Scratch Resistance Behavior of Automotive Plastic Coatings

Rose A. Ryntz and Dottie Britz—Visteon Corporation*

The sensitivity of automotive coatings, particularly coatings for plastics, to scratching has been a growing concern among automakers. Scratching may result from such predelivery events as polishing of minor defects embedded in the paint, or post-delivery events such as car wash bristles, dirt embedded under a cloth utilized in polishing the car, tree branches, and the like. Warranty cannot separate out which event is the more prevalent (e.g., predelivery or post-delivery to the customer) form of damage on plastics. Data available on coatings for metal, however, does suggest that isocyanate-based crosslinked systems perform more poorly than their melamine-based crosslinked counterparts when exposed to in-plant (predelivery) handling. This work attempts to correlate the scratch resistance behavior of coatings of plastics, both in their "green state" (right out of the oven, less than one week post-cure time) and in their infancy in the field (simulated 250 kJ Xenon arc Weather-ometer), to surface attributes such as toughness, hardness, and elasticity. Functional carbamate-melamine crosslinked one-component coatings and functionalized silane-melamine crosslinked one-component coatings appear to outperform selected two-component coatings, which in turn outperform one-component hydroxyl functional acrylic or polyester melamine crosslinked coatings. Material attributes such as surface hardness, toughness (as measured through the method of essential work), and the ability to recover from an applied load are most important in the ability of the coating to resist damage.

INTRODUCTION

Increased scratch resistance of coatings has been a long sought-after goal in the automotive industry. Predelivery (in-plant handling) and post-delivery (customer induced) scratching is known to occur from such events as polishing, car wash bristles, tree branches, and the like. Warranty, however, cannot separate out the most prevalent damage-induced event. Coatings on plastics, while lower in modulus than coatings on steel, are still subject to scratch events, albeit they have a greater tendency to self-heal once scratching events have occurred.

Several researchers have attempted to resolve the issue by varying the modulus,[1] toughness,[2] and hardness[3] of the coatings studied. The ability to quantify what the variances in coating attributes contribute to increased scratch resistance, however, remains a subject of controversy.

Conventional test methods utilized to quantify the scratch resistance of a coating are such measurements as: reduction in gloss of a coating after being subjected to a traversing tangential load of known particle size abrasive (crockmeter test); measurement of damage depth and recovery of damage depth of a coating after exposure to a single point indentor (nanoindentor[4,5]); or quantitative measurement of the fraction of elastic, viscoelastic creep, and fracture response of a coating after exposure to a single point indentor (scanning probe microscope[6]).

Courter[7] evaluated several acrylic/melamine formulations for automotive sheet and determined that a mar-resistant coating should possess a low modulus, which would translate to low yield stress and high toughness. She attributed the higher mar resistance of such coatings to their ability to resist cracking when scratched.

Gregorovich[8] related the scratch resistance, as determined through the conventional crockmeter test, of a coating to the mechanical toughness of the coating under applied uniaxial stresses. In the so-called "method of essential work" the toughness of a coating or film in plane strain was found to be independent of the geometry and dimensions of the specimen tested.[9] In calculating the essential work or toughness of a coating, sample preparation is important. Several free films of the coating studied

*401 Southfield, Dearborn, MI 48121.

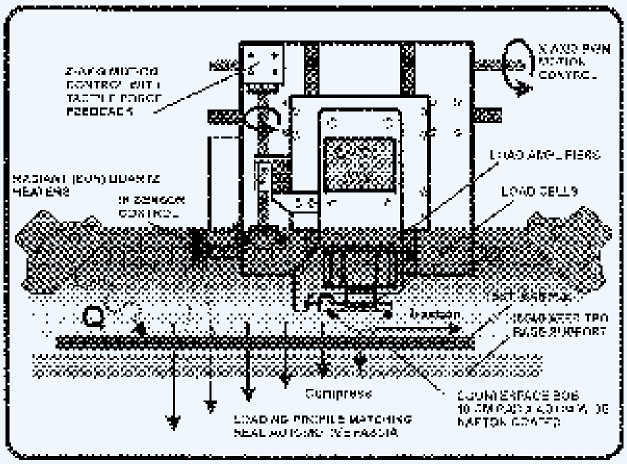

Figure 1—Schematic of SLIDO apparatus.

