Coating Evaluations of Decorative PVD Finishes

G.J. van der Kolk, T. Hurkmans, T. Trinh and W. Fleischer,
Hauzer Techno Coating Europe B.V., The Netherlands; and
M. Griepentrog and U. Beck, Federal Institute for Materials Research and Testing, Germany

Keywords: Adhesion; Characterization; Decorative PVD coating, other

ABSTRACT

PVD coatings are generally subjected to a series of testing methods. In this paper we give an overview of the current testing practices, concentrating on decorative coatings. Both ASTM and DIN testing practices will be briefly discussed.

Testing methods for PVD finishes can be split in a few main areas:

- General properties like: thickness/adhesion
- Mechanical properties like: hardness/brittleness/roughness
- Wear resistance
- Corrosion resistance
- Optical properties like: colour /brilliance

For practical purposes it is desired that the properties of the ensemble of substrate and coating remain constant during a long period. To test this adequately, most tests are simulating environmental conditions in an accelerated way, e.g. thermal cycling, heat quench. Fundamental film properties like structure and composition are not discussed.

So far most of the PVD coating testing methods have been developed for tool coatings. As PVD coatings for decorative applications is a relatively new area, there is not yet a standard set of tests. A few statements will be made about specific tests that are commonly used for decorative applications.

INTRODUCTION

PVD coatings have been used for over 20 years in functional areas like tool coating.

The application of tool coating has emerged from a standard coating like TiN to a series of different coatings, dedicated to specific purposes. Coatings like TiAlN, and modifications like TiAlYN [1] are being used. For tool coatings a kind of standard has been established to specify the coating.

For tribological coatings a set of standards has not yet been established. Obvious properties like adhesion, roughness and friction are well characterized. However, wear behavior is not yet fully understood. For some coating systems there is a linear relation between wear and hardness, for others it is inversely proportional [2]. Therefore a clear set of standards for tribological applications is still missing.

Decorative coatings have been applied already for over 15 years, mainly on rather small personal accessories like spectacle frames, pens, watches. For these applications most manufacturers have used an internal set of standards.

Recently the PVD production equipment has been advanced, resulting in commercial viability of PVD coatings for applications like door hardware, bathroom faucets etc., see Hurkmans et al [3]. At this stage it is important to be able to define a set of standards and parameters that characterize the performance of the substrate in combination with the coating, as the performance of PVD technology itself can vary within very wide ranges, depending on product pre-treatment, selected process, selected substrate materials etc. As the decorative PVD coating mostly replace electrochemically deposited layers testing methods used in the plating area are used initially. However, the PVD coating has properties which are in certain aspects superior to plated layers, therefore a generally accepted set of standards is needed for specific testing.

MAJOR TESTS

Thickness

The coating thickness can be measured in many ways during deposition *(in situ)* or after the deposition process *(ex situ)*. For the *ex-situ* determination of the coating thickness on products or specially prepared reference samples there are destructive and non-destructive methods. A review of measurement of thickness of metallic and other non-organic coatings is given in ISO 3882, Metallic and other non organic coatings—Review of methods of measurement of thickness.

Thickness: Non-Destructive Methods

<u>X-ray spectrometric methods:</u> X-rays are directed to a fixed area of the coated surface. The intensity of the secondary radiation emitted by the coating, or by the substrate and attenuated by the coating, is measured. A correlation exists between the intensity of the X-rays and the coating thickness. Commercial available instruments are capable of measuring coating thicknesses with an accuracy better than 10%. The accuracy is reduced if: i) constituents of the coating are

41st Annual Technical Conference Proceedings (1998) ISSN 0737-5921

present in the substrate, and vice versa; ii) when more than two coatings are superimposed; iii) when the chemical composition of the coating varies greatly from that of the calibration standard. (For most of hard coating/substrate combinations no certified standard is available.) The method is not suitable for larger thicknesses, depending on the wave length of the fluorescent radiation, density and atomic number of coating constituents. The method is described in ISO 3497; Metallic coating-measurement of coating thickness- X-Ray spectrometric methods.

