

# PVD Chromium Coatings Replacing Decorative Chromium Electroplated Coatings on Plastics

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## ABSTRACT

Traditional electroplated chromium coatings on plating-grade ABS which utilize hexavalent chromium (Cr6) baths are being phased out due to long standing issues of health and environmental hazards and waste stream reclamation. In Europe, the implementation of the REACH initiative will increase fees on companies still using Cr6 in 2017 and will require action plans to phase out Cr6 in the future. Leading industries such as automotive, sanitary, small appliances and durable goods are searching for reliable alternatives for plating on plastics (POP). Since the 1970s, PVD chromium coatings have been available, but have lacked production viability due primarily to a lack of environmental durability and/or a tendency to stress-crack when subjected to thermal cycling. Alloying and nano-layering the depositions have produced coatings that have controlled stress cracking, but have not been able to produce the true chromium appearance that designers demand. New techniques have been developed to produce chromium coatings that can withstand thermal cycling without stress-cracking and exhibit excellent environmental durability. These new sputtered chromium coatings do not require a protective paint top coat to pass exterior automotive trim specifications. Visually the chromium coatings match those of electroplated decorative chromium in color and appearance. They can also be altered to achieve certain design effects such as satin finishes. This paper will discuss the technical challenges and testing results of this new PVD coating technique.

## INTRODUCTION

Electroplated chromium coatings on polymer substrates incorporate numerous steps of chemical baths and rinses to produce the 35 to 50 microns of leveling and support metals under the final, thin, decorative chromium top layer (Figure 1).

These steps include: cleaning, conditioning, neutralizing, acid etching, catalyzing, accelerating, nickel flash, copper plating, nickel plating, chrome plating along with the necessary effluent care and disposal. Each step must be closely monitored and controlled to produce high quality chromium surfaces,

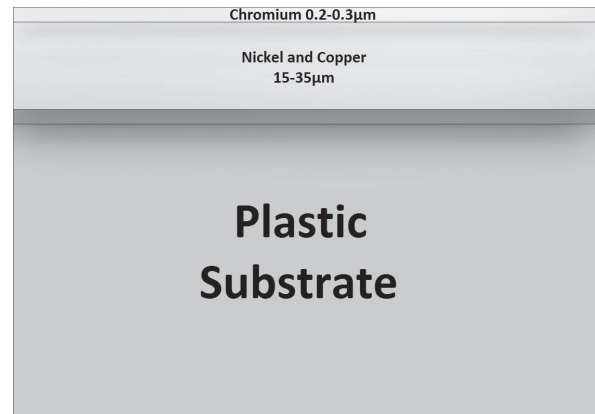


Figure 1: Electroplated chrome stack.

or a wide variety of subsequent quality issues will surface in the field. Most electroplating operations are permanent installations, require large amounts of floor space (upwards of a thousand square meters) and do not lend themselves to be easily integrated into LEAN synchronous manufacturing methods. To achieve the level of LEAN initiative required for optimum quality control, the manufacturer should have plastic injection molding and electroplating operations under the same roof. This minimizes the resident holding time that the substrates can pick up problematic contaminants which could affect quality. There are very few manufacturers with this capability, requiring the product to be molded at one company, shipped to a plating company, and then returned to the molder or contract manufacturer for final assembly. These methods increase the possibility of substrate surface contaminants that can affect the electroplated coating quality (Figures 2 and 3) and substrate damage due to shipping and handling.

The electroplated chromium color most popular with automotive designers belongs to Cr6 coatings. These coatings appear brighter (around 75 % reflectivity), and are more forgiving and less expensive to produce than trivalent chromium coatings that some electroplaters are using today. While the love affair

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Figure 2: Electroplated chromium delamination.

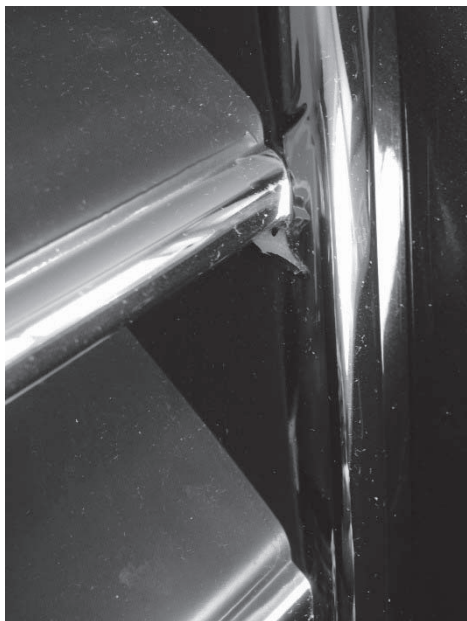


Figure 3: Electroplated chromium peeling.

of chromium on automotive components is primarily driven by the USA, there is an increasing demand in the sanitary, appliance and other consumer markets worldwide.

