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Standard Test Method for Measuring Mechanistic Aspects of Scratch/Mar Behavior of Paint Coatings by Nanoscratching[1]

This standard is issued under the fixed designation D7187; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers the nanoscratch method for determining the resistance of paint coatings on smooth flat surfaces to scratch/mar.

1.2 Previous methods used in scratch/mar evaluation first physically scratch or mar a sample's surface with multiple contact cutting, and then use visual inspection to assign a ranking. It has been recognized that loss of appearance is mainly due to surface damages created. The philosophy of this method is to quantitatively and objectively measure scratch/mar behavior by making the evaluation process two steps with emphasis on surface damages. Step one is to find the relationship between damage shape and size and external input (such as forces, contact geometry, and deformation). Step two is to relate damage shape and size to visual loss of luster. The first step is covered by this method; in addition, a survey in the appendix provides an example of an experiment to relate the damage to the change in luster.

1.3 There are three elementary deformation mechanisms: elastic deformation, plastic deformation and fracture; only the latter two both contribute significantly to mar. This method evaluates scratch/mar based on the latter two damage mechanisms.

1.4 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

1.5 *This standard does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D609 Practice for Preparation of Cold-Rolled Steel Panels for Testing Paint, Varnish, Conversion Coatings, and Related Coating Products

D823 Practices for Producing Films of Uniform Thickness of Paint, Varnish, and Related Products on Test Panels

D1005 Test Method for Measurement of Dry-Film Thickness of Organic Coatings Using Micrometers

D1044 Test Method for Resistance of Transparent Plastics to Surface Abrasion

D1186 Test Methods for Nondestructive Measurement of Dry Film Thickness of Nonmagnetic Coatings Applied to a Ferrous Base

D1400 Test Method for Nondestructive Measurement of Dry Film Thickness of Nonconductive Coatings Applied to a Nonferrous Metal Base

D3363 Test Method for Film Hardness by Pencil Test

D3924 Specification for Environment for Conditioning and Testing Paint, Varnish, Lacquer, and Related Materials

D5178 Test Method for Mar Resistance of Organic Coatings

D6037 Test Methods for Dry Abrasion Mar Resistance of High Gloss Coatings

D6279 ~~Test Method for Rub Abrasion Mar Resistance of High Gloss Coatings~~ Test Method for Rub Abrasion Mar Resistance of High Gloss Coatings

G171 Test Method for Scratch Hardness of Materials Using a Diamond Stylus

3. Summary of Test Method

3.1 This test method is based on representative samples of the paint film being scratched using a nanoscratch instrument. From

[1] This test method is under the jurisdiction of ASTM Committee D01 on Paint and Related Coatings, Materials, and Applications and is the direct responsibility of Subcommittee D01.23 on Physical Properties of Applied Paint Films.

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For ASTM Book of ASTM Standards volume information, refer to the standard's Document Summary page on the ASTM website.

information received during a scratch test, values for plastic resistance and fracture resistance can be determined.

3.2 From these values of plastic resistance and fracture resistance, the mechanistic aspects of scratch/mar behavior of the coating can be subsequently compared.

4. Significance and Use

4.1 This test attempts to address two major drawbacks in existing mar tests such as Test Methods D1044, D3363, D5178, D6037, and D6279, namely:

4.1.1 Measured damage is caused by hundreds of contacts with differing contact geometries making it difficult or impossible for mechanical quantities (force, displacement) at the contact points to be reliably determined.

4.1.2 The damage is evaluated using subjective visual assessments, which provide only a qualitative sense of wear with little information about mar mechanisms.

4.2 This test provides a quantitative assessment of a paint coating's mechanistic aspects of scratch/mar behavior in various conditions. The ability to control testing variables such as rate and temperature allow the study of the scratch/mar behavior in a variety of environments.

4.3 This test method is particularly suitable for measurement of paint coatings on laboratory test panels.

4.4 The accuracy and precision of scratch/mar performance may be significantly influenced by surface nonuniformity and irregularities.

4.5 A correlation has been observed between good mar resistance in field studies and a combination of high Plastic Resistance and high Fracture Resistance (terms are defined below). When coatings have had either high Plastic Resistance and low Fracture Resistance, or low Plastic Resistance and high Fracture Resistance, there have been contradictory results in field studies.