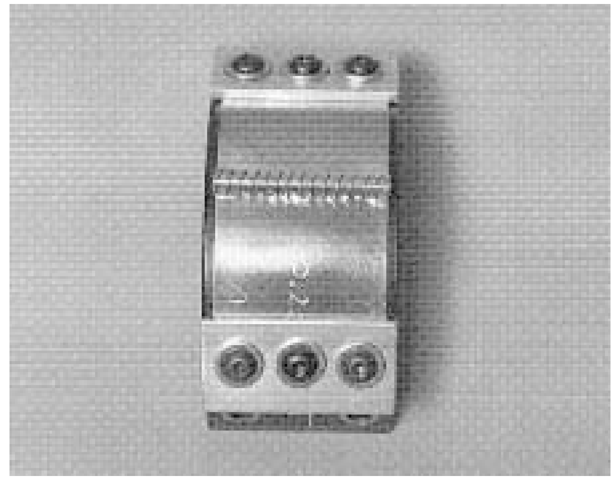

Figure 2—Helix scratch head utilized in Scratcho.

are selectively notched on both sides of a known, consistent gage length to produce a series of ligament lengths. The work of fracture is then calculated for each of the samples by taking the area under the stress-strain curve in a uniaxial stress-strain measurement. When the ligament length is plotted versus the work of fracture, the best-line fit extrapolation to zero ligament length is taken as the "essential work" value.

Two restrictions are applicable to the essential work method. The first restricts the maximum ligament length used for extrapolation[10] to one-third of the width of the sample so that it restricts the plastic deformation to the ligament area and ensures complete yielding of the sample before crack growth. The second restricts the maximum ligament length used for extrapolation to three to five times the sample thickness[11] to avoid the plane-stress to plane-strain transition region where the theory breaks down.

The intent of this paper is to present a concise description of what variations in coating attributes, such as toughness and hardness, contribute to the scratch resistance propensity of the coating. Such scratch methods as the essential work, the crockmeter method, the Ford five-finger test (a modified single point indentor method), and a newly described Scratcho testing methodology are utilized to prescribe coating attributes to scratch resistance. A variety of coating types, to include one-component and two-component crosslinked coating matrices, over flexible plastic are ranked by each of the scratch methods described.

EXPERIMENTAL

All solventborne flexibilized (for application onto flexible plastics) coatings utilized in this work were sprayed applied:

(1) as a clearcoat at nominal dry film build (35 to 50 microns) over untreated thermoplastic olefin (TPO) substrate supplied by Solvay Engineered Polymers (Sequel 1440) which was subsequently baked for 30 min at 121°C (for free film tensile specimens for essential work calculations) or;

(2) as a composite consisting of chlorinated polyolefin adhesion promoter (dry film build of eight microns)/black one-component melamine crosslinked basecoat (dry film build of 20 microns)/clearcoat (dry film build of 35 to 50 microns) over thermoplastic olefin substrate (Sequel 1440) which was applied wet-on-wet and subsequently baked for 30 min at 121°C.

The flexible clearcoats were either one-component hydroxyl-functional acrylic or polyester (1K) melamine-crosslinked systems, 1K functionalized carbamate-melamine crosslinked systems, 1K functionalized alkoxysilane-