Physical Vapor Deposition (PVD) and lacquering (thermally cured paint base and top coatings) have been partners for decades. Paint base coatings provided the adhesion and leveling layer for the PVD coating which was usually a thermally evaporated aluminum coating. To protect this bright aluminum coating from abrasion and environmental damage, a clear paint top coating was used with or without color tinting

(Figure 4). Thermal curing paint lines required large areas of the production floor, comparable to that of the electroplating lines not including the required effluent management systems. Ultraviolet (UV) curing paint lines used today, occupies less than half the floor area of a thermal curing paint line.

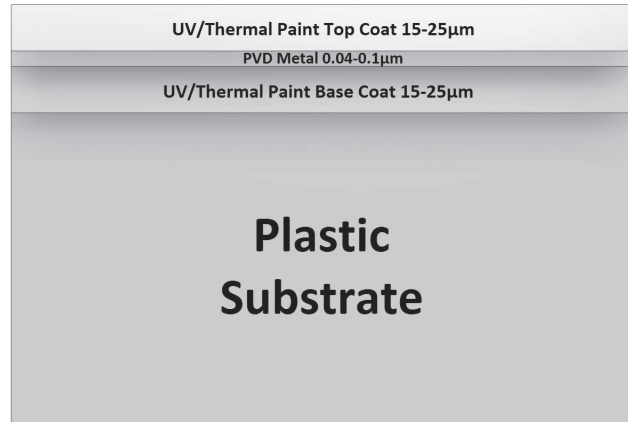


Figure 4: Traditional paint, PVD metal, paint triple stack.

Work starting around 1968 by Hella in Germany produced the Tri-Coat™ process which was later licensed for use to Stokes Vacuum in the USA around 1985. This process used a paint base coating to improve the specular surface of automotive lighting housings, followed by the PVD triple stack of highly reflective thermally deposited aluminum, a corrosion resistant hexamethyldisiloxane (HMDSO) barrier coating cross-linked with a DC plasma, finished with a thermally deposited SiOX top coating for scratch protection. The very thin HMDSO layer (around 0.03 µm) did not reduce the reflectivity as much as a paint top coating, but it was less resistant to scratching. The SiOX final top coating did improve scratch resistance, at least through the production assembly processes, but was prone to yellowing if the layer was applied too thick. This in-chamber vacuum process eliminated the paint top coating step for protected lens used in automotive lighting applications.

Around the same time, John Thornton at Telic Corporation in Santa Monica, California, published work of depositing thicker chromium coatings which did not require paint top coatings on ABS substrates for use in exterior automotive trim and other applications [1]. He reports success of sputtering up to 1.2 µm of chromium directly onto the ABS, as well as over a paint base coating (Figure 5). He also noted the sources of substrate heating in sputtering processes that can cause severe stress cracking includes: 1) heat of condensation of coating atoms, 2) kinetic energy of coating atoms, 3) ultraviolet radiation from plasma, 4) working gas heating and 5) plasma bombardment. This heating can also generate outgassing of the plastic substrate which can discolor the PVD coating [2]. The work that he and his colleagues performed led the way for today's versions of truer color PVD chromium coatings for the replacement of decorative electroplated chromium.

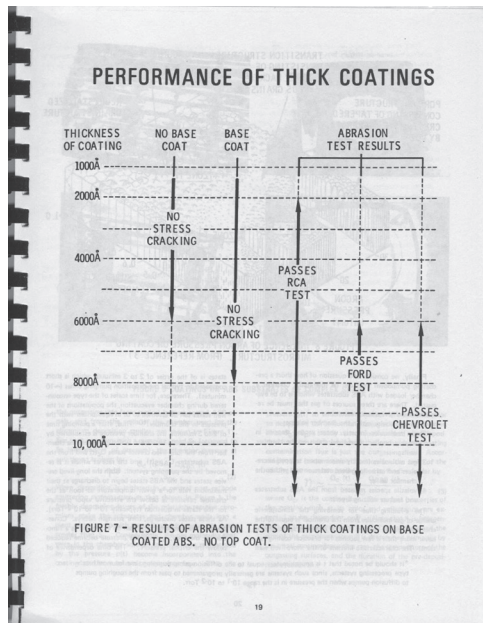


Figure 5: Performance of thick coatings, J.A. Thornton 1975.