4.6 Mar resistance characterizes the ability of the coating to resist light damage. The difference between mar and scratch resistance is that mar is related to only the relatively fine surface scratches which spoil the appearance of the coating. The mechanistic aspects of mar resistance depend on a complex interplay between visco-elastic and thermal recovery, yield or plastic flow, and micro-fracture. Polymers are challenging because they exhibit a range of mechanical properties from near liquid through rubber materials to brittle solids. The mechanical properties are rate and temperature dependent and visco-elastic recovery can cause scratches to change with time.

4.7 Since this method measures mechanical qualities, such as forces and displacements (deformations) during the damage making process, rate dependence, temperature dependence, and visco-elastic-plastic recovery can be further investigated and visual impacts of damage can be related to deformation mechanisms.

5. Apparatus

5.1 *Paint Application Equipment* , as described in Practices D609 and D823.

5.2 *Nanoscratch Instrument*, consisting of an instrument with a well-defined indenter, which translates perpendicular to the coating surface and has the capacity to produce an instrumented scratch of controlled and variable normal force and continuously measured displacement during testing. The normal force must be feedback controlled, in order to quickly respond to variations in surface morphology. The force of the instrument should have a maximum normal force of at least 50 mN (mN should be read as milli-Newtons) with a resolution of at least 0.1 mN. The maximum tangential force, if measured, should be at least 50 mN with a resolution of at least 0.5 mN. The range of the displacement sensors should be at least 50 μm with a resolution of at least 20 nm. Displacement and tangential force response of the coating should be measured with a high data acquisition rate, such as a maximum of five μm between data points.

5.3 *Suggested range for testing parameters*:

5.3.1 Indenter size should range from 1 to 100 microns and should be spherical in geometry. Indenter material should be diamond.

5.3.2 The scratch should be applied at a rate of 0.5 to 10 millimetres per minute.

5.3.3 The loading rate of the normal force should be applied at 5 to 200 mN per minute.

5.3.4 The scanning preload should be conducted with an applied force of 0.1 to 1 mN.

5.4 The following is an example of one particular application of the test ranges. This example is based on automotive clear coats on a metal substrate.

5.4.1 Indenter size of 2 microns.

5.4.2 Scratch rate of 3 millimetres per minute.

5.4.3 Loading rate of 40 mN per minute.

5.4.4 Scanning preload of 0.2 mN.

5.4.5 Data acquisition rate of 3 μm between data points.

NOTE 1—To optimize test parameters for a particular coating, it should be remembered that different combinations of applied load and indenter radius will cause differing damage in polymeric coatings. A smaller indenter radius (sharper tip) will tend to cut the coating and apply a higher contact pressure, whereas a larger indenter radius (blunter tip) will tend to tear the coating and apply a lower contact pressure.

6. Test Specimen

6.1 The substrate for the paint coating should be a smooth, plane, rigid surface, such as those specified in Practices D609 and D823.

6.2 The thickness of the coating being tested, determined in accordance with either Test Methods D1005, D1186, or D1400, should be uniform within 500 nm. In order to minimize the effect of the substrate for maximum accuracy, the penetration depth should not exceed one-half the coating thickness.

6.3 At least three scratches should be performed on each test specimen.

6.4 The surface of the specimens should be free of any dirt and oils.

6.5 The specimen size should be sufficient to be adequately secured to the nanoscratch instrument, but not so small as to interfere with the movement of the indenter tip or its supporting cantilever.

NOTE ~~1—It~~ 2—It is recommended that substrates with similar compliances be used when comparing different coatings.

7. Conditioning

7.1 Cure the coated test specimens under conditions agreed upon between the purchaser and seller that reflect the conditions of curing of the paint in actual service.

7.2 Condition and test the test specimens at 23 ± 2ºC (73.5 ± 3.5ºF) and a relative humidity of 50 ± 5 % for at least 24h, unless the purchaser and seller agree on more suitable test characteristics, as specified in the Standard Atmosphere of Specification D3924.

8. Procedure

8.1 Secure the specimen to the moveable stage on the instrument with the surface to be measured located perpendicularly to the indenter tip. Ensure the panel is held rigidly to the stage and cannot be moved by the action of the subsequent scratch test.