Table 1—Coating Properties and Scratch Resistance

Coating	Microhardness	$E/(1 - v^2)$	W_r/W_t	7N Scratch Depth* (microns)	7N Scratch Recovery (%)	Scratcho (lb)	Scratcho WOM (lb)	Crockmeter (% Gloss Loss)	Wess (J x 10^{-4})	Wess (R^2)
A1K	81.9	1.1	0.58	0.99	0	4.6	4.8	38.1	0.22	0.6
A2K	128	1.7	0.61	0.9	1	9.1	3.7	33.9	6	0.52
Bcarb	221	1.9	0.47	0.9	8.1	14.52	5.97	14.6	18.7	0.93
B1K	29.5	0.7	0.63	1.2	0.4	7.57	2.3	28.6	1.46	0.64
B2K	66.2	1.3	0.69	1.14	2.1	8.48	6.25	13	2.27	0.96
Dsilane	34.3	0.7	0.65	1.16	0	8.18	6.53	9.9	6.45	0.91
D1K	95.8	1.5	0.64	1.07	0	4.4	3.15	36.1	2.64	0.9
D2K	61.8	1.2	0.66	1.2	0.2	7.5	5.1	15.3	0.91	0.95
Pcarb	122	1.4	0.56	0.95	0	5.91	4.14	32	1.29	0.89
P1K	35.4	1.2	0.68	1.1	0	5.16	3.3	42.1	0.71	0.57
P2K	91.4	1.5	0.66	0.96	3.1	7.88	3.72	26.1	4	1

Table 2—Results of Tests on Flexible Coatings

	Scratch Resistance			
Coating	7N	Crockmeter	Scratcho	Scratcho (WOM)
A1K				
A2K	X		X	
BCarb	X	X	X	X
B1K				
B2K	X	X	X	X
D1KS		X	X	X
D1K				
D2K		X		X
PCarb				
P1K				
P2K	X			

melamine crosslinked systems, or two-component hydroxyl-functional acrylic or polyester (2K) isocyanate crosslinked systems. Coatings were obtained from the commercial paint suppliers utilized in the automotive components business (e.g., BASF Coatings, PPG Coatings, Akzo Nobel, PPG Industries, or DuPont Automotive Coatings).

The essential work values were obtained on each clearcoat-only system by methods described previously on an Instron 5565 electromechanical testing apparatus. Tensile tests were performed at 25°C and 50% relative humidity. The displacement rate was 0.033 mm/sec. Clearcoat-only films were prepared as previously discussed, peeled from the TPO substrate, and cut into gage lengths of 25.4 mm. Double-edged notch tension specimen geometry of different ligament lengths was utilized. The notches were made perpendicular to and at the mid-gage length using a razor blade with a tip radius of 0.01 mm. To obtain sharp crack tips, the razor blade was drawn from the inside of the notch to the outside edge of the gage length. Three specimens each of five different ligament lengths were tested for each clearcoat. The ligament lengths were chosen to maintain plane strain conditions within the specimens. Essential work values were calculated by plotting the ligament length (x-axis) versus the work of fracture (area obtained under the stress-strain plot) (y-axis) and extrapolating the best straight line through the data points back to the zero-ligament length. The correlation coefficient to straight-line goodness of fit, R^2, is also reported.

Ford five-finger (FLTM 108-13) scratch ratings were obtained at room temperature (25°C) on adhesion promoted/basecoat/clearcoat TPO composites with the 7N finger. In this method the coated panel is placed onto a moveable platen onto which is placed a beam containing the scratch pin. The beam is 250 mm long and is equipped with a scratch pin that consists of a highly polished steel ball (1 mm ± 0.1 mm in diameter). The beam is driven by compressed air to draw the pin across the surface of the coated plaque to generate a scratch. Sliding velocity was maintained at approximately 100 mm/sec. Recovery values reported were achieved by placing the scratched panel in a dessicator (maintained at 98% relative humidity and room temperature) for a period of 24 hr prior to measurement. Measurements of the scratch "ditch" depth, scratch "shoulder" threshold, and scratch "ditch" volume removed, were obtained with a Wyko interferometer at a magnification of 5X.

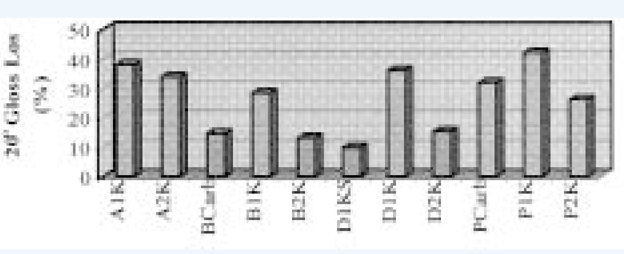

Figure 3—Crockmeter results as a function of coating type.