Since the late 1980s, OEM approved PVD coatings have been applied directly to high surface quality molded polymer substrates (PC and ABS/PC behind clear lens, ABS behind colored lens) with no paint base coating or top coating for applications that were protected from physical contact. For automotive lighting, sputtered or cathodic arc stainless steel and chromium coatings took the place of low reflectivity argentine paints (20 % reflective); chromium, or aluminum coatings (with HMDSO in-chamber top coating) were applied directly to high quality optical housings behind clear lens, bringing visual excitement and new design possibilities to a utilitarian application. While the use of these techniques did not apply to all automotive lighting applications, it eliminated the need for painting and brought true LEAN manufacturing to the production floors with injection molding and PVD operations. For those applications that required specular finishes, extreme environmental, and abrasion resistance, UV curable base and top coatings became available to bring the advent of synchronous LEAN manufacturing into the metalizing and painting arena.

In the mid 2000s, new paint base coating chemistries started to emerge with low or no (regulated) volatile organic compounds (VOCs) in an effort to reduce air pollution. These newer paint products provided both the structural support for the chromium films and an improved stress management system between the soft substrate and the harder chromium films.

Chromium is a very hard metal, has a very low coefficient of thermal expansion (CTE) and can exhibit brittleness. It is self-passivating, and will not oxidize beyond a few atomic layers, protecting its metallic shine without the need for

secondary treatments. These are all excellent properties from a durability point of view; however, they can present significant challenges when trying to deposit chromium directly on polymers or within a deposition matrix including a base coating. Chromium is easily cracked if subjected to external thermal shock or impact stresses. The response to external stresses interacts with intrinsic stresses generated during the PVD process. The negative effects of these stresses can be minimized by keeping the chrome film as thin as possible, while still achieving the desired look. Films of 30 nm to 80 nm can retain flexibility and will not fracture when subjected to moderate temperature excursions. However, these films are quite fragile relative to impact and abrasion and require secondary protection with a painted top coating that could reduce the brightness and reflectivity. Conversely, thicker chrome films of 200 nm to 600 nm exhibit excellent abrasion resistance, but often fail due to cracking, as discussed previously. There are no one-size-fits-all solutions when it comes to the selection of the coating matrix. Specific application requirements will define the materials and methods that can be deployed, as we will review next.

Exterior automotive applications are probably the most challenging to achieve. The coating matrix must pass a wide variety of tests including: thermal shock, thermal cycling to extreme temperatures, bird droppings, Russian mud, grav-elometer, UV/weatherization, Florida/Arizona sunshine, car wash chemicals and brushes, and others. The impact and shock requirements dictate a thin film of chrome with a clear top coating. However, most clear-coats do not have sufficient hardness to provide long term abrasion resistance, have difficulty passing UV exposure and/or sunshine tests. The highest level of success has been seen using low or no VOC paint base coatings and thicker chromium films of 200 to 400 nm on smaller substrates, such as badges and insignias.

Interior automotive trim applications have relaxed specifications in some areas, but have a more difficult abrasion test. Thin chromium films are used with or without top coatings. Exposed surfaces can be subject to mild abrasion with a soft cloth and certain chemicals for cleaning. Testing protocols vary widely per application and manufacturer and can include tests for specific chemical resistance, such as sunscreen, mustard, cleaning chemicals, hand cream, etc. If the trim piece will be permanently mounted behind a protective cover, such as inside an instrument panel, the thin chromium film does not need the clear-coat.

In addition to automotive, the appliance industry and the bathroom/kitchen sanitary fixture markets offer great opportunities for PVD chrome (as well as other metallic finishes, such as stainless steel). Abrasion, chemical, and thermal requirements are all moderate when compared with automotive requirements. Since most of the electroplated chromium on laundry appliances is currently Cr6, it is expected that PVD

chromium and other materials will continue to see market share growth as the world seeks environmentally friendly surface solutions.