Beta backscatter method: When beta particles impinge upon a substrate a fraction is backscattered. The backscattered fraction depends on the atomic number of the material. If a body is coated and the atomic numbers of coating material and substrate are sufficiently different, the intensity of the backscatter will be between two limits: backscatter intensity of substrate and that of the coating. Using calibration standards thicknesses can be derived.

Thickness: Destructive Methods

Microscopic method: The coating thickness is measured on a magnified image of a cross-section of the coating. (Preparation of the cross section requires metallographic experience). With an optical microscope the method is capable of giving an absolute measuring accuracy of 0.8 µm, so not suitable for decorative PVD coatings. With a Scanning Electron Microscope the detection limit is much lower. The accuracy can be very good if proper reference standards are used.

Contact probe profilometer: For this method a special sample preparation is needed. In order to create a step part of the substrate has to remain uncoated. This can be done by masking a part of the substrate during deposition, or by dissolving a small area of the coating without attacking the substrate. Afterwards the step height is measured with a contact probe or optical probe profilometer. The suitability of this method depends on the profilometer used and the surface roughness. The step height should be remarkably higher than the surface roughness. Commercially available profilometers can identify steps in the range of 2 to 5 nm. Calibrated standards for different measuring ranges are commercially available. The European standard is described in ENV 1071-1.

Cap grinding method (Calo tester): A cavity is ground into the coated part. The test procedure is normally carried out with a steel ball of defined diameter wetted with a suspension of alcohol and diamond particles. The pattern of a plane monolayer shows two concentric circles due to surface and interface. With the two observed diameters the coating thickness can be calculated. Care has to be taken of i) possible interface layers not being visible; ii) polishing effects due to improper grinding speed or grinding suspension; iii) the roughness of the coated substrate. Under good conditions, when using a polished substrate, the method is capable of giving an absolute accuracy of 0.3 µm for TiN coatings of 3 mm thickness. The European standard is described in ENV 1071-2.

Adhesion

Adhesion is defined as the attractive force existing between coating and substrate. This force can be measured as the force required to separate the coating and substrate for a unit surface area. For organic coatings (paint and varnishes) and metallic coatings there are some tests using direct determination of the force. The method is described in ISO 2819. A test used for coatings is:

Cross hatch adhesion test: Flat coated area is cut with a scalpel (6 parallel cuts and 6 perpendicular to the first cuts) and covered by pressure sensitive tape, the tape is smoothed and subsequently rubbed by pencil. The tape is pulled off and the surface area is inspected for removal of coating. A rating is according to ASTM D3359, varying between 0 and 5 (5 being no flaking observed). For properly applied PVD coatings a value of 5 is expected in this test.

Tests related to this test are the Peel-off test, see ASTM D2861 and ASTM B533, the Pull-off test, see ASTM D5179 and ISO 4624, and the Twist-off test.

For most PVD coatings the adhesion is much better, and a simple separation of coating and substrate is not possible. The behavior of the coating under test conditions is not only determined by adhesion but also by other properties of the coating (hardness, E-modulus, strain, thickness, ductility) and by the same properties of the substrate. Therefore a number of indirect methods has been accepted by most users of functional coatings for characterisation of the adhesion of coating and substrate system:

Rockwell Indentation test: A standard hardness test according to the Rockwell C standards is being executed. (Standards are, a diamond tip with 120° between diamond faces, and a tip radius of 0.2 mm). Minor cracking of the film around the indentation area is allowed. Major cracks and flaking off is not allowed. A proper description of this test is given in [4, 5] with classifications between 1 and 6 for good to bad adhesion, see Figure 1. The test is only standardized for TiN coatings on High Speed Steel substrates. The substrate hardness should be at least 54 HRC. For other coating/substrate conditions a further validation is necessary.

For applications where more severe conditions are expected, like decorative apllications on front end of cars or on motor cycles we recommend the Rockwell indentation test with classification 2 or better.