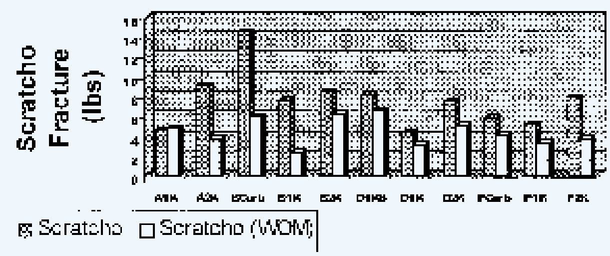

Figure 4—Scratcho results as a function of coating type and exposure.

Microhardness measurements on the basecoat/clearcoat composite structures were made with a Fischer Microhardness H-100 apparatus equipped with a Vickers indentor and a 100 mN load. The load rate was applied in 60 steps, with one second between steps. Unloading was accomplished after seven seconds of creep in 60 steps, with one second between steps. Values reported include the plastic hardness, H_{plas}, which is a measure of the plastic deformation component of the indentation; the plastic component, W_r, reported as a percentage of the total work (W_t) applied in the indentation process; and $E/(1 - \upsilon^2)$, which is the Young's modulus (E) divided by a factor of (1 – Poisson's ratio (υ) squared), the value being somewhat representative of the compressibility as a function of material stiffness.

Gloss retention of marred surfaces was measured with a 20° gloss meter and reported as a percentage of the initial unmarred surface gloss. Marring was performed on an AATCC crockmeter equipped with a cloth pad (DP-cloth, HQ manufactured by Struers, Copenhagen, Denmark and distributed by VWR Scientific) fitted with 0.01 gram of 63 micron (220 grit) alumina oxide. The load was

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Figure 5—7N scratch performance as a function of coating type.

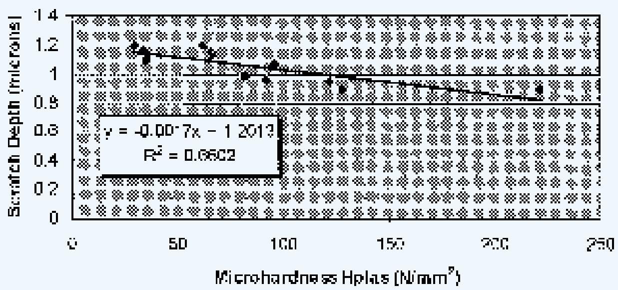

Figure 6—7N scratch depth vs. microhardness Hplas.

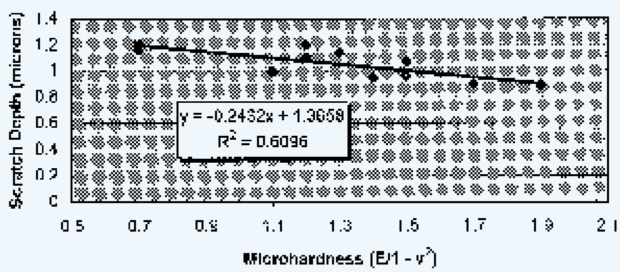

Figure 7—Microhardness $E/(1 - \upsilon^2)$ vs. 7N scratch depth.

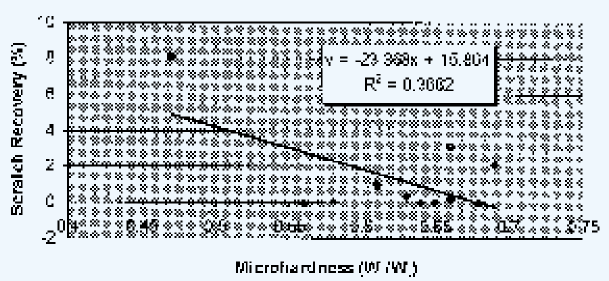

Figure 8—Microhardness (W_r/W_t) vs. scratch recovery.