### COST DISCUSSIONS

Today's strides in reducing effluents and synchronous LEAN manufacturing of molding/base coating/PVD, have brought PVD chromium directly into competition with decorative electroplated chromium. When comparing the true cost per part produced between electroplating and PVD solutions, analysis has shown PVD pricing to be up to 15% less expensive than electroplating. Factors that come into these estimates include: processing equipment capital, labor, consumables, utilities, floor space, effluent management/disposal and product scrap.

### TECHNICAL CHALLENGES AND ACCOMPLISHMENTS

As with electroplated chromium, a very thin outer layer of pure chromium on top of the coating matrix provides the color and visual depth that designers and consumers like from Cr6. Alloying the chromium with other materials and nano-layered metals to control the intrinsic stresses (Figure 6), can change this appearance and the performance characteristics of the matrix. Some coating providers use controlled micro-cracking of the chromium (Figure 7) to keep the visual appearance and the thermal expansion within balance. Understanding the relationships between the myriad of factors including thermal expansion, stress management, adhesion, surface finish and durability play key roles in the success of PVD chromium.

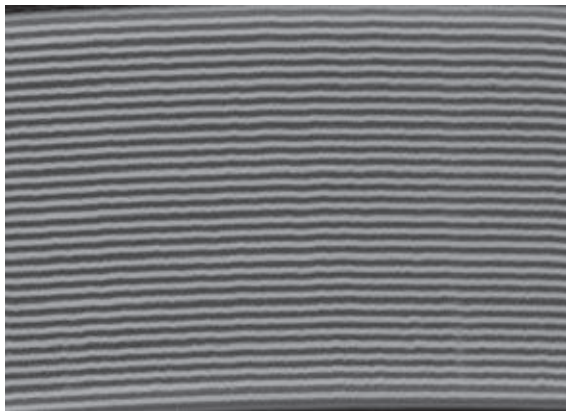


Figure 6: Nano-layered 10  $\mu\text{m}$  coating on acrylic.

A new patent-pending technology called SuperChrome™ PVD Coating, by Vergason Technology, Inc. (Figure 8), utilizes controlled ion and thermal energies throughout the film deposition process. As mentioned earlier, substrate heating sources for reactive magnetron sputtering fall into six categories: 1) electron bombardment, 2) kinetic and condensation heat of sputtered atoms, 3) bombardment of argon ions reflected from the target, 4) bombardment of reactive gas ions from the target, 5) radiation from the sputter target and 6) radia-

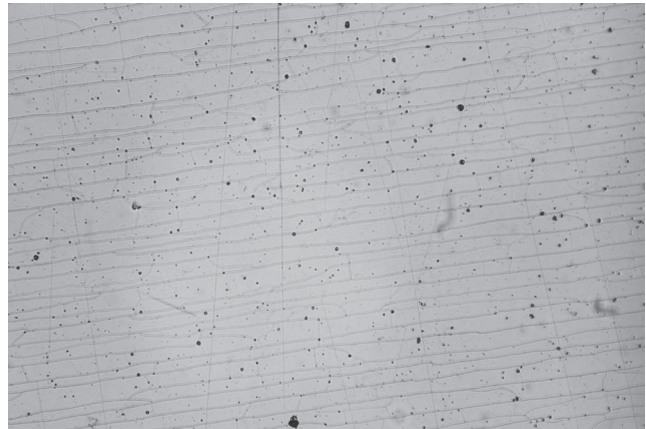


Figure 7: Bamboo micro-cracking of chrome coating on ABS.

tion from the plasma [3]. While the heat of condensation is unavoidable, some degree of control over heating is achieved through magnetron design and chamber geometry as well as specific levels of total pressure, reactive gas partial pressure, and power during film growth. Stress levels also respond strongly to total pressure. These interactions require a complex, multidimensional optimization. At the interface, the coating stress closely matches the intrinsic stress of the paint base coating and is finitely altered to the thin chromium layer at the top of the matrix. This multi-layered coating stack provides the adhesion, corrosion protection, abrasion protection and surface color to closely match that of electroplated chromium. The color of SuperChrome™ is a direct match with General Motors Z150 electroplating standard.