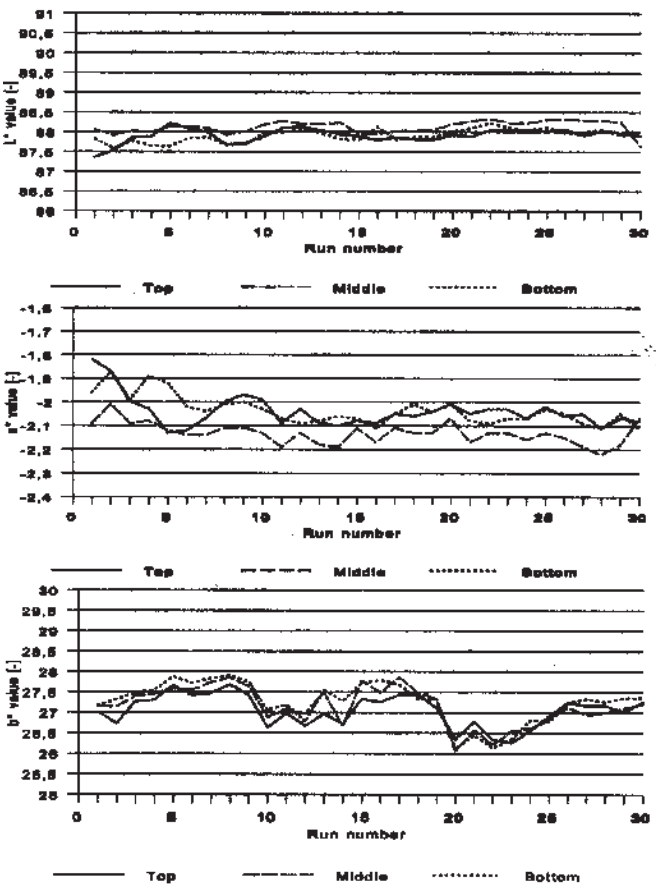

Figure 1. L*, a* and b* values, batch to batch, top to bottom in HTC 1500.

Scratch test: The test has been described by Perry [6,7]. In Europe a standard is defined (DIN V ENV 1071-3). In the most common version of the test a diamond stylus (standard a Rockwell C indentor) is drawn across the coated surface under an increasing load. Normally used is a force between 5 and 200 N. The critical load is defined as the load at which failure occurs, like coating detachment. The critical load can be used as a qualitative measure of the coating/substrate adhesion. The adhesion is considered to be good when the track does not show any flaking off at the edges at vertical load values of 50 N or higher. However, it is well known that a range of possible failure modes may occur and only some of these (spallation and buckling) are related to adhesion [8]. Furthermore the reported result includes the observers interpretation. This generally limits the suitability for the assessment of adhesion of hard coatings on soft substrates. A lot of work to improve the accuracy and the reliability of the scratch test has been reported in [9].

Bend test: Parts are bent with the coated surface outside, untill two legs are parallel. The deformed area is examined for peeling or flaking off of the coating. (ASTM B571-91-3)

This test is very suitable for practical conditions, as it is very easy to apply.

Heat Quench test: Coated samples are heated up to 250 °C (depending of course on substrate) and kept at this temperature for 5 minutes. Subsequently the samples are immersed in water at Room Temperature. Flaking and or peeling off of the coating is evidence of unsatisfying adhesion. The test is described in ASTM B 571-91-9. For PVD coatings this test is very suitable to check for initial adhesion problems.

Mechanical Properties: Hardness and E-Modulus

The deformation and fraction behavior of thin hard coatings is determined by the plastic and elastic properties of coating and substrate material, as well as by the coating adhesion to the substrate. The plastic and elastic behavior can be described by the parameters hardness and modulus.

Hardness: It is defined as the resistance of a solid against the penetration of another hard state during the penetration. The Hardness of, e.g., polymeric coatings on electroplated layers is normally measured with the 'pencil hardness test' (ASTM D3363). High density graphite drawing pencils are moved over a coating surface—the hardness of the pencils increases. The hardness of the coating is correlated to the hardness of the pencil that cuts into the film surface.

For thin hard PVD coatings this test is completely insufficient, as i) the hardness of the coating is much higher than of a polymeric layer, and ii) the coating thickness is much less so that the substrate hardness is also measured, therefore the microhardness is determined.

