PVD matrix.

[†] VTI Superchrome®, Vergason Technology, Inc., Van Etten, NY, USA over Mankiewicz CYCON®, Mankiewicz Gebr. & Co. (GmbH & Co. KG), Hamburg, Germany.

Figure 2 - Comparison of chromium plating with traditional and advanced PVD systems.

UV-cured base Coating

The UV base coating is as important to the performance of the PVD chromium as is the chromium layers itself. The UV base coat (monocure), contains a low level of volatile organic compounds (VOCs), involves short process times, and cures in seconds (Fig. 3). The formulation of the basecoat must optimize adhesion to the substrate and its support of the PVD chromium. Known paint issues must be considered, including adhesion for multiple substrate part design, paint rheology and application methods. Optimal smoothness is required since the reflective surface exacerbates any flaws (orange peel, dust inclusion, etc.).

UV-cured painting sees a low level of heat (<80°C) from flash heat to optimize paint flow-out prior to UV curing. Matching the type and set up of the lamps (arc, microwave, LED; stationary mounted or robot mounted) and the energy required for curing, must take into account the heat sensitivity of the substrate.

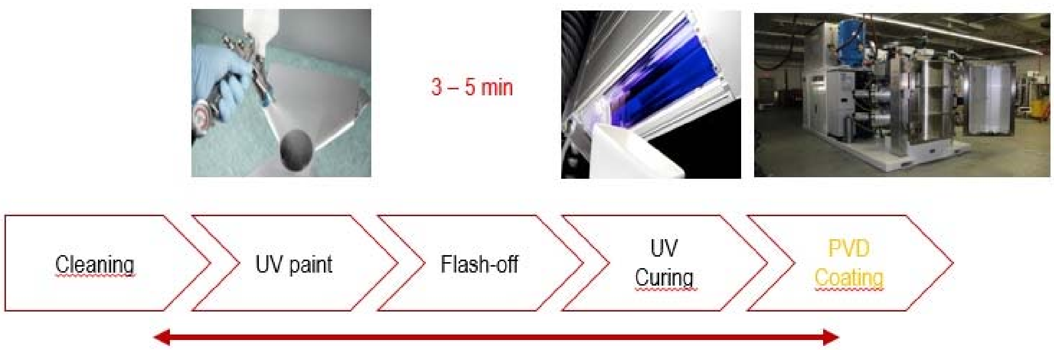

Figure 3 - UV-cured base coat process.

PVD chromium performance

The PVD chromium meets virtually all major test requirements for automotive interior and exterior trim components (Audi-Volkswagen, BMW, Renault, PSA, Ford, Porsche, Daimler), using the proprietary system. As well, those specifications for home and commercial appliances (Bosch, Miele) are met with PVD chromium and a standard UV base coat (See Appendix).

Industrial scale production

Figure 4 illustrates the available industrial scale processing, from molding, through cleaning, to UV coating and PVD chromium. With single point loading and a cycle time of 15 minutes, the productivity of the system is quite favorable.

Manual Doors Batch size: 660mm Ø X 1220mm tall Cycle time: 15 minutes Single Point Loading

Figure 4 - PVD chromium in industrial production.

Summing up

In summary, PVD chromium is gaining rapid acceptance with OEMs for the safe replacement of automotive trim, sanitary and appliance applications of electroplated chromium on plastic substrates. The key work for chromium coatings on plastic substrates with no top coating was started four decades ago, and batch and inline processing is now available.

Job coating services available at SPPP, Saint-Berthevin, France (http://www.sppp53.com).
Application coatings are available at VTI® in the USA (www.vergason.com)

APPENDIX
Performance Test Results for PVD Chromium

AUDI / Volkswagen Exterior VW TL 211 / 528	VTI SUPERCHROME - Mankiewicz CYCON®		
	Bright	Medium	Dark
Initial adhesion	✓	✓	✓
Stone chipping	✓	✓	✓
Constant climate KK	✓	✓	✓
High pressure cleaning	✓	✓	✓
FAM test fuel	✓	✓	✓
Gaoline E10	✓	✓	✓
Diesel B7	✓	✓	✓
Isopropanol	✓	✓	✓
Sodium hydroxide 5%	✓	✓	✓
Sulfuric acid 10%	✓	✓	✓
Hydrochloric acid 10%	✓	✓	✓
Bird drop	✓	✓	✓
Liquid pitch	✓	✓	✓
PV1200 climate change test	✓	✓	✓
PV1200 climate change test - NSS salt spray	✓	✓	✓
PV3930 Florida light resistance – 4800 h Arizona light resistance – 3000 h	✓	✓	✓
Car wash resistance / Car washing brush	✓	✓	✓
CASS	✓	✓	✓

AUDI / Volkswagen Interior TL226	VTI SUPERCHROME - Mankiewicz CYCON®
Visual appearance	✓
Initial adhesion	✓
Cream A	✓
Cream B	✓
Visual appearance after 2d 60°C	✓
Adhesion after 2d 60°C	✓
Visual appearance after 24 h 90°C	✓
Adhesion after 24h 90°C	✓
Visual appearance after KK (240h 40°C, >96% relative humidity)	✓
Adhesion after KK (240h 40°C, >96% relative humidity)	✓
Hydrolysis	✓
Crockmeter dry (100/2000 cycles)	✓
Martindale	✓
Abrex	✓

Figure A1 - Audi-Volkswagen (Exterior and Interior).