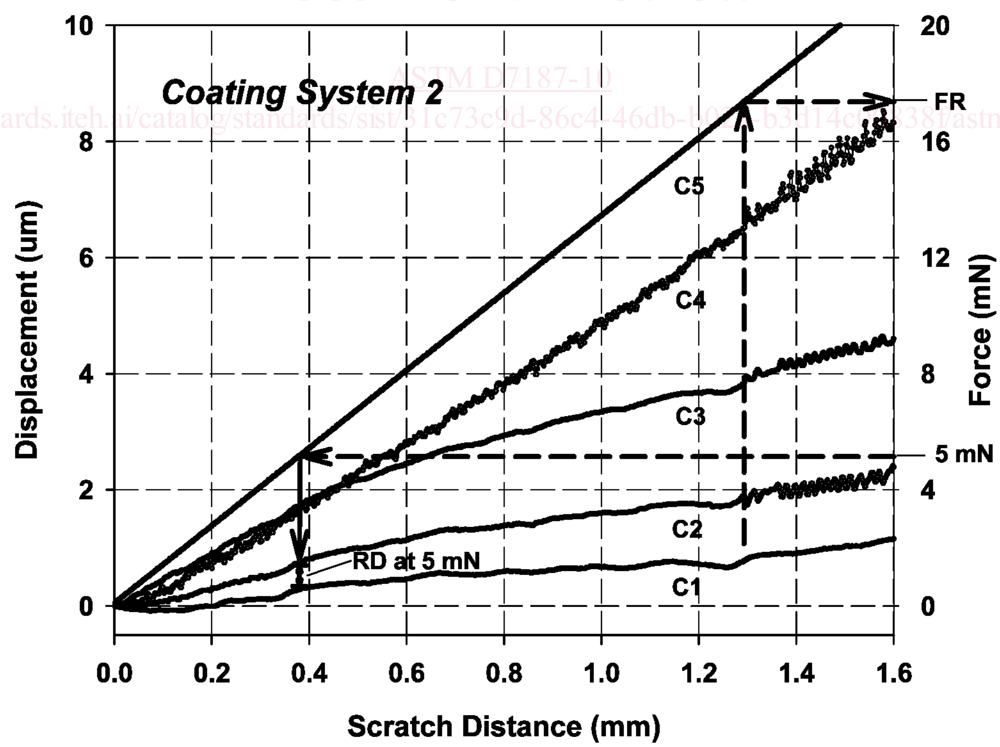
8.2 Carefully move this area under the indenter and bring the indenter tip close to the sample surface.

8.3 The complete scratch test consists of three distinct steps. In all three steps, the indenter follows the exact same path across the sample surface.

NOTE ~~2—A~~ 3—A set of sample test parameters can be found in 5.4

8.3.1 Perform a prescan to measure the topography of the undamaged coating. Apply the lowest load that the instrument can apply but that makes no permanent damage. The prescan, scratch, and postscan should all be performed on the same line.

8.3.2 Instruct the instrument to begin making a scratch to produce damage to the coating. Allow the instrument to ramp to the



NOTE—The unit "mN" is meant to be read as mili-Newton.

FIG. 1 Typical Data from a Nanoscratch Experiment C1 – Vertical Displacement of the Indenter During the Pre-scan C2 – Vertical Displacement During Post-scan C3 – Vertical Displacement During Scratch . C4 – Tangential Force C5 – Applied Normal Force (1)

desired normal force at a controlled rate. At the end of the scratch, return the indenter tip to its starting position at the beginning of the scratch.

8.3.3 Perform a postscan, where the indenter tip is scanned along the scratch, measuring the residual topography of the damaged area. This should be done with the lowest load the instrument can apply.

NOTE ~~3~~4—Prescan and postscan should only be used if the instrument has force feedback control, otherwise significant error may be incurred.

8.4 The complete scratch test should be repeated 2 more times at different locations so that there are a total of 3 scratches per test panel.

8.5 Typical results of a nanoscratch test are presented in Fig. 1.[3] The graph consists of five curves labeled 1 through 5. If needed, correct the data by curve fitting so that zero indenter penetration and residual depth corresponds to zero applied normal force.