Microhardness: the most used method is to determine optically the indentation area made by a diamond stylus. Basically Vickers and Knoop diamond tips are defined. For the Vickers and Knoop test see ISO 4545, ISO 4546, ISO 4547 and ISO 6507-3:1997. The penetration depth of the diamond tip should be less than one tenth of the coating thickness, otherwise the substrate hardness is also measured (the Buckle rule, see [10]). With normal test equipment therefore the minimum coating thickness should be 3 µm with Vickers indentors and 1.5 µm for Knoop indentors.

An alternative method is the measurement of hardness using depth sensing indentation experiments.

Hardness under load, or universal hardness: An indentor penetrates the sample either under load control or displacement control during which load and displacement are monitored both at loading and unloading. The hardness value is calculated from the indentation depth under working test load. The hardness value contains information about both the plastic and elastic properties of the coating. (Hardness values from conventional microhardness measurements give only information about the plastic behavior). With this method nano hardnesses can be determined. The resolution depth and load measurement determine the accuracy (taking into account the Buckle rule). Considerable effects can be expected from the surface roughness, the coating uniformity (e.g. small droplets) and the real indentor geometry. One cannot assume that the nano indentor has the theoretical shape. The standards are described in ISO TR 14577 and in DIN 50359, parts 1 to 3.

Modulus: The elastic modulus quantifies elastic properties of the coating. Young's modulus can be determined by accoustic microscopy, Brillouin scattering or bending tests. There are no standards for these methods. In principle the slope of the unloading curve in the universal hardness experiment can be used to derive the elastic modulus, see above. Recently a laser accoustic technique has been developed for determination of the elastic modulus, see [11,12]. A German pre-standard is described in DIN V 32939. The surface wave dispersion phase velocity is measured as a function of frequency. Frequencies up to 200 Mhz allow reliable measurements of the e-modulus fore film thicknesses less than 50 nm. The results show remarkable agreement with those obtained from depth sensing indentation.

Mechanical Properties: Roughness

One of the most important factors influencing the decorative impression of a product is the surface topography. Generally the PVD coating has no levelling effect, and the roughness prior to PVD deposition is reproduced after deposition. The testing methods for PVD are not different from test methods for uncoated surfaces. A short description of a few methods follows.

Contact Methods for Roughness Measurement

Surface roughness measurements with a contact stylus are currently the most widely used industrial method. Several devices are commercially available and suitable for different measuring ranges (with a vertical resolution of 10 nm). A load is applied to the stylus when traversing the surface. The vertical movements of the stylus are used to trace surface roughness. Most commonly used are the parameters Ra (average of the absolute distance between middle value and actual surface) and Rz (average of the peak to bottom maximum of 5 different measurement tracks). A major disadvantage of the method is that the dimension of the stylus influences the measurement. A major advantage is that the method is well characterized and quantifiable for given stylus geometires. The tests are described in ISO 468-1982, ISO 5436, ISO 4287, DIN ISO 4288, DIN ISO 3274.

Non-Contact Optical Methods for Roughness Measurement

Many of the optical methods use a laser beam for illumination. In autofocus detection systems this laser beam is used as an optical stylus moving over the surface. A wide aperture objective focusses the beam onto the surface, the reflected light from the surface is collected with a photo detector which receives maximum signals when the surface is at the focal point. When the laser beam is out of focus the intensity change is registered and used to control the movement of the objective until the focal point is reached again. The vertical movements of the objective are used as a measure for detecting the surface profile. The lateral resolution is determined by the diameter of the laser beam and the wave length of used light. The method is not yet standardized.

To get information about surface topography in the nanometer scale the Atomic Force Microscope (AFM) is often used. AFM measures repulsive forces between a surface and a flexible cantilever with a silicon nitride tip. The interatomic forces between the tip and the surface deflect the cantilever. The movements of the cantilever are used as a measure for the surface profile. The vertical resolution of the AFM is in the 0.01 nm range. The method is not yet standardized.

Wear Resistivity of ceramic PVD coatings is generally much higher than that of Organic Coatings. Therefore the standard test method for Organic Coatings by falling abrasive _D 968-93) should not be used for ceramic PVD coatings like brass coloured ZrN or TiN. A wear test that can be used there is e.g. the Tabor Abrasor test as described in D 4060-95. Recommended values to be achieved by standard ceramic PVD coatings are that the Tabor Abrasor test is performed for over 500 to 1000 cycles, depending on the type of abrasive wheels.