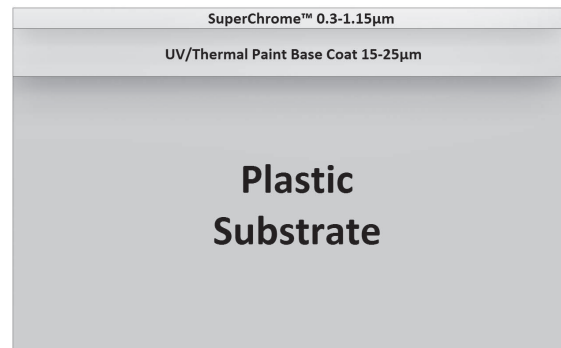


Figure 8: UV cured base coating with PVD chrome matrix.

### RESULTS AND ANALYSIS

SuperChrome™ PVD Coating produces the deep, rich, Cr6 appearance without any negative environmental issues. Separate of the paint base coating, the coating process takes place in one coating cycle and requires no paint top coating to pass a variety of automotive specifications. Current, as tested European results for SuperChrome™ PVD Coating applied over Mankiewicz Cycon UV cured base coat are shown with Table 1.

Table 1: External automotive trim specification for VW/Renault/PSA.

	<b>SuperChrome™ with UV Base Coat</b>
Visual Appearance	PASS
Initial Adhesion	PASS
Visual Appearance after 2d 60°C	PASS
Adhesion after 2d 60°C	PASS
Visual Appearance after 24 h 90°C	PASS
Resistance to Gritting (Renault 47-03-003/L-2013)	PASS
Stone Chipping, Volkswagen spec (VWTL211)	PASS
Stone Chipping, PSA spec (PSA B72 0200/2013-04)	PASS
Visual Appearance after Constant Climate (VWTL211) (240h 40°C, >96 % relative humidity)	PASS
Adhesion after Constant Climate (VWTL211) (240h 40°C, >96 % relative humidity)	PASS
Water Absorption BAC FORD (PSA B72 0200/2013-04)	PASS
Cream A (VWTL226)	PASS
Cream B (VWTL226)	PASS
High Pressure Cleaning (VWTL 211)	PASS
Resistance to Scratching by Abrasion (Renault 47-03-003/L-2013)	PASS
FAM test fuel (VWTL211)	PASS
Gasoline E10 (VWTL 211)	PASS
Diesel B7 (VWTL211)	PASS
Isopropanol (VWTL 211)	PASS
Sodium Hydroxide 5 % (VWTL 211)	PASS
Sulfuric Acid 10 % (VWTL 211)	PASS
Hydrochloric Acid 10 % (VWTL 211)	PASS
Bird Droppings (VWTL 211)	PASS
Liquid Tree Pitch (VWTL 211)	PASS
PV1200 Climate Change Test (VWTL 211)	PASS
NSS (VWTL 528) Salt Spray	PASS
Artificial Aging UVB Procedure A (PSA B72 0200/2013-04)	PASS
PV3930 Florida Sunshine (VWTL 211) 830 Hours	PASS
Car Wash Brush Resistance (VWTL 211)	PASS

Third party tests performed on SuperChrome™ coated ABS plaques yielded the following results: ASTM B117-11 Salt Spray Test, 1000 hours, no change observed. ASTM B368-09 and GM4372M CASS Test, 22 hours, no change observed.

HESD 6001-71 Section 4-4-4-3 Test Condition 1, Thermal Cycling, 168 hours, no change observed. Post-test pictures of the SuperChrome™ chrome coated plaques and electroplated chrome coated plaques are shown below in Figures 9 - 12:



Figure 9: Salt spray resistance test on plaques.

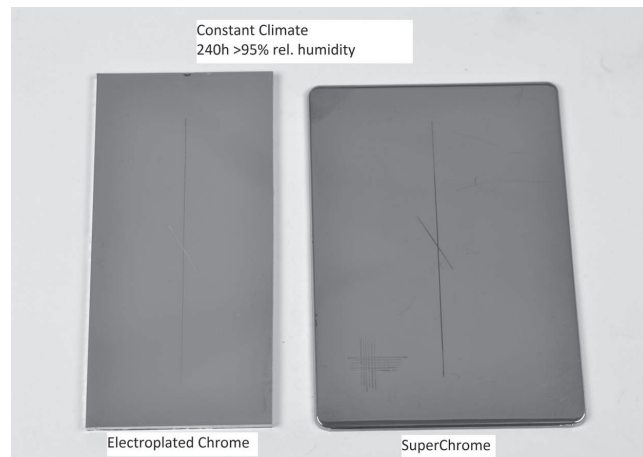


Figure 10: Constant climate test on plaques.