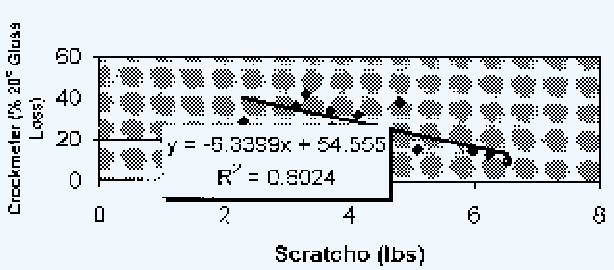

Figure 9—Scratcho vs. crockmeter results.

kept constant at 940 grams, the sliding velocity maintained at approximately 21 mm/sec, and a total of two double rubs was performed on each sample.

Scratcho results were obtained on a commercially available SLIDO apparatus (shown in *Figure* 1) equipped with a scratch head comprised of a stainless steel helix, where each helix head of the 15 heads comprising the helix is approximately 0.8 mm in diameter, with 2 mm between each helix head (*Figure* 2). In this scratch methodology, the painted sample is placed onto an insulated TPO base support and the sample is heated to 155°F by means of radiant quartz heaters, maintained at temperature with an infrared sensor control. The helix scratch head is then loaded onto the sample at a ramped load rate of 10 to 300 lbs over a distance of six inches, with an acceleration of 20 in./sec^2 and a velocity of 2 in./sec.

Scratch deformation imparted to the painted panel is analyzed under a MacBeth white light at a 45° angle. The first sign of fracture within the paint is reported as a load function, e.g., pounds (lb) to first fracture. Painted panels were also exposed to modified SAE J1960 conditions in a Xenon arc Weather-ometer (WOM) equipped with borosilicate/borosilicate inner and outer filters. Exposure time was 250 kJ. The scratch testing methodology was reproduced on the weathered (WOM) panels and the pounds to first fracture reported.

RESULTS AND DISCUSSION

The results obtained in all testing performed on the flexible coatings studied in this work are tabulated in *Table* 1. For discussion purposes, tabulated data is represented graphically comparing either material attribute (microhardness and essential work values) to mechanical properties (Scratcho , crockmeter, and 7N scratch) or comparing scratch data results to each other. For simplicity, nomenclature utilized in *Tables* 1 and 2 is as follows: 1K represents an acrylic or polyester hydroxyl-functional melamine crosslinked system, 2K represents an acrylic or polyester hydroxyl-functional isocyanate crosslinked system, silane represents a functionalized alkoxysilane melamine crosslinked system, and "Carb" represents a functional carbamate melamine crosslinked system.

A comparison is made in *Table* 2 of the scratch resistance ratings afforded for each of the coating types evaluated. The "X" rating was afforded for the top four performing coatings per each test performed. Quite consistently, as is seen in the Table, the carbamate (B) and two-component (B) coatings outperformed the silane (D1KS), which outperformed the two-component coatings (A, P, D). These ratings were based on the coating types that received the most "Xs" across the various scratch methodologies tested. As can be seen in *Table* 2, none of the hydroxyl-functional acrylic or polyester one-component melamine crosslinked systems formulated for plastics afforded "superior" scratch resistance in these tests.

As depicted in *Figures* 3 through 5, the scratch resistance of the various coatings as measured by the crockmeter (*Figure* 3), 7N Ford five-finger (*Figure* 4), and the Scratcho (*Figure* 5) are depicted. These results were then tabulated in *Table* 2 by selecting the top four performing coatings in each of the test methodologies.

In *Figure* 6, the results of microhardness H_{plas} are shown as a function of the 7N five-finger scratch data obtained on each of the flexible coating systems. The data suggests that as the H_{plas} of the coating increases, the scratch depth obtained decreases. Correlation to a straight line as determined by the least square methodology was 66%.