Decorative Properties

Colour: The colour of PVD coatings is established with methods similar to normal uncoated objects. The most widely used system is the CIELAB colour system. Basically colours are characterized by three parameters:

a* and b* defining a plane with colours ranging from green (-a*), to red (a*) and blue (-b*) to yellow (b*). The L* value is used to indicate the contribution of white light, black (L*=0) and white (L*=100). The colour distance ΔE^*_{ab} is given by:
$\Delta E^*_{ab} = \sqrt{((L1^*-L2^*)^2 + (a1^*-a2^*)^2 + (b1^*-b2^*)^2)}$

Depending on the application colour differences in between 5 and 16 are acceptable. With a proper PVD process colour reproducibility can be achieved within $\Delta E_{ab} = 3$. See Figure 1.

The colour is normally measured with the test sample facing the colour detector, and the light source at 45° relative to the sample surface (test method 45/0). Important settings are the illumination source (e.g. D65), aperture and observer angle (2° or 10°).

Coating Stability

Corrosion resistivity: Mainly used are Neutral Salt Spray test (NSS), Copper Accelerated Acetic Salt Spray test (CASS test) and the Kesternich test. The NSS test is typically done with Sodium Chloride solution of 50 g/l ± 5 g/l. Tests are done with saturated demi water spray (particle size less than 5 µm at a temperature of 35°C). Criteria for coatings range from 500 hours to 2000 hours.

The test is described in ASTM B 117, DIN 50021, ISO 9227.

The CASS test is described in ASTM B 368. Typical test times are between 4 and 8 hours.

The Kesternich test is described in ISO 6988. The coating is tested with SO_2 (0.2 dm^3 in a volume of 300 dm^3) in an atmosphere with huidity of 75% at 40°C for one or two cycles of 24 hr.

What can be expected from a PVD coating is, that the NSS results of uncoated parts are reproduced. Improvement is hardly achieved; the corrosion resistance is comparable to that of the initial coatings of Ni and Cr. However, if the PVD coating has a high porosity, the performance will be less than that of uncoated parts because of the formation of electrochemical cells. After the treatment described in the test method, it shall be examined for flaking off of the coating, corrosion of one of the metal layers below the coating. Corrosion ratings are given in ASTM B 537.

Water immersion: The test is described in ASTM D870-92. Typically parts are immersed in water in a corrosion resistant container. The water temperature is 38°C (100°F). The parts should not show any coating degradation. For PVD coating a more stringent test is to submerge coated parts in water at 79°C (175°F) for 24 hr. Colour changes afterwards should be very limited. Changes that can be expected for good coatings are for the Δa* value less than 0.3 and for the Δb* value less than 3.5.

Cyclic humidity test: The test is described in DIN50017. Parts are subjected to a 24 hr cycle, with 8 hr slow temperature rise up to 40°C at 100% humidity, followed by cooling to Room Temperature at humidity lower than 75%. The cycle is repeated each 24 hr. The surface should not be detoriated after a pre-set number of cycles. Recommended for proper ceramic PVD coatings is a minimum number of 50 cycles.

Humidity test: The test is analogous to the cyclic humidity test without the cooling down cycle.

Thermal cycle: The test is described in ASTM B125 or ISO 4525. Basically the thermal cycle test is intended to assess adhesion. There are three basic versions:

A: thermal cycling between 75°C and 20 ± 5°C

B: thermal cycling between 75°C and -20°C

C: thermal cycling between 75°C and -40°C

Minimum number of cycles is 4. Products are supposed to be kept at the temperatures for at least 1 hr.

UV/Humidity test: It is a test that simulates the detoriation caused by water, like rain and dew, and the ultraviolet energy in sunlight. It does not include local extraordinary conditions like atmospheric pollution. Basically samples are subjected to UV irradiation (wavelength 1220 nm) and to condensation in alone in a repititive cycle. The test is described in ASTM G 53. Practical values for PVD coatings are to keep the samples at a temperature of 60°C and continue the test for at least 1000 hours.