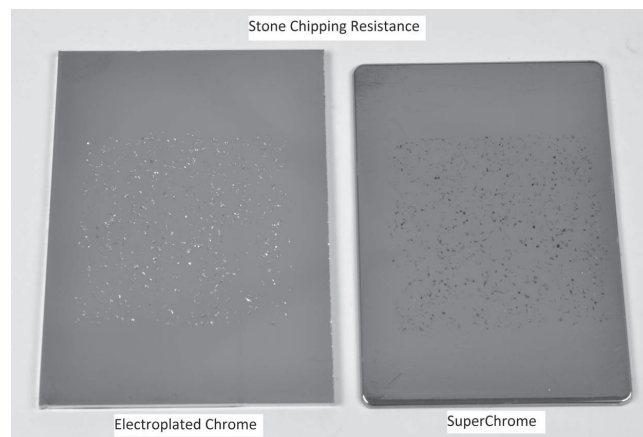


Figure 11: Stone chipping resistance test on plaques.

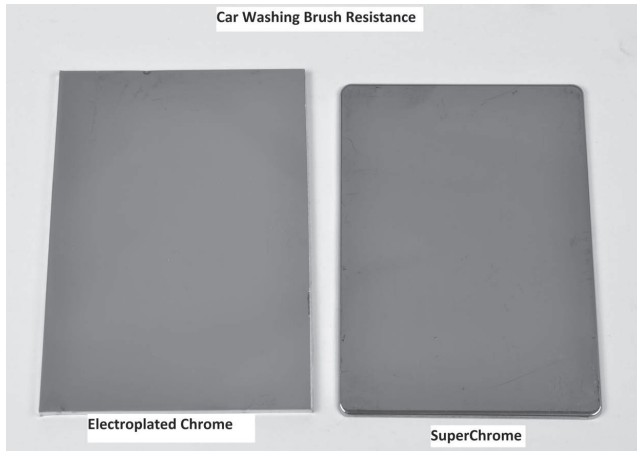


Figure 12: Car washing brush resistance test on plaques.



Figure 13: Scratch tester.

Destructive tests were performed to compare the mechanical behavior of electroplated chromium and PVD chromium. These tests include scratch at various loads using an Erichsen Model 413 tester (Figure 13) with a  $90\ \mu\text{m}$  diameter diamond tip stylus (Figure 14), and 10 kg load Braille C diamond indentation on the coated ABS plaques (Figures 15 -17). Table 2 contains micrographs of the various scratch tests and profilometer scans across the scratches. Static loads of 5, 10 and 15g were applied at linear rates of 2.7 to 3.9 mm/sec. The substrate moved from right to left. The combination of a hard coating on a soft substrate is expected to produce tensile and Hertzian cracks in the coating at lower loads, with chipping and spallation of the coating as the substrate is deformed at higher loads. The image for 15g on SuperChrome™ shows concave arcs in the wake of the tip that indicate Hertzian cracking. At 10g, profilometry shows the depth of the groove is comparable to the thickness of the coating, yet there is no evidence of coating delamination. At this magnification, there is the suggestion of cracks only at the sharp groove edge parallel to direction of motion. This signifies that while the coating is hard, it also has some measure of toughness to remain conformal without yielding. Using a Calotest device [4], the electroplated sample had a total metal thickness of  $50.0\ \mu\text{m}$ . The comparatively shallow depth of penetration of the electroplated sample is to be expected with 166 times the PVD thickness.

The  $50.0\ \mu\text{m}$  thick electroplated Cr sample in figure 15 has the smallest diameter crater, and like the SuperChrome™ sample in figure 16, shows excellent adhesion. Stress cracking and adhesion loss of the sample in Figure 17, is mostly due to the tensile stress cracking and hardness of the single layer chrome coating.