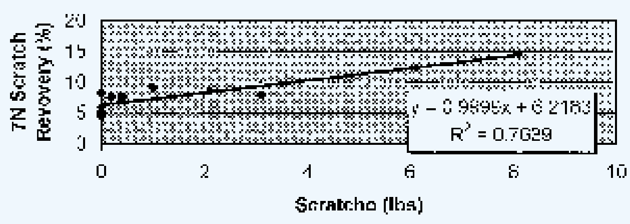

Figure 10—Scratcho vs. 7N scratch recovery.

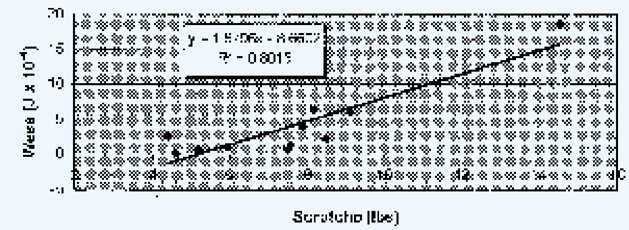

Figure 11—Scratcho vs. Wess

The Young's modulus/compressibility function ($1 - \upsilon^2$) of each coating is plotted versus the 7N scratch depth obtained in *Figure* 7. As shown in *Figure* 7, as the Young's modulus/compressibility function of the coating increases, the resultant scratch depth decreases.

The scratch recovery in the 7N five-finger scratch as it is influenced by the plasticity of the coating (W_r/W_t) is shown in *Figure* 8. As is shown in *Figure* 8, there is a pattern developing which depicts that as the coating exhibits a greater total plasticity (e.g., higher W_r/W_t) the scratch recovery decreases. This assumes that total deformation in the microhardness experiment is either plastic or elastic. If the plasticity increases, the elasticity decreases, thereby decreasing the extent or ability of the coating to self-heal. This relationship is not very concrete as the correlation to a straight line, as determined through the method of least squares, is only approximately 37%. This "poorness of fit" could be attributed to other factors that are not accounted for in the indentation process, but do occur in the scratch process, e.g., fracture.

The results of various scratch resistance methodologies as compared to one another are shown in *Figures* 9 and 10. As can be seen in *Figure* 9, the crockmeter and Scratcho results correlate with each other quite well, with a 60% goodness of fit to linearity. As Scratcho results increase, e.g., pounds required to produce first fracture, the crockmeter mar resistance increases, e.g., less 20° gloss loss.

A similar correlation (0.76 correlation to goodness of fit) exists when Scratcho results are compared to the results obtained in 7N scratch resistance (*Figure* 10). As the pounds required to produce first fracture in a coating increase, the percent recovery attained within a scratched sample increases.

Finally, Scratcho results are compared to a coating material attribute, namely essential work of fracture, in *Figure* 11. It can be seen in *Figure* 11 that as the essential work of fracture of a coating increases so too do the pounds required to produce the first fracture within the coating. This relationship supports the statement that as the toughness of a coating increases, e.g., the work required to fracture the coating increases, so too does its scratch resistance. It is quite interesting to note that (as seen in *Table* 1) the functional carbamate one-component melamine crosslinked system has the highest essential work to break (a factor of three higher than the next highest value) and it is one of the better performing coatings for scratch resistance.

SUMMARY

Known scratch methodologies, namely the crockmeter and Ford five-finger laboratory test methods, in addition to a newly described compressive shear loading device (herein termed Scratcho), are used to compare flexibilized clearcoat systems as applied over one-component hydroxyl-functional acrylic or polyester melamine crosslinked black basecoats. It is shown that the scratch testing methodology utilized to assess the scratch resistance of the coating system dictates results, and that Scratcho compares very well with crockmeter results. Functional carbamate melamine crosslinked one-component coatings and alkoxysilane functional one-component melamine crosslinked coatings appear to outperform selected hydroxyl-functional acrylic or polyester isocyanate crosslinked two-component coatings, which in turn outperform hydroxyl-functional acrylic or polyester melamine crosslinked one-component coatings. Material attributes such as surface hardness, toughness (as measured through the method of essential work), and the ability to recover from an applied load are most important in the ability of the coating to resist damage.

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