8.5.1 Curve 1 shows the topography of the unscratched surface along the scratch path. It is a measure of the vertical displacement of the indenter tip during a low (~0.2 mN) constant load prescan.

8.5.2 Curve 2 shows the topography of the damaged surface along the scratch path immediately after the scratch test was concluded. It is a measure of the vertical displacement of the indenter tip during a low (~0.2 mN) constant load scan through the completed scratch.

8.5.3 Curve 3 shows the vertical displacement of the indenter tip during the scratching process.

8.5.4 Curve 4 shows the tangential force that arises between the coating and the indenter tip.

8.5.5 Curve 5 shows the applied normal force on the coating surface.

9. Calculations

9.1 From analysis of the Force/Displacement versus Scratch Distance plot produced (Fig. 1), plots of various quantities relating to the mechanical behavior of the coating vs. scratch distance can be generated:

9.1.1 The penetration depth (PD) of the indenter under the applied normal force can be calculated by subtracting the surface topography measured from the prescan, Curve 1, from the displacement measured during the scratch, Curve 3.

$$PD = C_3 - C_1$$

where PD means Penetration Depth, and C_3 and C_1 correspond to Curves 3 and 1 respectively.

9.1.2 The magnitude of residual depth (RD), otherwise known as permanent plastic deformation, to the coating can be calculated by subtracting the surface topography before the scratch, Curve 1, from the topography after the scratch, Curve 2.

$$RD = C_2 - C_1$$

9.1.3 The difference between the displacement during the scratch, Curve 3, and the surface topography after the scratch, Curve 2, is the elastic recovery (ER) of the coating.

$$ER = C_3 - C2$$

9.1.4 The ratio of tangential force, Curve 4, to the normal force, Curve 5, is a form of the friction coefficient (C_f).

$$C_f = C_4/C_5$$

NOTE~~4—The~~ 5—The prescan and postscan need to be conducted consistently (with the same scanning parameters done within less than 10 minutes) before and after the scratch load is applied. This is done to accurately measure recovery aspects since these aspects will vary with time.

9.2 Plastic resistance (PR) at a particular normal force can be calculated by dividing the normal force by the magnitude of the permanent damage at that normal force before fracture occurs. Selecting the spot for measurement to be at a higher applied normal force results in values that reflect a more true plastic resistance. This gives a value for plastic resistance that is relatively constant that is in units of force per unit of damage depth, or mN/μm.

$$PR = F_N/RD$$

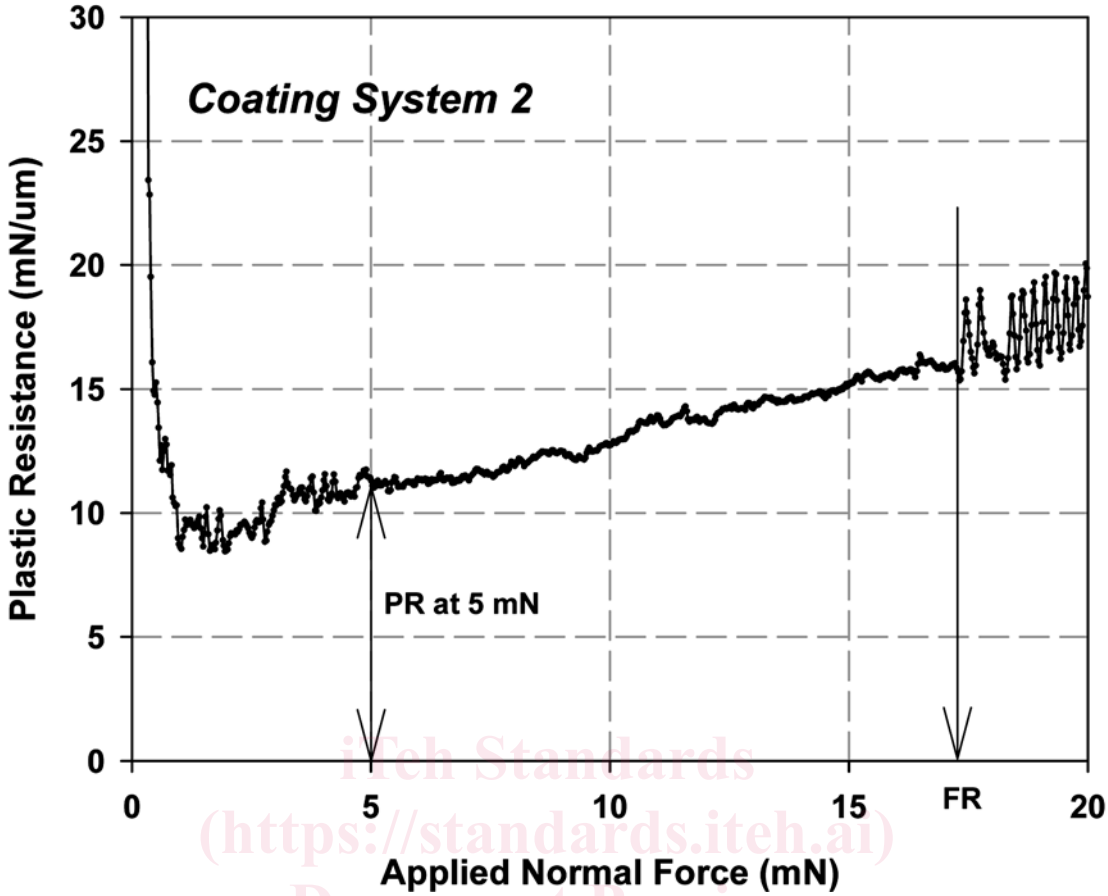
where:

PR = plastic resistance,
F_N = the normal force in mN, and
RD = permanent plastic deformation or residual depth in microns

NOTE~~5—Only~~ 6—Only at very low normal force values does the plastic resistance differ radically. In our tests, we selected the measurement point to be at 5 mN. In the case of Fig. 2, the material has fractured at 5 mN so plastic resistance should be measured at a lower force. Plastic resistance values should be evaluated in the area of the curve that is relatively constant and in the area before fracture occurs.

9.3 Fracture resistance can be determined by locating the point where normal force, tangential force, penetration depth of the indenter and permanent damage begin to fluctuate wildly. This is the point where the first fracture occurs. Any subsequent increase in normal force only leads to increased fracture. This mechanical quantity is known as the *critical load* and has units of mN.

[3] The boldface numbers in parentheses refer to the list of references at the end of this test method.



NOTE—The unit "mN" is meant to be read as mili-Newton.

FIG. 2 Variation of Plastic Resistance (PR) with Respect to Applied Normal Force. Note that the constant plastic resistance value at higher (greater than 3 mN) applied loads. FR refers to the Fracture resistance, or critical load. (2)

9.4 Plastic deformation and fracture are the two damage mechanisms that will have an effect on the coating performance. As shown in Fig. 3a and b, the morphology of these two types of deformation is quite different. This difference in morphology is what has the most profound influence on the appearance of the coating. Plastic deformation is calculated in 9.1.2 and is also known as the magnitude of permanent damage or residual depth (RD).

9.5 Data for several coatings may be compared using a graph of Plastic Resistance versus Fracture Resistance, as shown in Fig. 4.

9.6 For some coating types, it may be of interest to calculate the plastic resistance based on the width of the scratch. In this case, the plastic resistance can be defined as the ratio of applied normal load divided by the width of the scratch at that point along the scratch. This methodology is similar to that described in Test Method G171 for the measurement of scratch hardness. It requires a means of directly measuring the scratch width; this can be achieved by microscopy or by stylus profilometry.

10. Report

10.1 Report the following information:

10.1.1 Mean and range of fracture resistance and plastic resistance or residual depth values, and where these values are measured (5 mN in our example), obtained for each sample.