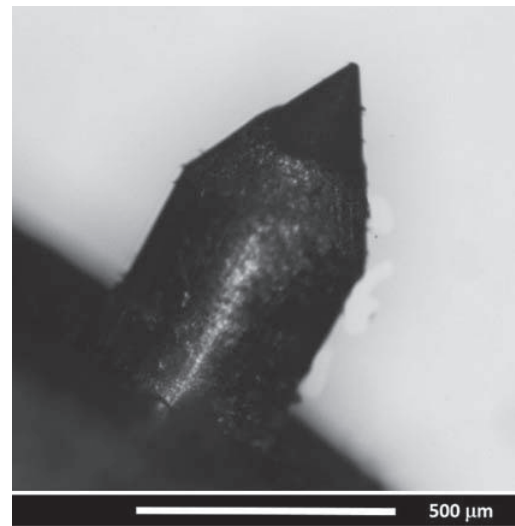


Figure 14: Diamond stylus.

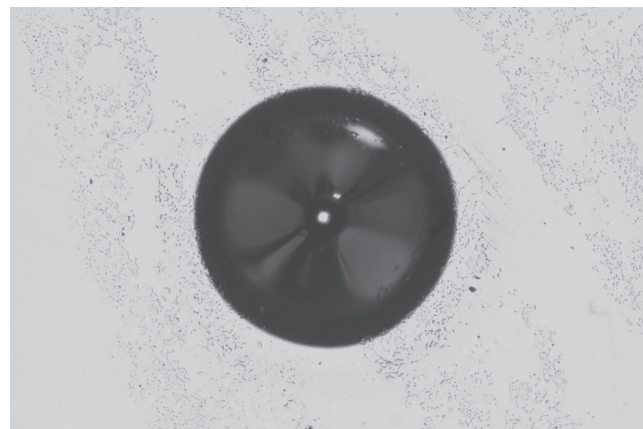


Figure 15: Diamond indentation of electroplated ABS  $740\ \mu\text{m}$ .

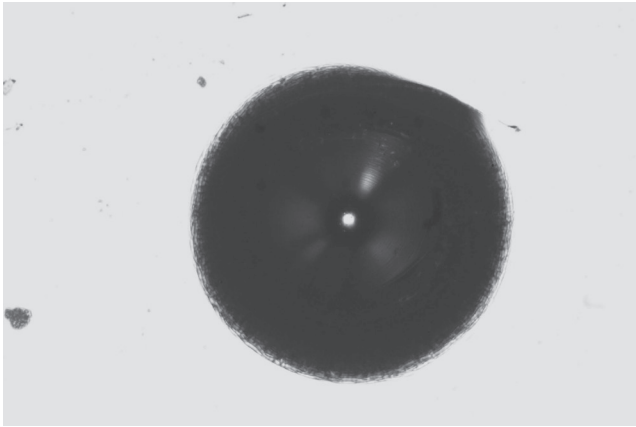


Figure 16: Diamond indentation of SuperChrome™ ABS 820  $\mu\text{m}$ .