This paper gives only very brief information about the most important standards. A list of surface related standards is on the BAM home page at [13]. A more complete presentation can be found in [14].

Table 1. Coating Evaluation for PVD Finish

Description	Standards			Comments
	ASTM	ISO	DIN (ENV)	
Thickness				
Review of measurement of thickness		3882		
Cross sectioning by SEM		1463		
Profilometer		4518	1071-1	
X-ray spectrometer		3497		
Cap grinding (Calo test)			1071-2	
Adhesion				
Review of adhesion testing methods		2819		
Rockwell indentation			VDI 3198	CVD/PVD coating of cold forging tools
Scratch test			1071-3	
Cross hatch adhesion	D3359-95a	2409		
Pel-off test	D 2861			
	B533		DIN 53494	
Pull-off test		4624		for paints and varnishes
	D 5179			adhesion of organic coatings to plastic
Bend test	B571-91-3			
Hardness				
Pencil hardness test	D33363-92			not suitable for hard PVD coatings
Vickers macro hardness		146 and 4545		Vickers and Knoop hardness test
Vickers micro hardness		4546		Verification of Vickers/Knoop hardness testing machines
Vickers micro hardness		4547 and 6507-3		Calibration of standardized blocks for hardness test
Vickers micro hardness	B578-93			microhardness testing of electroplated coatings
Universal hardness		TR 14577		Metallic materials, universal hardness test
Universal hardness			DIN 50359	Universal hardness testing, method/verification/calibration
Laser acoustic of e-modulus			DIN V 32939	
Roughness				
Roughness measurement		468-1982		surface roughness, parameters, their values and general rules
Roughness calibration		5436		Calibration specimen, stylus instruments
Determination of parameters		4288		Determination of surface roughness parameters using stylus
Scratch resistivity				
Falling abrasive	D 968-93			
Taber abraser	4060-95			
Color				
Cielab colour measurement	JIS Z8729	7724	DIN 5033	
Color chart			DIN 6164	
Color matching			DIN 6173	general rules
Colorimetric evaluation			DIN 6174	according to CIELAB form
Coating stability				
Neutral Salt Spray Test	B117	3768 and 9227	DIN 50021	
CASS test	B 368			corrosion ratings in ASTM B 537
Kesternich test		6988	DIN 6988	
Water immersion	D870-92		DIN 50905	
Heat quench	B 571-91-9			
Cyclic humidity			DIN 50017	
Thermal cycle	B 125		4525	
UV/humidity	G 53-95			
Gold alloy/general		ISO 3160-1		specific for watches
Gold alloy/fineness, thickness		ISO 3160-2		specific for watches

REFERENCES

1. L.A. Donohue, I.J. Smith, W.-D. Munz, I. Petrov and J.E. Greene, Proc of ICMCTF, 1997.

2. S.J. Harris, A.M. Weiner and W.-J. Meng, Wear, 211, 208-217, 1997.

3. T. Hurkmans, F. Hauzer, B. Buil, K. Engel and R. Tietema, Surf And Coat Technol 92, 62-68, 1997.

4. J. Guttler and J. Reschke, Surf and Coat Technol, 60, 531-535, 1993.

5. VDI ("Society of German Engineers") 3198, Coating (CVD, PVD) of cold forging tools.

6. A.J. Perry, Surf Eng 2, 183-190, 1986.

7. A.J. Perry, J. Valli and P.A. Steinmann, Surf Coat Technol 36, 559-575, 1988.

8. S.J. Bull, Tribology International 30(7), 491-498, 1997.

9. Development and validation of test methods for thin film hard coatings (FASTE) Final report, (SMT contract number MAT-Ct 940045).

10. H. Buckle, Micro hardness testing (in German), VDI-Ber 41, 14-20, 1961.

11. D. Schneider and Th. Schwartz, Surface and Coatings Technology, 91,136, 1997.

12. D. Schneider, B. Schultrich, H.-J. Scheibe,H. Ziegele and M. Griepentrog, to be presented at the ICMCTF '98 in San Diego, CA.

13. BAM home page at:
http://www.bam.de/a_viii/g3viii20.html

14. G. Reiners, Standards for thin film technologies, Short courses held on TATF '96.