10.1.2 Type of coating, substrate and coating techniques used.

10.1.3 Time and temperature of sample conditioning.

10.1.4 Indenter size and shape.

~~10.1.5Applied scratch rate and loading rate as well as the scanning force.~~

10.1.5 Applied load range (minimum and maximum), loading rate and scanning force.

10.2 An example of reported test parameters can be found in 5.4.

11. Precision and Bias

11.1 *Precision*—Six samples, each of three automotive clearcoats with differing chemistry, named System 1, 2, and 3, were tested at Dupont Marshall Labs, CSM Instruments and FPL for repeatability and reproducibility and discrimination. Statistically,

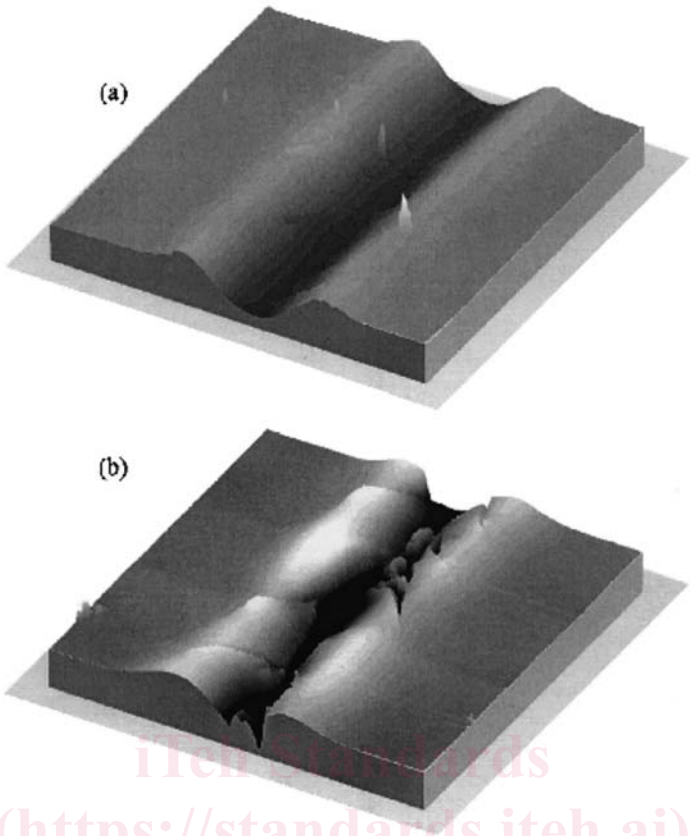


FIG. 3 AFM Images of a Scratch both before Fracture (a) and after Fracture (b)

the rule of thumb is at least 30 data points are needed to assess variability. The data set with three laboratories, three different samples (systems) and six measurements each, yields a total of 54 results for analysis and is used to demonstrate the method's repeatability and reproducibility. In all cases, the CSM Instruments Nano-Scratch Tester was used. The software MINITAB was utilized to perform the statistical analysis.

11.1.1 Fracture Resistance:

11.1.1.1 Table 1 shows the statistical results of fracture resistance. Here Sr is the average value of standard deviation measured by the three individual groups, and SR is the overall standard deviation of all 18 samples from the three groups. Values of r and R are 2.8 times of Sr and SR, respectively. Repeatability is characterized by the values of Sr and r. Reproducibility is characterized by the values of SR and R.

11.1.1.2 Fig. 5further illustrates the repeatability, reproducibility and discrimination of the test method regarding fracture resistance measurements. A Gage R&R study with ANOVA method is given in Fig. 6.

11.1.2 Residual Deformation:

11.1.2.1 Table 2 shows the statistical results of residual deformation. Fig. 7 further illustrates the repeatability, reproducibility and discrimination of the test method regarding residual deformation measurements. A Gage R&R study with ANOVA method is given in Fig. 8.

11.1.3 Plastic Resistance:

11.1.3.1 Table 3 shows the statistical results of plastic resistance. Fig. 9 further illustrates the repeatability, reproducibility and discrimination of the test method regarding plastic resistance measurements. A Gage R&R study with ANOVA method is given in Fig. 10.

11.1.4 The data in Tables 1-3, indicate that relatively large errors (ratio of deviation to mean) occur during the residual deformation measurement and plastic resistance measurement of coating system 3. This is due to the unusual, rubbery behavior of the material, which results in more than 97 % immediate deformation recovery (in comparison to 70 to 80 % for most coatings) and makes measurement of residual deformation more challenging. The errors are further exaggerated when calculating plastic resistances because a low value of residual deformation in the denominator greatly impacts the plastic resistance calculation.

11.2 *Bias*—This procedure has no bias because the values for plastic deformation and fracture resistance, though resembling fundamental mechanical properties, are defined only in this test and in that respect are highly subject to the variables of the test itself, such as the scratch speed and loading rate.