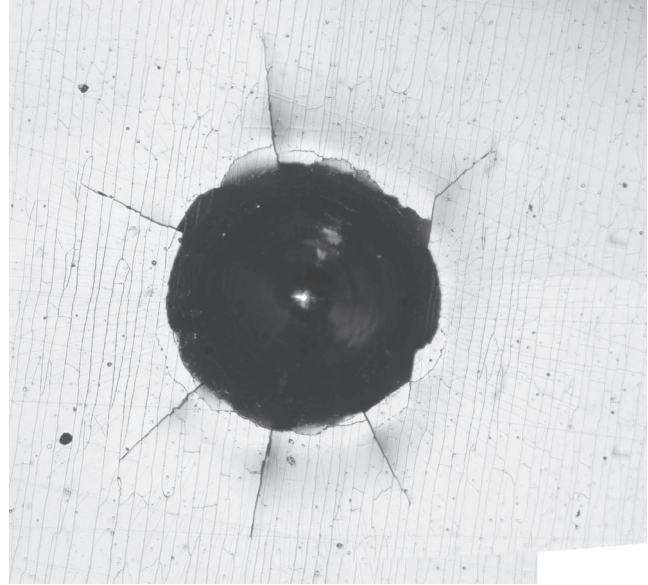
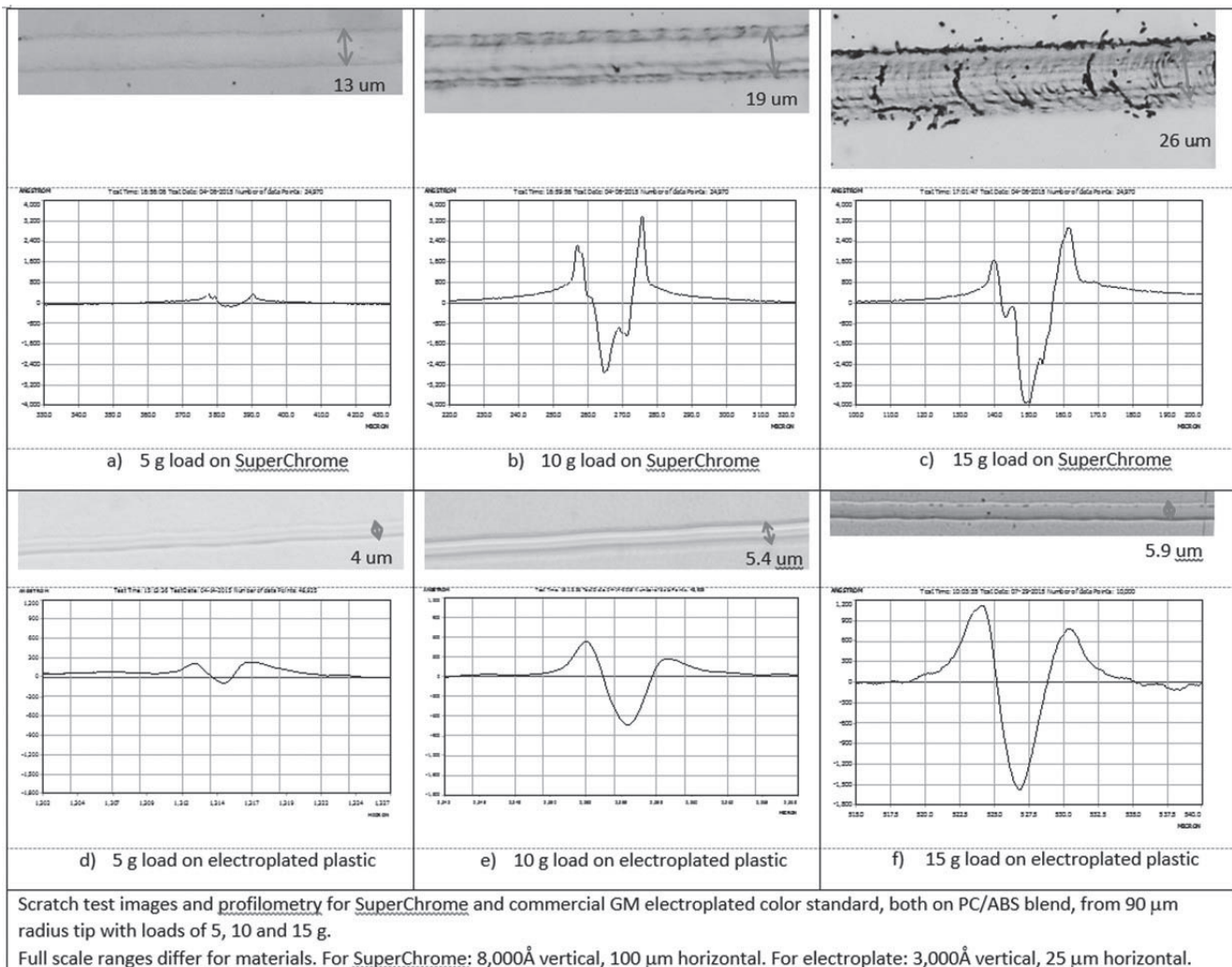


Figure 17: Diamond indentation of micro-cracked PVD Cr 848  $\mu\text{m}$ .

Table 2: Scratch and profilometer tests.



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## CONCLUSION

Today's designers have more environmentally safe choices when looking for bright chromium finishes with greatly reduced or eliminated harmful effluents as competition and technologies increase. SuperChrome™ coatings have been demonstrated to stand up to the harsh OEM tests for external automotive applications. This speaks very highly for a PVD thin film solution that is significantly thinner than electroplated chromium coatings. Appliances, sanitary, aerospace and general consumer products stand to benefit with durable finishes from a wider group of providers.

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