	BMW - Exterior	VTI SUPERCHROME - Mankiewicz CYCON®
	Gitterschnitt - resistance to cross-cutting	✓
	Steinschlag - stone chipping	✓
	Druckwasserstrahl - high pressure cleaning	✓
	Crockmeter - crockmeter	✓
	Car wash resistance / Car washing brush	✓
Chemikalienbestandigkeit – chemical resistance	36% Schwefelsäure – sulfuric acid	✓
	Hohlraumkonservierer – underbody sealant	✓
	Ethanol/Wasser – ethanol/water	✓
	Felgenreinigergel – wheel cleaner	✓
	1% Schwefelsäure – sulfuric acid	✓
	10% Salzsäure – hydrochloric acid	✓
	Baumharzlösung – liquid tree pitch	✓
	Pankreatin - vomit	✓
	VE-Wasser – demineralized water	✓

BMW - Interior	VTI SUPERCHROME - Mankiewicz CYCON®
Haftung - adhesion	✓
Kondenswasserkonstantklimalagerung - Constant climate	✓
Crockmeter	✓
Alterungsbeständigkeit – aging proof	✓
Klimawechseltest – climate change	✓
Abrasion acc. to AA-0471	✓
Crème - cream	✓
Hydrolysis	✓

Figure A2- BMW (Exterior and Interior).

Renault – PSA - Ford	VTI SUPERCHROME - Mankiewicz CYCON®
Adhesion after cross-cut	✓
Resistance to scratching by abrasion (Renault 47-03-003/--L_2013)	✓
Stone chipping, PSA spec (PSA B72 0200_2013-04)	✓
High pressure test (Kaercher) PSA spec	✓
Thermal shock test PSA D45 1234 C	✓
Stone chipping, Renault spec Up to 150 km/h	✓
BAC FORD (PSA B72 0200_2013-04) water absorption	✓
High pressure test (Kaercher) Renault spec	✓
Heat ageing, Renault spec	✓
Resistance to fuel, cleaning agents Renault spec	✓
Crockmeter, wet/dry Renault spec	✓

Porsche – Exterior (VW-TL 161)	VTI SUPERCHROME - Mankiewicz CYCON®
Gitterschnitt - resistance to cross-cutting	✓
Verhalten im Dampfstrahltest (Anlieferzustand) Steam jet (condition as delivered)	✓
Verhalten im Dampfstrahltest (120 h KK + 1 h Konditionierung RT) - Steam jet	✓
Verhalten im Dampfstrahltest (120 h KK + 24 h Konditionierung RT) - Steam jet	✓
Steinschlagprüfung RT -20°C Stone chipping	✓
Politur nach VW 50002-A16 - polish	✓
5% Schwefelsäure (4h 50°C) – sulfuric acid	✓
5% Schwefelsäure (24h 50°C) – sulfuric acid	✓
Klimawechseltest PV1200	✓
Crockmeter dry (100/1000 cycles)	✓

Figure A3 - Renault-PSA (Peugeot, Citroen, DS, Opel and Vauxhall)-Ford and Porsche (Exterior).

Bosch directive LV 74 A	VTI SUPERCHROME - UV Base Coat
Adhesion - Haftung	✓
Condensing water 24 h bei 40°C - Schwitzwasser	✓
Resistance to detergent 70°C - Waschlauge	✓
Resistance to steam 70°C - Wasserdampf	✓
Alternating climates - Klimawechsel 8 h 40°C / 16 h room temperature 21 cycles	✓
Heat 70°C 3 weeks - Wärmelagerung	✓
Resistance to commercial detergents – Reinigungsmittel (Haushaltsreiniger) 16 h at room temperature	✓
Crockmeter with Ethanol 15 DH	✓

Bosch directive: 5700 1709918181, F1	VTI SUPERCHROME - UV Base Coat
Temperature cycling - short test 4 h at RT / 2 h at 0 to - 20 °C	✓
Temperature cycling short test 16 h 60 °C / 30 min. RT / 4 h - 20 °	✓
storing 168 h at 60 °C	✓
Isopropanol resistance 15 sec rubbing (app. 10 N/cm²)	✓
cleaning agent: 0,3 % "Pril" solution on sponge , 37 double strokes per minute, 1,000 strokes in total, app. 470 g weight load	✓
hand sweat (from TL 226 Norm) 24 h	✓
adhesion of metal layer	✓
temperature cycling 3 Zyklen 8 h 70 °C - 12 h RT - 12 h - 25 °	✓

Figure A4 - Bosch Directive LV 74A (Appliances).

Miele directive	VTI SUPERCHROME - UV Base Coat
Adhesion (2 times tear-off)	✓
condensation water alternating climate (20 cycles 8 h / 40 ° - 16 h / 20 °)	✓
light fastness Suntest (100 h, then color measurement)	✓
temperature changing test (80 ° and - 20 ° change after 1 h, 3 cycles)	✓
MEK Test (Methyl-Ethyl-Keton) (2 times 60 double strokes with batting, Crockmeter)	✓
acetic acid 25 %	✓
caustic soda solution 10 %	✓
color fluid	✓
2-Propanol	✓
Olive oil	✓
Paraffine oil	✓
Incidin N	✓
formic acid 5 %	✓
Suds Test 20 g/L with Persil Megaperls 24 h bei 60 °C	✓

Figure A5 - Miele Directive (Commercial Washers).

About the author

Gary Vergason has been working in the PVD field for over 37 years in the field of vacuum coatings, beginning with Multi-Arc Vacuum Systems in St. Paul, Minnesota and Perkin-Elmer Corporation in Eden Prairie, Minnesota before founding Vergason Technology in Van Etten, NY in 1986, where he is currently its CEO and Chairman. His areas of expertise include physical vapor deposition, chemical vapor deposition and plasma-enhanced chemical vapor Deposition. He has authored and co-authored numerous patents, technical papers and articles. Mr. Vergason has served as President of the Society of Vacuum Coaters since May 2016.